# APPLICATIONS OF HIGH PRESSURE PLASMA CHEMISTRY TO THE ABATEMENT OF PERFLUOROCOMPOUNDS FROM MICRO-ELECTRONICS MANUFACTURING

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## ABSTRACT

It is well known that exhaust gases from the manufacturing, transportation, and utility industries can contribute to ozone-induced smog and acid rain, as well as to the climate change by their potential global warming and atmospheric ozone depletion mechanisms. In order to achieve compliance with future legislative limits intended to reduce air pollution, it is necessary to develop alternative abatement methods for a wide variety of harmful gaseous compounds. These compounds can contribute to the global warming effect both directly and indirectly. Direct effects occur when the gas itself is a greenhouse gas like water vapor, carbon dioxide ($CO_2$), methane ($CH_4$), nitrous oxide ($N_2O$), and ozone ($O_3$). Indirect radiative forcing occurs when chemical transformations of the original gas produce other greenhouse gases, when a gas influences the atmospheric lifetimes of other gases, and/or when a gas affects atmospheric processes that alter the radiative balance of the earth. Very powerful greenhouse gases that are not naturally occurring include *hydrofluorocarbons* (HFCs), *perfluorocarbons* (PFCs), and *sulfur hexafluoride* ($SF_6$), which are generated in a variety of industrial processes [1].

In the semiconductor industry, for example, PFCs are used extensively for plasma enhanced chemical vapor deposition (PECVD), plasma etching and plasma cleaning. In general, only a small portion of these gases is consumed during semiconductor fabrication, so the effluent stream from a particular process may contain relatively large quantities of environmentally harmful compounds. While the ideal solution to this problem would be to develop cleaner processing methods, or to recover and recycle unused process chemicals, achieving the zero emission goal sought by the semiconductor industry will probably require continued use of some form of post-treatment.

The present work describes the development and application of a non-thermal plasma system sustained by 2.45GHz frequency microwaves (MW) and operated at atmospheric pressure against a wide variety of pollutant molecules of

interest to microelectronics industry. The technology has been tested on gas flows containing $C_2F_6$, $CHF_3$, $NF_3$, $SF_6$ and particularly $CF_4$ to illustrate its effectiveness. A schematic diagram of the experimental system is shown in figure 1:

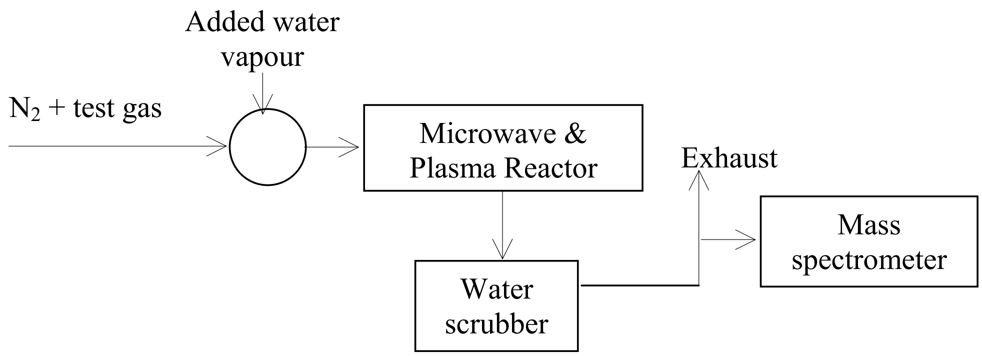


Figure 1. Schematic diagram of the experimental system

Microwave discharge is one technique used to obtain a non-equilibrium plasma, even under atmospheric pressure. In a non-equilibrium plasma the mean electron energy, or temperature, is considerably higher than that of the bulk-gas molecules. Because energy is added to the electrons instead of the ions and background gas molecules, the electrons can attain energies of 1-10eV, while the background gas can remain at ambient temperature. This non-thermal condition can be created at both atmospheric and sub-atmospheric pressures, but high volume throughput, and therefore high treatment rates, can only occur at atmospheric pressures. Because the electrons are preferentially excited in a non-thermal plasma, leaving the more massive ions with lower energy, significant energy savings can be realized [2-4].

Microwave induced atmospheric plasma destruction of PFCs in the presence of water (source of hydrogen and oxygen) was tested over a range of flow rates, power levels, and PFC concentrations. The carrier gas was nitrogen.

The chemical abatement of perfluorocarbons in the presence of water can be represented by equation 1:

$$C_nF_m + \frac{m}{2}H_2O \rightarrow nCO_2 + mHF \qquad (1)$$

This equation describes the predominant product formation as long as there is sufficient oxygen to convert all the carbon to $CO_2$ and sufficient hydrogen to convert all the fluorine to HF. Since HF (water soluble) is the desired product for fluorine, it is necessary to increase the hydrogen concentration; one approach for increasing the hydrogen content is to add excess water.

It was found that successful abatement is dependent on the total gas flow, the total power level, the ratio PFC:$H_2O$, and the concentration of $CF_4$. Destruction and removal efficiencies of $CF_4$ up to 99% have been achieved using 1.9 kW of microwave power. Fluorine by-products resulting from the plasma treatment of the PFCs have been determined to be water-scrubbable. It has been also proved that water abatement of PFCs results in less-oxidized by-products such as CO and HF; this is probably due to the significant presence of fluorine-scavenging H species from water within the plasma that will react with fluorine to form HF rather than to recombine with carbon to form $CF_4$. The preferential formation of HF can be attributed to the high bond strength of the H-F bond, which is on the order of $570 kJmol^{-1}$, while the C-F bond strength in $CF_4$ is approximately $540 kJmol^{-1}$. The destruction and removal efficiencies of the process increases with increasing microwave power level and decreasing pollutant initial concentration and total gas flow.

## REFERENCES


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