

# Remote microwave plasma source for cleaning chemical vapor deposition chambers: Technology for reducing global warming gas emissions

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The semiconductor industry uses a large amount of perfluoro compounds (PFCs), and their impact on global warming has become a major environmental concern. In the semiconductor industry, PFC are used to periodically remove deposits from the chamber walls of chemical vapor deposition (CVD) reactors after film deposition. These chamber clean processes account for typically 50%–70% of the PFC usage in a semiconductor wafer fabrication site, the rest being mainly used for wafer-etching processes. With a conventional parallel plate radio frequency (rf) plasma reactor, the PFC gas utilization is incomplete and a large fraction of unreacted gas can be emitted in the atmosphere. This paper describes a microwave plasma source that provides as high as 99.9% utilization removal efficiency (URE) of the reactant gas ( $\text{NF}_3$ ) during chamber clean. This technology brings the million metric tons carbon equivalent (MMTCE) of a chamber clean to negligible levels and also enhances the chamber clean efficiency and the system throughput. Here we review the requirements for the manufacturability of a remote plasma clean process. Gaseous Fourier transform infrared and quadrupole mass spectroscopy techniques have been used to characterize the clean process, the by-products of the reaction, and the efficiency in reducing the MMTCE of CVD chamber cleans. © 1999 American Vacuum Society. [S0734-211X(99)06802-X]

## I. INTRODUCTION

Perfluoro compound (PFC) molecules absorb strongly in the infrared, and their release into the atmosphere can contribute to the green house effect by modifying the radiation balance of the planet.<sup>1</sup> PFC gases have very long lifetimes (up to 50 000 years for  $\text{CF}_4$ ) and large global warming potentials (GWPs) that are several thousands of time that of  $\text{CO}_2$ .<sup>2–4</sup> Recently, impacts of an increase of the earth's surface temperature have been observed.<sup>5–9</sup> Still, further understanding of the meteorological aspects of global warming is needed to allow prediction and correlation with modifications of the climate patterns. However, it is largely accepted by the scientific community that "the world's changing climatic conditions are more than the natural variability of weather."<sup>10</sup> At the recent "Earth summit" in Kyoto (Dec. 97), the Conference of the Parties agreed to include PFC gases in a yet-to-be-defined limitation agreement.<sup>11</sup>

The PFC usage by the U.S. semiconductor industry is steadily increasing, and the emission of these gases in the atmosphere could double by the year 2000 without imminent action. Considering the negative impact of global warming gas emissions, the major U.S. semiconductor manufacturers have taken a voluntary approach to limit or eliminate PFC emissions in the atmosphere and have signed a memorandum of understanding (MOU) with the U.S. environmental protection agency (EPA) in 1995. More recently, other agreements have been signed between semiconductor manufacturers and governmental institutions in Europe and Asia.

Several strategies are investigated, including process and hardware optimization, abatement, capture and recycling, or alternate chemistries.<sup>12–18</sup> Among the diverse solutions that are currently under development or evaluation, plasma assisted processes present an efficient use of energy, can practically attain close to 100% utilization removal efficiency, are easy to implement and can be economically sound. It has been demonstrated that efficient PFC conversion (to nonglobal warming gases) can be obtained by designing reactors with high plasma density, long gas residence time, and generally by addition of an oxidizer to the process.<sup>19–21</sup> For a particular gas flow ( $F$ ), and a given processing time  $t_1$ , the utilization removal efficiency is defined as

$$\text{URE} = \frac{\int_0^{t_1} F(t)_{\text{Plasma OFF}} dt - \int_0^{t_1} F(t)_{\text{Plasma ON}} dt}{\int_0^{t_1} F(t)_{\text{Plasma OFF}} dt}, \quad (1)$$

where  $\int_0^{t_1} F(t)_{\text{Plasma OFF}} dt$  represents the integrated gas flow which would result from an equivalent process with no plasma.

We developed a remote clean technology based on a microwave plasma source placed upstream of the wafer processing chamber (see Fig. 1).  $\text{NF}_3$  molecules are ionized and dissociated by means of a high density plasma in order to generate fluorine free radicals ( $F$ ) and also excited radicals ( $F^*$ , ...) and negative and positive ions.<sup>22–24</sup> The by-products of the reaction are injected in the process chamber so that the fluorine radicals can dry etch the residues deposited on the chamber walls. Because the  $\text{NF}_3$  plasma is confined in the remote applicator, and because ions and elec-

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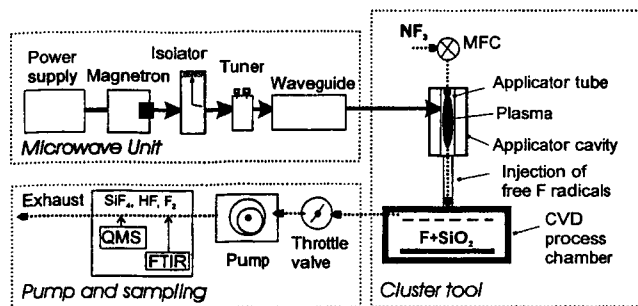


FIG. 1. Schematic of the remote microwave clean technology integrated to a PECVD cluster tool. The high density remote plasma source is placed upstream of the process chamber and provide both higher clean efficiency and complete utilization removal efficiency of  $\text{NF}_3$ . Free fluorine radicals are injected in the chamber to react with, and remove, deposition residues. Gaseous by-products were sampled downstream of the vacuum pump.

trons have a short lifetime, the concentration of charged species in the main chamber is negligible, compared to an *in situ* plasma clean process. In other words, the chamber clean process is purely chemical, therefore avoiding aggressive ion bombardment of the chamber components (i.e., a soft clean).

During the development of this technology, the initial objective was to understand the excited species recombination mechanisms, characterize the gaseous by-products, and study their effect on the chamber clean efficiency. Three main phenomena can occur after the fluorine radicals leave the applicator:

(1) A gas phase recombination of the radicals into the initial molecule or into other nonreactive molecules. Of course, one would like to minimize this probability. Gas phase recombination is related to the pressure and resulting mean-free path for any gas molecule. At relatively low pressure (<5 Torr), the recombination probability is small for  $\text{NF}_3$ , but recombination can occur for fluorocarbons such as  $\text{CF}_4$  or  $\text{C}_2\text{F}_6$ , as will be seen later.

(2) A wall recombination of the reactive species, especially for fluorine atoms that are highly reactive. This problem is a major concern with a remote source because it is often separated from the main chamber by a showerhead to ensure uniform gas distribution. To keep the fluorine radical recombination to reasonable levels was challenging and required evaluation of different designs, radical injection schemes, and reactor materials.

(3) The third phenomenon is the chemical reaction of the active species with the residues present in the main chamber to form gaseous by-products that are nonglobal warming gases. This desired reaction must be effective to remove residues in the shortest possible time, to enhance the overall system throughput.

With the remote microwave clean technology, the concentration of free radicals is enhanced compared to a standard radio frequency (rf) clean technology using capacitive coupling. Typically, a chamber rf clean process presents a URE as low as 5%–20% for  $\text{CF}_4$ . Higher efficiency can be obtained with molecules such as  $\text{C}_2\text{F}_6$  or  $\text{C}_3\text{F}_8$ , but fluorocarbon chemistries generate polymeric residues or other PFCs: it was observed in the case of a conventional plasma reactor

with capacitive rf clean, that increased dissociation of  $\text{C}_2\text{F}_6$  lead to generation of  $\text{CF}_4$  which has even longer atmospheric lifetime than  $\text{C}_2\text{F}_6$  (see Table III). To remedy this problem, an abatement approach with a high density plasma source placed downstream of the main chamber can be adopted, but is not favored because, in turn, it requires spending additional energy to compensate for a front-of-the-line inefficient process.

The remote microwave clean technology approach can be classified as a hardware and process optimization rather than an abatement technology.<sup>25,26</sup> It uses  $\text{NF}_3$  as a clean gas, does not require addition of an oxidizer ( $\text{O}_2, \text{O}_3, \text{N}_2\text{O}, \dots$ ), and provides as high as 99.9% URE of  $\text{NF}_3$  in standard conditions. The technology virtually eliminates the environmental concerns associated with PFC emissions from chemical vapor deposition (CVD) chamber clean processes. In addition, the chamber clean time can be reduced by as much as a factor 2.

In the following, we will describe the operating conditions and characterize the effluents using quadrupole mass spectroscopy (QMS) and gaseous Fourier transform infrared (FTIR) techniques. We present a characterization of the effluents from three different CVD chambers equipped with remote microwave clean units: a standard capacitively coupled plasma enhanced CVD (PECVD) reactor, a sub-atmospheric CVD (SACVD) chamber used for thermal deposition of dielectric films, and a high density plasma CVD (HDP CVD) chamber which is an inductively coupled plasma reactor. Thin film materials such as silane-based and tetraethyl-orthosilicate (TEOS)-based silicon dioxide, silicon nitride, fluorine-doped low-*k* materials, and antireflective coatings have been deposited and the gas emissions during the clean processes have been characterized. Finally, the efficiency of the technology with respect to the emission of green house gases from CVD tools is assessed.

## II. EXPERIMENT

### A. Hardware and process regimes

A schematic description of a remote microwave source installed on a PECVD chamber is given in Fig. 1. In this configuration, the source is mounted on top of the deposition chamber to minimize the distance between the applicator and the chamber to be cleaned.

Several challenges faced the development of a production-ready remote clean technology. First, the microwave applicator must be designed to efficiently transmit high microwave power to the plasma (up to 6 kW in some cases). Several configurations were modeled, tested, and optimized to minimize the microwave reflected power, increase the plasma density, and saturate the molecule dissociation efficiency. Second, the applicator must be designed to survive the very harsh, high density, fluorine plasma environment on a production system. Therefore, great attention must be taken in the choice of the materials (sapphire, ceramics, Teflon™, . . .), and in the dissipation of energy. Indeed, the desired microwave power dictates the cooling scheme of the

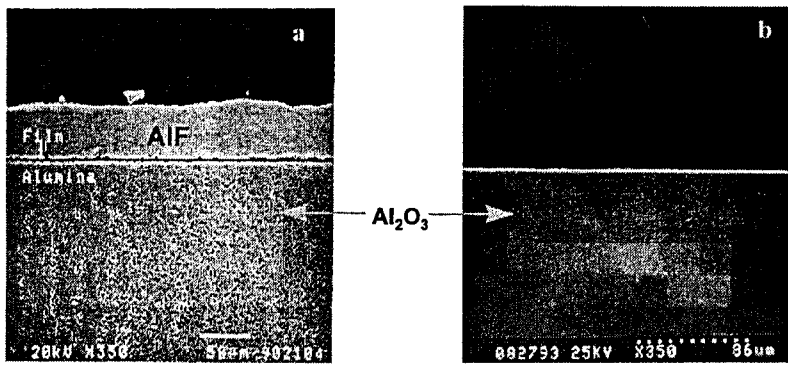


FIG. 2. Surface of the  $\text{Al}_2\text{O}_3$  ceramic dome of an HDP CVD chamber after: (a) 150 h *in situ* clean (left) and (b) 150 h of remote microwave clean (right).

applicator (air versus liquid cooling). On the PECVD and SACVD chambers, the surface area of the exposed walls was minimized by design ( $\sim 600 \text{ cm}^2$  for a 200 mm wafer size). Therefore, a low-power ( $< 2200 \text{ W}$ ) microwave clean unit was sufficient. For the HDP CVD chamber, the ceramic dome through which the plasma is inductively coupled with a rf antenna presents a large surface area, and the total HDP CVD chamber wall surface area ( $\sim 6500 \text{ cm}^2$ ) is more than ten times that of the PE and SACVD chambers. At comparable microwave power and gas flow, the HDP CVD chambers would require longer clean time. To compensate, a higher power microwave applicator was designed.

A benefit of a remote clean technology is that it greatly increases the lifetime of the chamber components and process kit. Since no plasma is sustained in the main chamber, the critical components (ceramic dome, liners, heater, electrostatic chuck) are not subject to fluorine ion bombardment. This is particularly crucial for an inductively coupled source where the presence of a radial electric field can cause ion acceleration toward the dome with energies often higher than 100 eV. An *in situ* clean results in chamber wall erosion, and formation of an  $\text{AlF}_3$  film at the surface of the Al chamber material or the ceramic components. Figure 2 presents scanning electron microscopy (SEM) pictures of the surface of  $\text{Al}_2\text{O}_3$  ceramic domes of a HDP CVD chamber after 150 h of chamber clean (*in situ* vs remote clean). In Fig. 2(a), the case of an *in situ*  $\text{NF}_3$  plasma clean process, one can observe the growth of a  $\sim 60\text{-}\mu\text{m}$ -thick  $\alpha\text{-AlF}_3$  at the surface of the dome [determined by energy dispersive x-ray (EDX) and x-ray diffraction techniques]. This  $\alpha\text{-AlF}_3$  film does not adhere well to the surface of the dome, and the film can delaminate and generate particles after a critical thickness is reached. These particulates ( $0.1\text{--}10 \mu\text{m}$  in diameter and higher) are catastrophic defects for integrated circuits, reducing the yield and increasing preventive maintenance frequency. On the contrary, a remote plasma clean is much softer, does not lead to wall sputtering, and the formation of  $\text{AlF}_3$  is dramatically reduced. Instead, a well adherent, passivation layer can form ( $< 5\text{-}\mu\text{m}$ -thick) and protect the ceramic surface if the temperature of the chamber component is correctly controlled [Fig. 2(b)]. An increase of the wall temperature is beneficial for the clean efficiency, but is often not practical for safety reasons (the maximum allowable

temperature of a wall exposed to a system operator being  $60^\circ\text{C}$ ).

The choice of the clean gas is also of utmost importance. Figure 3 shows the etch rates of PECVD silicon nitride films deposited on Si substrates placed at an increasing distance from the applicator. Two alternative clean chemistries were tested. The first one uses a mixture of  $\text{CF}_4$  and  $\text{N}_2\text{O}$  with a ratio of 3/1. The total gas flow was 2000 sccm, and the pressure in the chamber was 5 Torr. With this clean chemistry, addition of oxygen has been shown to improve etch efficiency and is necessary to avoid formation of polymeric residues after repeated chamber cleans.<sup>25–28</sup> With the  $\text{NF}_3$  chemistry, the process conditions were optimized to obtain an equivalent etch rate of  $1.8 \mu\text{m}/\text{min}$  at a distance of 10 cm downstream of the plasma. This was attained with pure  $\text{NF}_3$  and a total gas flow of 700 sccm at a chamber pressure of 1.5 Torr. Addition of oxygen to the discharge was not favored because of the generation  $\text{NO}_x$  species which are classified as hazardous air pollutants (HAPS). The  $\text{CF}_4$  experimental results indicate that the etch rate decreases significantly with increasing distance from the applicator. On the contrary, the etch rate remains fairly constant when using  $\text{NF}_3$  as a precursor gas. This could be attributed to the fact that dissociated  $\text{CF}_4$  molecules tend to recombine after leaving the plasma region, or that dissociated  $\text{CF}_4$  molecules react with oxygen to form species such as  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{COF}_2$ , which would reduce the etch rate. On the contrary,  $\text{NF}_3$  molecules do not significantly recombine in the gas phase. This was

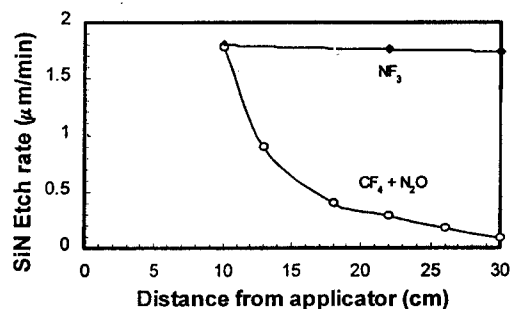


FIG. 3. Etch rate measured on  $\text{Si}_3\text{N}_4$  coupons as a function of the distance from the applicator for two chemistries:  $\text{CF}_4 + \text{N}_2\text{O}$  (circles) and  $\text{NF}_3$  (diamonds).

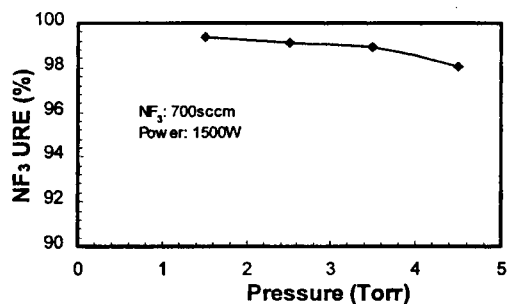


FIG. 4. NF<sub>3</sub> utilization removal efficiency as a function of the pressure in the microwave applicator.

confirmed by using quadrupole mass spectroscopy to monitor the NF<sub>3</sub> partial pressure at three positions: (1) at the chamber exit, (2) at the pump inlet at a distance of ~10 m from the chamber, and (3) downstream of the vacuum pump at atmospheric pressure. These measurements showed no increase in NF<sub>3</sub> concentration downstream of the chamber or the pump, and the NF<sub>3</sub> URE was better than 90% at all positions. For these reasons, we chose NF<sub>3</sub> as the clean gas versus CF<sub>4</sub> or other fluorocarbon gases. In particular, CF<sub>4</sub> is a very stable molecule that is difficult to break apart, and higher power density, gas residence time, and gas flow are required to obtain an equivalent URE, compared to NF<sub>3</sub>.

Figure 4 presents the URE of NF<sub>3</sub> as a function of the gas pressure in the PECVD chamber. For this experiment, the magnetron power was fixed at 1500 W and the NF<sub>3</sub> gas flow was 700 sccm. The results indicate that the URE decreases slightly as the pressure is increased. However, for a pressure of 4.5 Torr, the URE is still higher than 98%, which confirms that the gas phase recombination is not a limiting factor in the case of NF<sub>3</sub>, in this pressure range. Figures 5 and 6 indicate that the URE will decrease if one increases the gas flow or decreases the magnetron power. This suggests that the power per gas molecule is a key parameter to attain high utilization removal efficiencies. The remote clean unit is operated in a saturation regime so that the URE is maximized in a large process window.

## B. Process effluent analysis

The experiments were carried out in CVD chambers equipped with remote microwave clean units (Fig. 1). To provide a fluorine balance for the reaction, and estimate the

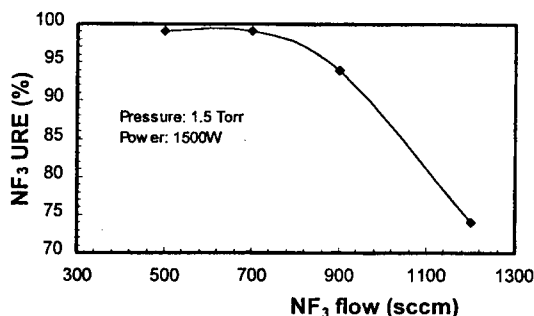


FIG. 5. NF<sub>3</sub> utilization removal efficiency as a function of the NF<sub>3</sub> gas flow.

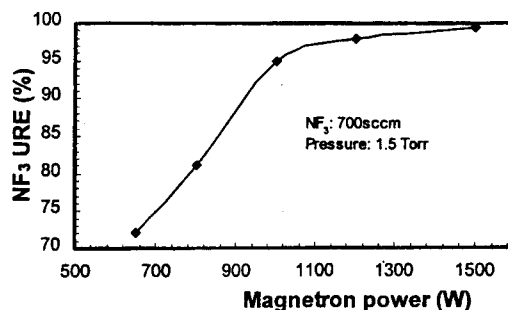
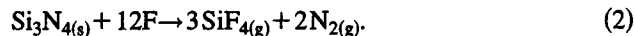


FIG. 6. NF<sub>3</sub> utilization removal efficiency as a function of the magnetron power.

environmental impact of the technology on the release of PFCs in the atmosphere, we used QMS and FTIR spectroscopy to sample the effluents downstream of the vacuum pump. The effluents are diluted with N<sub>2</sub> and sampled at atmospheric pressure. We calibrated the instruments using NF<sub>3</sub>, HF, F<sub>2</sub>, and SiF<sub>4</sub> gas standards. The URE of NF<sub>3</sub> was calculated by recording the partial pressure at 52 and 71 atomic mass units (amu) which correspond to NF<sub>2</sub><sup>+</sup> and NF<sub>3</sub><sup>+</sup> ions, respectively, and integrating the response for microwave ON/microwave OFF cycles during chamber clean. We also quantitatively determined the major by-products of the clean process by integration of the partial pressure during the clean using QMS spectroscopy for SiF<sub>4</sub>, NF<sub>3</sub>, and F<sub>2</sub>, while the HF emissions were quantified using the integration of the FTIR response. Several thin film materials with a thickness of typically 750 nm were deposited on 200 mm wafers. The sequence was as follows: (1) during film deposition, a capacitively coupled (PECVD) or inductively coupled (HDP CVD) plasma was maintained in the chamber, in an atmosphere of the appropriate deposition gas. For the SACVD process, a film was deposited at high temperature and at nearly atmospheric pressure. (2) The wafer was removed and (3) a chamber clean was performed. During chamber clean, no plasma was sustained in the deposition chamber, but the remote plasma microwave source was turned on. The purpose of the clean is to remove the silicon-containing residues. For example, in the case of a silicon nitride residue removal, a basic equation could be written



Of course, the real reaction sequence is much more complex and must account for a wide variety of excited species and reaction paths, the formation of dangling bonds at the surface of the material, . . . ,<sup>22,28-30</sup> in particular, other by-products (HF and F<sub>2</sub>) have been observed in the present case (see Fig. 7). Other deposited films correspond to typical CVD applications in integrated circuit manufacturing. PE-TEOS oxide and PE-silane oxide refer to SiO<sub>2</sub> films obtained by PECVD in a parallel plate plasma reactor using, respectively, TEOS+O<sub>2</sub> and SiH<sub>4</sub>+N<sub>2</sub>O as reactant. HDP CVD oxide refers to an SiO<sub>2</sub> film deposited in the inductively coupled reactor using SiH<sub>4</sub>+O<sub>2</sub> as reactant gases. SACVD oxide refers to SiO<sub>2</sub> films, thermally deposited using TEOS and

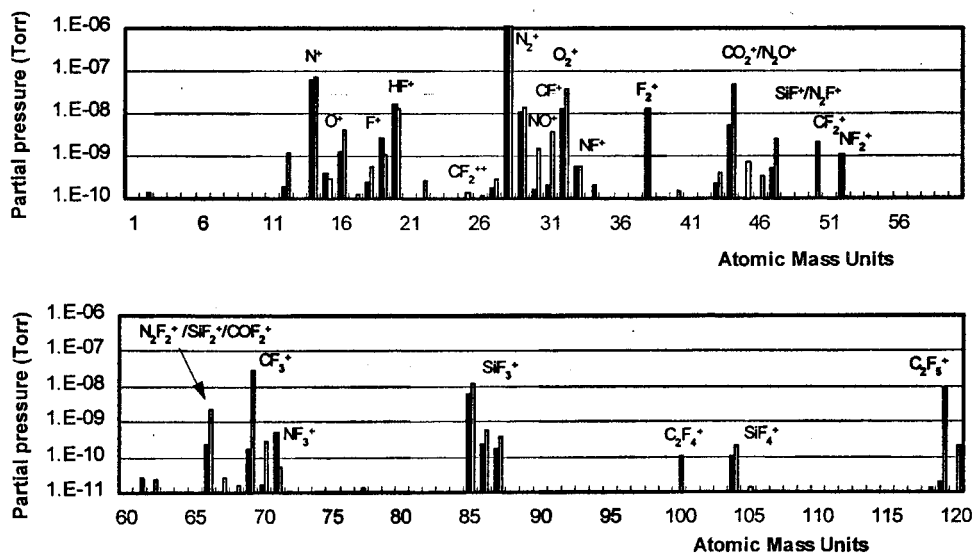


FIG. 7. QMS spectra recorded at the exit of the vacuum pump during the clean process after TEOS-oxide film deposition in a PECVD chamber. The remote microwave clean using  $\text{NF}_3$  (dark bars) is compared to a standard rf clean using  $\text{C}_2\text{F}_6$  (white bars).

ozone as reactant species. These films are extensively used for pre-metal dielectric (PMD), intermetal dielectric (IMD), and device passivation applications. For the  $\text{SiO}_2$  films, the refractive index (R.I.) was typically 1.46 (at 633 nm). The fluorinated silicate glass (FSG) is a common low dielectric constant film used for IMD applications in  $0.25 \mu\text{m}$  device generation and refers to a fluorine-doped  $\text{SiO:F}$  film ( $\text{F}=4$  at. %) deposited in the PECVD chamber using  $\text{SiH}_4/\text{N}_2\text{O}/\text{SiF}_4$  gases and tuned with a R.I.=1.40 and a compressive stress of  $-50$  MPa. The silane nitride film can be used for device passivation, diffusion barriers, or liners and is a PECVD  $\text{Si}_3\text{N}_4\text{H}_2$  film turned with a R.I.=1.98 and a stress of  $-150$  MPa using  $\text{SiH}_4/\text{NH}_3/\text{N}_2$  as precursor gases. Finally, the antireflective coating (ARC) film consists of a silicon-rich  $\text{SiO}_x\text{N}_y$  film deposited with a R.I.=2.1 and a stress of  $-100$  MPa using  $\text{SiH}_4$ ,  $\text{N}_2\text{O}$ , and He gases. Figure 7 shows the 120 amu QMS spectra recorded at the exhaust of the pump during the chamber clean process (PETEOS-oxide process). We compare the effluent emissions of a standard (optimized)  $\text{C}_2\text{F}_6$  rf clean with a remote microwave  $\text{NF}_3$  clean. As mentioned earlier, the standard  $\text{C}_2\text{F}_6$  clean requires addition of oxygen to avoid polymeric residues deposition on the chamber wall, and a small fraction of  $\text{NF}_3$  was also added to improve plasma stability. For the rf clean, one can observe the  $\text{C}_x\text{F}_y$  peaks while the  $\text{N}_x\text{F}_y$  peaks are apparent during the microwave clean, due to the dissociation of the  $\text{NF}_3$  molecules. For both clean processes, the main byproduct is  $\text{SiF}_4$  ( $m/e = 104, 85, 66, 47$ ). Note that the HF peak is very similar for both cleans, but that the  $\text{F}_2$  emission is significantly higher in the case of the microwave clean, due to the very high dissociation efficiency of the  $\text{NF}_3$  molecules. The fact that  $\text{F}_2$  molecules can be detected downstream of the pump suggest that the clean process is not limited by the concentration of F free radicals but by the reaction rate on the chamber walls, which is driven by temperature. The peak at  $\text{amu}=44$  is attributed to  $\text{CO}_2$  and  $\text{N}_2\text{O}$  in the case of the  $\text{C}_2\text{F}_6$  clean. In the case of the  $\text{NF}_3$  microwave clean, no evidence of  $\text{NO}_2$  formation was found (see FTIR study) and the peak

at  $\text{amu}=44$  is attributed to background  $\text{CO}_2$ . From comparison of the peak ratios of the CF-related species, and from comparing a  $\text{C}_2\text{F}_6$ -only and a  $\text{CF}_4$ -only QMS response, one can determine that the  $\text{C}_2\text{F}_6$  rf clean leads to the formation of  $\text{CF}_4$  molecules, which have longer atmospheric lifetimes (cf. later Table III). The  $\text{NF}_3$  clean, on the contrary, has by-products that are nongreenhouse gases.

Figure 8 shows the FTIR spectrum recorded at the outlet of the vacuum pump for three different conditions. The bottom curve shows the  $\text{NF}_3$  peak appearing at  $\sim 920 \text{ cm}^{-1}$  when the gas is flowing without turning the plasma on. When the plasma is turned on, at the beginning of the clean, the  $\text{SiO}_2$  residues are dry etched by the fluorine free radicals. The main by-product of the clean process is confirmed to be  $\text{SiF}_4$  ( $1045 \text{ cm}^{-1}$ ), as can be seen on the outer curve (Fig. 8). A spectrum was also recorded during an overetch step (top curve) to confirm that no  $\text{NF}_3$  recombination occurs, even after the chamber is cleaned. Instead, by-products such as  $\text{N}_2$  and  $\text{F}_2$  are expected but cannot be detected in the given wave number interval. No other by-products were observed with the FTIR technique in the range of  $400\text{--}4600 \text{ cm}^{-1}$ . In par-

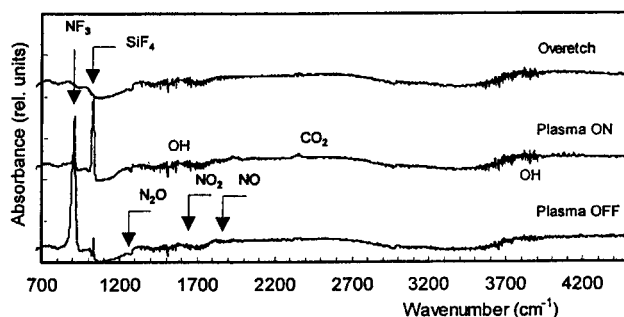


FIG. 8. FTIR spectrum recorded at the exhaust of the vacuum pump at different stages of the clean process. Bottom:  $\text{NF}_3$  ON, plasma OFF, gas only. Center:  $\text{NF}_3$  ON, plasma ON, chamber cleaning. Top:  $\text{NF}_3$  ON, plasma ON, chamber overetch.

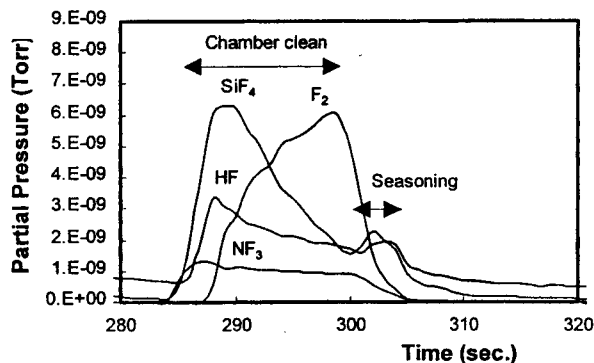


FIG. 9. Dynamic partial pressure of the main by-products during chamber clean as recorded by QMS. Also shown is the removal of trapped fluorine on the reactor walls during a seasoning step.

ticular, no trace of NO ( $1875\text{ cm}^{-1}$ ), NO<sub>2</sub> ( $1613\text{ cm}^{-1}$ ), or N<sub>2</sub>O ( $1264\text{ cm}^{-1}$ ) were found within the lower detection limit of the technique ( $<55\text{ ppm}$ ). From this observation, it is suggested that the oxygen from the SiO<sub>2</sub> film is removed during the clean as O<sub>2</sub>.

In Fig. 9, the QMS time profile during one chamber clean is presented for the various by-products of the reaction. The initial NF<sub>3</sub> "bump" is due to a few seconds stabilization time to attain the correct gas flow and pressure. At the beginning of the clean, the SiF<sub>4</sub> response rapidly increases. After the chamber clean, the SiO<sub>2</sub> residues are removed from the walls and the SiF<sub>4</sub> emission vanishes. As can be observed, the HF peak follows the shape of the SiF<sub>4</sub> signal, and it can be concluded that the main source of hydrogen comes from the highly hydrogenated SiO<sub>2</sub> residues deposited on the walls at low temperature ( $60\text{ }^{\circ}\text{C}$ ). The typical H content of such residues is  $\sim 30\text{ at. } \%$ .<sup>25,26</sup> As the clean process progresses, the F<sub>2</sub> signal rises, due to continued dissociation of NF<sub>3</sub> and rarefaction of the source of silicon. After the chamber clean is performed, a chamber seasoning step is initiated prior to introduction of a wafer for the next film deposition. The seasoning consists of coating the chamber walls with a few hundred nanometers of (SiO<sub>2</sub>) film. This step is intended to seal off any residual particles that might otherwise flake off during deposition, and to remove excessive fluorine adsorption from the chamber walls. Indeed, one

can observe that the HF signal strongly rises due to recombination with the deposition gas precursors (TEOS+O<sub>2</sub>). In conjunction with the remote clean, this seasoning step allows to increase the process stability during several thousands of deposition/clean cycles, and to reduce particle contamination in the chamber.

Table I presents the utilization efficiencies and a quantitative analysis of the effluents for the reaction of NF<sub>3</sub> with different film residues and process chambers (PECVD, SACVD, and HDP CVD). The remaining NF<sub>3</sub> emissions (NF<sub>3out</sub>) are also indicated, completed by the utilization removal efficiencies. For each process, a fluorine mass balance was performed. In the case of the PECVD chamber, the plasma was initiated with NF<sub>3</sub> gas after a few seconds gas flow stabilization step during which NF<sub>3</sub> is introduced but no plasma is sustained. This stabilization step accounts for the remaining 50–100 scc of NF<sub>3out</sub> (PECVD chamber). For the SACVD and HDP CVD chambers, the plasma was initiated with a carrier gas (N<sub>2</sub>), and NF<sub>3</sub> was introduced only when the plasma was stable. Therefore, one can observe UREs as high as 99.9% in standard operating conditions. The table reports the emissions of the clean process in standard cubic centimeters (scc), and the results were normalized to a constant volume of 820 scc of NF<sub>3</sub> gas introduced into the system. As can be observed, the amount of HF emissions is fairly constant for the PECVD and SACVD films and is practically independent of the deposition chemistry or method (PE or SA) for the silicon oxide-type films. Indeed, the H concentration of residues deposited on the chamber walls at low temperature ( $60\text{ }^{\circ}\text{C}$ ) does not vary significantly ( $\text{H} \sim 20\text{--}30\text{ at. } \%$ ) in these chambers, as measured by the intensity of the SiOH peak of residues deposited on Si coupons, using FTIR spectroscopy. For the HDP CVD process, the record low HF emission (15 scc) is due to the fact that better SiH<sub>4</sub> dissociation efficiency is reached during deposition, resulting in lower hydrogen incorporation in the deposited HDP film. It is also interesting to remark that the volume of SiF<sub>4</sub> produced while etching the silicon nitride residues is much greater than for the other chemistries (381 scc vs  $\sim 100\text{--}200\text{ scc}$ ). This is attributed to the fact that the downstream etch process is more efficient for the nitride film than the oxide films, and because the number of Si atoms is

TABLE I. Quantitative analysis of effluents during chamber clean after deposition of various thin films in different chambers. Measurements were performed at the exit of the pump (rows 1–7) and at the outlet of a conventional point-of-use (POU) abatement unit (row 8).

Chamber	Film	Total NF <sub>3</sub> used (NF <sub>3in</sub> scc)	By-products				Fluorine balance	NF <sub>3</sub> URE (%)
			NF <sub>3out</sub> (scc)	SiF <sub>4</sub> (scc)	HF (scc)	F <sub>2</sub> (scc)		
PECVD	PE-SiH <sub>4</sub> -oxide	820	96	117	44	753	0.94	88.9
PECVD	PE-TEOS-oxide	820	63	158	51	640	0.87	92.3
PECVD	SiO:F	820	51	135	40	939	1.06	93.7
PECVD	Darc™	820	84	227	56	638	1.01	89.7
PECVD	SiH <sub>4</sub> -nitride	820	77	381	100	14	0.77	90.6
SACVD	SACVD oxide	820	1.06	180	172	705	0.94	99.9
HDP CVD	HDP CVD oxide	820	4	38	15	1052	0.93	99.5
POU abat.	HDP CVD oxide	820	1	1	9	3	N/A	99.9

TABLE II. Lifetime, radiative forcing, induced increase of temperature and global warming potential for 100 years and infinite integrated time horizons (ITH) of green house gases used in the semiconductor industry.

Gas	Lifetime (years)	Rad. forcing ( $\text{W m}^{-2}/\text{ppbv}$ )	$\Delta T_x$ ( $^{\circ}\text{C}/\text{ppbv}$ )	GWP (100 years ITH)	GWP ( $\infty$ ITH)
$\text{CO}_2$	100	0.000018		1	1
$\text{CF}_4$	50 000	0.10	0.06	6500	850 000
$\text{C}_2\text{F}_6$	10 000	0.23	0.13	9200	230 000
$\text{C}_3\text{F}_8$	7000	0.24	0.14	7000	130 000
$\text{SF}_6$	3200	0.64	0.43	23 900	230 000
$\text{NF}_3$	740	0.21	0.07	8000	18 000
$\text{CHF}_3$	250	0.18	0.12	11 700	11 000

higher per molecule of  $\text{Si}_3\text{N}_4$ , compared to  $\text{SiO}_2$ . This is in agreement with previous studies showing that the etching process of silicon oxide materials is more efficient when the reaction is ion assisted, and that the etching of  $\text{Si}_3\text{N}_4$  is more chemical in nature.<sup>27-29</sup> Compared to  $\text{SiO}_2$ , the remote cleaning of  $\text{Si}_3\text{N}_4$  presents the greatest decrease in clean time, with an improvement of 40% over an optimized *in situ* rf clean process. Another particularity of the  $\text{Si}_3\text{N}_4$  case, is that the F balance is not perfect (0.77) compared to other chemistries (0.93–1.06). This probably comes from a recombination of the F atoms with  $\text{Si}_x\text{N}_y\text{H}_z$  residues accumulated in the foreline to form  $(\text{NH}_4)_2\text{-SiF}_6$ ,<sup>25,26</sup> which is a solid material and therefore cannot be detected using QMS spectroscopy.

Finally, one can observe in Table I that the  $\text{F}_2$  emissions are the highest in the case of the HDP CVD chamber. This can be attributed to the specific design and large surface area of this chamber. In any case, the remaining emissions of HF and  $\text{F}_2$  (which are classified as HAPS, or hazardous air pollutants) can be readily taken care of with traditional point-of-use abatement techniques. An appropriate scrubbing technique consists of reacting the  $\text{F}_2$  molecules into HF by thermal reaction at high temperature (typically 600–900  $^{\circ}\text{C}$ ) using hydrogen gas as a reactant. The remaining HF can be easily water scrubbed and the water recycled using a calcium hydroxide fluorine press, delivering  $\text{CaF}_2$  solid material as a by-product, which is inert and nontoxic. The last row of Table I gives an example of the abatement efficiency attainable with a commercially available point-of-use (POU) scrubber.

### III. RESULTS AND DISCUSSION

To compare the environmental impact of the different clean processes and technologies, we took into account the different utilization removal efficiencies and the emission of global warming gases (unreacted gas and by-products). For example, in the case of the  $\text{C}_2\text{F}_6$  rf clean processes, one must account for the formation of  $\text{CF}_4$  as a by-product. For the calculations, we used the global warming potentials and molecule lifetime reported in Table II. The GWP, using both infinity and 100 years as the integrated time horizon (ITH), is defined for a given gaseous species ( $x$ ):

$$\text{GWP}_{x,\text{ITH}} = \frac{\int_0^{\text{ITH}} \Delta T_x C_x(t) dt}{\int_0^{\text{ITH}} \Delta T_{\text{CO}_2} C_{\text{CO}_2}(t) dt}, \quad (3)$$

where  $\Delta T_x$  is the increase in temperature induced by the molecule (proportional to its absorption in the infrared), and  $C_x(t)$  is the concentration of the gas during the considered period. While the GWP values are estimated, and accurate only to  $\pm 20\%$ , the radiative forcing of PFC molecules are well known and measured. The radiative forcing (in  $\text{W m}^{-2}/\text{ppbv}$ ) helps to determine the effect of a gas on climate.<sup>2</sup> An increase in concentration of a green house gas in the atmosphere results in stronger absorption of the infrared emission that would normally be radiated to space when the earth's surface cools down (at night). In other words, this reduces the efficiency by which the earth cools to space, and tends to warm the earth's surface temperature.

In order to estimate the environmental impact of the process, one has to calculate the MMTCE for each clean operation. The MMTCE/wafer (normalized per clean process) is a measure of the equivalent mass of  $\text{CO}_2$  that would result in an equal radiative forcing. This allows to compare different clean processes, even when using different chemistries ( $\text{NF}_3$ ,  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , ...). With  $Q$  being the mass of the emitted gas, the MMTCE can be expressed as

$$\text{MMTCE}_{\text{ITH}} = \frac{Q(\text{kg})(12/44)\text{GWP}_{\text{ITH}}}{10^9}. \quad (4)$$

In Table III and Fig. 10, we compare the performance of different chamber clean processes and technologies developed over the past three years. The clean processes referred to were developed for PE-TEOS  $\text{SiO}_2$  thin films. During the

TABLE III. Improvement in the processes and hardware as measured by gas utilization removal efficiency, clean time, and gas flow for production-proven PECVD chamber clean processes over the past years ( $\text{SiO}_2$  film deposition). Note that increased  $\text{C}_2\text{F}_6$  utilization leads to increased  $\text{CF}_4$  production.

Process/hardware	Clean gas	Year	Rel. clean time	Rel. gas flow	$\text{C}_2\text{F}_6$ URE (%)	$\text{CF}_4$ prod. (%)	$\text{NF}_3$ URE (%)
RF clean/A	$\text{C}_2\text{F}_6$	1995	1.0	1.0	20	15	...
RF clean/B	$\text{C}_2\text{F}_6$		0.85	0.7	35	18	...
RF clean/C	$\text{C}_2\text{F}_6$	1996	0.65	0.7	55	25	...
RF clean/D	$\text{C}_2\text{F}_6$		0.55	0.45	70	30	...
Microwave clean/E	$\text{NF}_3$	1997	0.45	0.7	...	...	>95

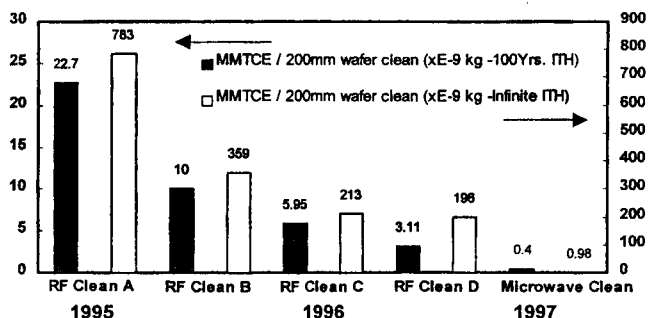


FIG. 10. Improvement in green house gases emission reduction over the past three years as measured by million metric ton carbon equivalent for various clean processes and technologies.

past years, each of the recipes and hardware configuration were optimized to decrease emissions, enhance clean time and reduce gas flows. On a production system, the requirement for changing the processes are drastic. Any change must be process transparent (no drift of the film properties for typically 3000–5000 consecutive wafers). This clean time must be equivalent or faster to maintain or increase the chamber throughput. Finally, any new technology or recipe must be economically sound, and parameters such as hardware cost, gas cost and hardware lifetime are of importance.

Processes A to D are based on  $C_2F_6$  clean processes. Processes A, B, C refer to standard production clean processes that were implemented on PECVD chambers from 1995 to 1996. Process A was the common process on production chambers in 1995 and is taken as reference for the gas flow and clean time (see Table III, columns 3 and 4). Process D is the optimized rf clean process used on a new generation PECVD chambers (introduced in 1996). Finally, process E refers to the remote microwave clean technology.

One can see in Fig. 10 that, compared to the process of record in 1995, the  $MMTCE_{100yrs}$  of the chamber clean processes was reduced by a factor of 50 (22.7/0.4) while the  $MMTCE_{\infty}$  was reduced by a factor close to 800 (783/0.98).

For the first three processes (A, B, C), the reduction in MMTCE was obtained by changing the clean process from a two-step process to a single-step process and reducing the total amount of clean gas. The  $C_2F_6$  utilization was increased to 55% (process C) by increasing the rf power density. With the introduction of a new chamber (process D), an increase of the  $C_2F_6$  utilization to 70% was attained. This was obtained by designing a process chamber with a smaller wall surface area and less exposed parts, and an even higher rf power density during clean. Also, the chamber uses ceramic material liners to protect the chamber walls, better confine the plasma, and limit the wall recombination of F radicals. For the  $C_2F_6$ -based chemistry (processes A to D), one can see that while the clean times and gas flows are reduced when one optimizes the clean process, the production of  $CF_4$  from  $C_2F_6$  increases. For process E ( $NF_3$  remote clean), this concern is eliminated. Compared to the process of record in 1995, one can see that the clean time has been reduced by 55% with a gas flow 30% lower and virtually no emission of global warming gases. Previous studies have shown that

the etching of  $SiO_2$  material is enhanced by ion bombardment.<sup>27–29</sup> In the present case, the remote clean is purely chemical, and it is observed that ion bombardment is not required to attain high clean rates on  $SiO_2$  residues. It can be concluded that the dominant factor to improve the clean efficiency is the concentration of fluorine radicals, much higher in the case of the remote  $NF_3$  clean, compared to an *in situ*  $C_2F_6$  process.

The major advancements made using the remote microwave source would not be possible without the unique chemical and physical properties of  $NF_3$ . This gas has the ability to provide an effective, carbon-free source of fluorine. With respect to the environmental impact, the choice of  $NF_3$  is favored over other molecules, because most fluorocarbon have higher GWP and lifetime (except  $CHF_3$  with a lifetime of 250 years). Especially,  $CF_4$  has a lifetime of 50 000 years with an infinite  $GWP_{\infty}$  of 850 000, versus 740 years and  $GWP_{\infty}$  of 18 000 for  $NF_3$ .

It must be noted that the cost of  $NF_3$  is nearly four times that of more commonly used fluorocarbon molecules ( $CF_4$ ,  $C_2F_6$ ). This must be taken into account to evaluate the cost-worthiness of the technology, but, in fact, the increase in gas cost is largely compensated by the improvement in process performance and tool productivity (reduced clean time, lowered wear of chamber components, extended runs between preventive maintenance). Also, attempts to achieve similar fluorine atom delivery rates using other commonly employed fluorocarbon molecules require higher gas flows, compared to  $NF_3$ .

Users should also be aware of the handling procedures of  $NF_3$ ; it should be treated with the same precautions used in handling of many other gaseous substances that present inhalation hazards. A detailed discussion of the toxicology and safety precautions associated with  $NF_3$  is beyond the scope of this article, but such information is readily available.<sup>30,31</sup> Although relatively inert at ambient temperature and pressure,  $NF_3$  is a strong oxidizing agent such that at higher temperature ( $>300^\circ C$ ),  $NF_3$  will dissociate into reactive fluorine species which react with most materials. The threshold limit values (TLV) and immediately dangerous to life and health (IDLH) values for  $NF_3$  fall both above and below those of many other commonly used gases ( $HF$ ,  $AsH_3$ ,  $Cl_2$ ,  $NH_3$ , ...). Because  $NF_3$  has very little odor, it cannot be detected by humans at concentration within the TLV, and adequate monitoring should be used. To enhance safe operating conditions in systems using  $SiH_4$  and  $NF_3$ , dilution with  $N_2$  is required to maintain concentrations outside the flammability limits. Dilution with nitrogen provides a three component flammability limit of 2.0%  $SiH_4$ /2.5%  $NF_3$ /95.5%  $N_2$ . Appropriate engineering and operational controls of the  $NF_3$  delivery and exhaust system should be implemented. Fortunately,  $NF_3$  has been widely used in the semiconductor industry for nearly 20 years, and adequate procedures are well implemented and documented.

#### IV. CONCLUSION

We have presented a remote microwave clean technology that has been developed for CVD chamber clean in a production environment. The remote plasma source was designed to sustain very harsh conditions due to fluorine corrosion and high plasma density. The source allows full dissociation of the  $\text{NF}_3$  molecules and injection of free fluorine radicals in the process chamber where no plasma is sustained. This leads to an efficient chamber clean due to the very high concentration of fluorine radicals. The clean process uses  $\text{NF}_3$  rather than  $\text{C}_2\text{F}_6$  which is known to form  $\text{CF}_4$  as a by-product. When using  $\text{CF}_4$ , it was observed that dissociated  $\text{CF}_4$  molecules can recombine downstream of the plasma region. A study of the effluent during chamber clean shows that  $\text{SiF}_4$ ,  $\text{HF}$ , and  $\text{F}_2$  are emitted as by-products of the reaction. No other by-products have been detected, in particular no  $\text{NO}_x$  species. The utilization removal efficiency for  $\text{NF}_3$  can be as high as 99.9% in standard operating conditions, and the reduction of the MMTCE due to CVD chamber clean is drastic. The remote clean technology reduces process kit damage due to the absence of ion bombardment in the main processing chamber, and improved process performance has been observed over thousands of deposition/clean cycles (particle contamination, mean time between preventive maintenance).

This demonstrates that environmental problems can be addressed in an economically sound manner, e.g., reducing PFC emissions while increasing the tool efficiency and productivity. As the concern for global, sustainable development is growing, design for the environment is becoming a significant part of research and engineering in the semiconductor industry.

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