

# Using Point-of-use Plasma Sources to Shape a Fab's Environmental Footprint

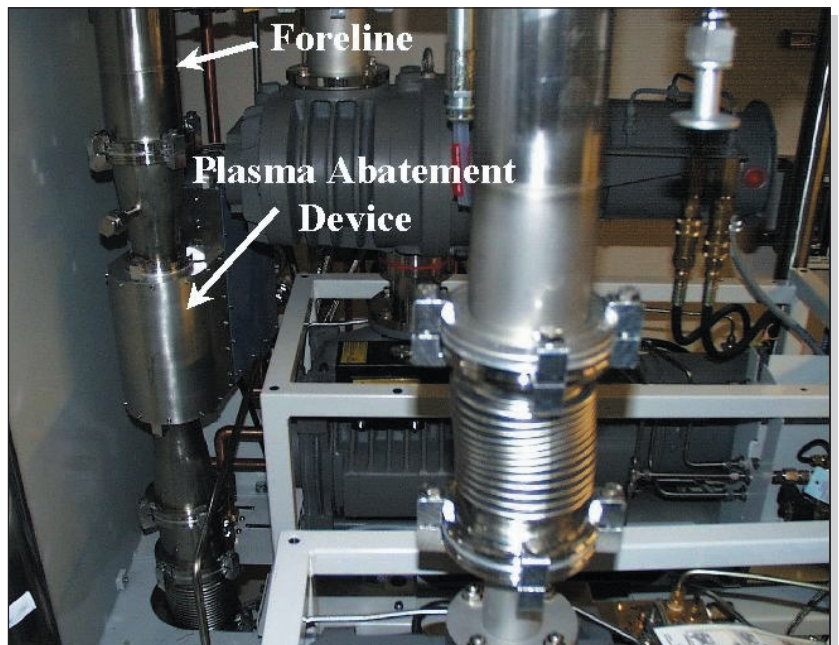
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## ABSTRACT

The chemicals and processes used to transform a raw wafer into a functional device are quite varied and present a daunting challenge to facilities engineers working to minimise waste emissions. For example, a silicon nitride deposition PECVD process uses  $\text{SiH}_4$  and  $\text{NH}_3$  to form a dielectric layer on a wafer, and later  $\text{C}_2\text{F}_6$  or  $\text{NF}_3$  to clean the process chamber. The process exhaust would contain unused original gases as well as by-products from the deposition and cleaning plasma chemistries ( $\text{F}_2$ ,  $\text{CF}_4$ ,  $\text{HF}$ ,  $\text{SiF}_4$ , etc.). Following the wafer through to the etch step, that process exhaust contains unused  $\text{CHF}_3$ ,  $\text{CF}_4$ , and  $\text{SF}_6$  from the process and  $\text{SiF}_4$ ,  $\text{HF}$ ,  $\text{F}_2$ ,  $\text{COF}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{SO}$ ,  $\text{SO}_2$ ,  $\text{SOF}_x$ , and others as exhaust. Both of these processes are performed under a plasma environment—useful for controlling precisely the film characteristics. However, the plasma produces multiple chemical by-products that are toxic to humans and/or the environment. This article reviews older treatment methods and introduces a relatively new application of plasma sources used to treat multiple component exhaust streams from etch and CVD equipment.

## EXHAUST TREATMENT TECHNOLOGIES

Wet scrubbers are among the most common exhaust treatment systems in use today, ranging from large factory acid scrubbers through small point-of-use systems for a single chamber. They are useful for removing particulates and water-soluble gases from the exhaust stream. Point-of-use water scrubbers can remove  $\text{SiF}_4$ ,  $\text{HF}$ ,  $\text{COF}_2$ ,  $\text{SO}$ ,  $\text{CO}$ , and  $\text{SOF}_x$  from the sample nitride application exhaust. Absorbing the fluorinated components of the exhaust makes the water more acidic, so it must be neutralised later, before discharge from the factory. The end product is largely  $\text{CaF}$  solid (with some sulphate content). Scrubbing with water, as is apparent, only partially treats the multi-component gas stream. Still remaining are the perfluorinated compounds (PFCs)  $\text{CHF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ , and  $\text{NF}_3$ , as well as the  $\text{F}_2$  and  $\text{SO}_2$ . Until recently, the PFCs on this list were not subject to any emissions standard. Now, however, all



countries with a significant semiconductor industry presence are signatories to a memorandum of understanding which sets guidelines for emission of PFCs.

Another method for treating the exhaust is dry absorption, which can be both chemical and physical in nature. In a dry scrubbing system, the exhaust passes through a bed of porous beads. Reactive components of the exhaust are absorbed onto the surface of the beads. Bead material must be chosen for the chemicals that might be present in the exhaust. For example,  $\text{HF}$  can be absorbed using a  $\text{CaCO}_3$  base material. As the  $\text{HF}$  passes through the bed, it reacts with the  $\text{CaCO}_3$  to form  $\text{CaF}_2$  (solid),  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .  $\text{SiF}_4$  can be trapped in a similar way, using a different material. The reactive sites are consumed in the process of treating the gas, so the bead material must be replaced (usually by exchanging canisters) after a period of time. In the nitride sample exhaust,  $\text{SiF}_4$ ,  $\text{HF}$ ,  $\text{COF}_2$ ,  $\text{SO}$ ,  $\text{CO}$ ,  $\text{SOF}_x$ ,  $\text{SO}$  and  $\text{SO}_2$  can all be treated with this method.

In an effort to address some of the shortcomings of water and solid scrubbing packages, some manufacturers have added a heat-based destruction module. In this style system, a flame or electric heater is used to warm a porous ceramic or catalyst material; the exhaust gas passes through the heated material. Some of the gas components are oxidised in the process. In

Figure 1  
An LB1200 plasma abatement tool installed in the subfab. It operates directly above the roughing pump, using no floor space while consuming about the same energy as a handheld hair dryer. This facility uses the abatement tool to remove PFC content from the exhaust

this way, it is possible to treat all of the gases present in the original exhaust stream:  $\text{CHF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{SiF}_4$ ,  $\text{HF}$ ,  $\text{F}_2$ ,  $\text{COF}_2$ ,  $\text{CO}$ ,  $\text{SO}$ ,  $\text{SO}_2$  and  $\text{SOF}_x$ . Usually, the ceramic to gas heat exchanger assembly is susceptible to clogging or, in the catalytic case, poisoning, so a water-based pre-scrubbing stage is often included to eliminate particulates and  $\text{SiF}_4$ . The by-products of

the oxidation process are  $\text{COF}_2$ ,  $\text{F}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}$ ,  $\text{SO}_2$ , all of which must be scrubbed again, usually with a canister-type solid absorption column.

Plasma sources, which enjoy wide acceptance on the manufacturing side of the factory, are relative newcomers to the field of exhaust gas treatment. Surprisingly, they have been recommended for some time as a method for improving automobile emissions, but have never seen commercial use [1]. In the past few years, however, several plasma sources have been introduced for exhaust treatment applications in the semiconductor industry. Electrochemical Technologies Corporation (ETC) [2] introduced in the early 1990s the DryScrub™, a foreline plasma source to prevent solids buildup in CVD tool forelines. In 1998, Litmas introduced the Litmas Blue™ system for PFC emission reduction on etch tools. ASTeX, also in 1998, released the ASTRON™, a fluorine radical source for CVD cleans [3]. In 2000, a second plasma conversion system (Litmas Red™) was developed for CVD applications. This year, at least 5 other companies from Korea, Japan and the USA will introduce plasma tools for effluent treatment.

The use of plasma to treat semiconductor equipment exhaust offers several advantages over traditional burn and scrub techniques:

- *size*: plasma conversion systems typically are installed in areas using no valuable floor space (directly on a foreline drop, for example);
- *low energy usage*: direct excitation of the gas is inherently more efficient than a 2- or 3-stage heat transfer process, and treatment in the foreline occurs before dilution from dry pump purge gas;
- *low operating cost*: a full year of operation costs about \$500 USD for a typical nitride etch application.

Perhaps the most useful aspect of using plasmas to clean exhaust streams is the almost endless variety of chemistries possible. Flame burner and catalytic systems are limited to oxidation processes. Plasmas can be used as oxidisers, or with a change in mixing gas, can be reducing. With yet another change in chemistry, the plasma can reduce one species, while oxidising another. There is a corresponding change in the type of gases emitted. This flexibility allows facilities engineering to choose an exhaust gas composition that best fits the existing or planned equipment for handling factory exhaust gas.

Consider as an example a Litmas Blue™ plasma pollution treatment system installed in the foreline. It deposits 1200 W inductively into the exhaust gas prior to its dilution in the dry pump. A typical install on an etch system is shown in Figure 1. A mixing gas is introduced to the foreline just prior to the plasma system. When used on an etch exhaust, larger molecules of both the exhaust and mixing gas are broken into fragments in the plasma. They then flow through the plasma region, and recombine to form a new set of exhaust gases more suitable for treatment via existing facilities. Two chemistries are discussed as examples: one suitable for water scrubbing, and another ideal for dry absorption treatment.

The raw exhaust gas stream on a 40 sccm  $\text{CF}_4$  and argon etch process consists predominantly of  $\text{CF}_4$ ,  $\text{F}_2$ ,  $\text{COF}_2$  and  $\text{SiF}_4$ , as shown in Figure 2. For water scrubbing it is desirable to have as many of the fluorine atoms arrive as  $\text{HF}$ , a form with a high water capture probability. Formation of  $\text{HF}$  is a reduction process, and requires the presence of available hydrogen. But it would also be desirable for the carbon to be converted to  $\text{CO}_2$ , so some free O is also necessary. Water vapour contains the ideal 2:1

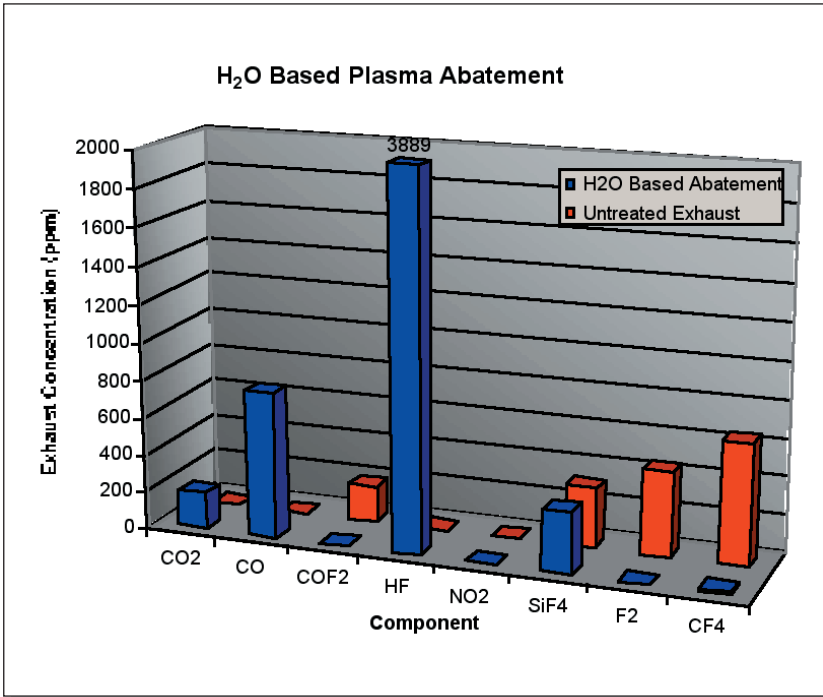


Figure 2 Gas product distributions for untreated etch tool exhaust and exhaust that has passed through a water vapour-based abatement plasma. Notice that the fluorine atoms leave the plasma in the form of  $\text{HF}$  or  $\text{SiF}_4$ , both of which are easily caught in a water scrubber

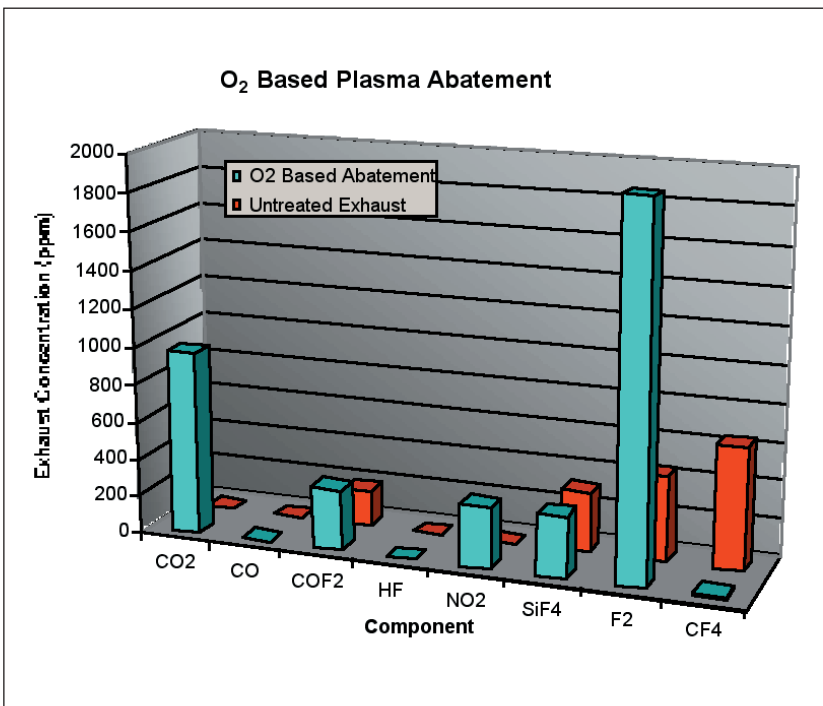


Figure 3 Gas product distributions for untreated etch tool exhaust and exhaust that has been treated in an oxygen-based abatement plasma. In this case, the fluorine atoms leave as  $\text{F}_2$ , a form that is readily absorbed in a dry absorption treatment system.

ratio of H to O for  $CF_4$  conversion, thus it is chosen as the mixing gas. The components of the resulting gas stream are also shown in Figure 2.  $CF_4$ ,  $F_2$ , and  $COF_2$  are nearly eliminated—converted to  $CO$ ,  $CO_2$  and HF. After a water scrubber, only  $CO_2$  remains.

Suppose the factory was located in an area which has severe restrictions on water usage (Phoenix, Arizona, USA, for example). In this case, the facilities manager might choose a dry treatment system over a water-based scrubber. In this case,  $F_2$  is more desirable than HF in the exhaust. If the mixing gas in the foreline plasma is changed from  $H_2O$  to just  $O_2$ , then the exhaust gas chemistry is changed as well, as is shown in Figure 3. The exhaust is still low in  $CF_4$ , but now there is little HF. The incoming fluorine molecules leave in the form of  $F_2$  (and a small amount of  $COF_2$ ).

The use of plasma sources to modify exhaust characteristics is not limited to the foreline. An atmospheric plasma system can be used after the roughing pump to obtain a similar result. Atmospheric discharges differ from their low pressure cousins in that the electrons and ions have temperatures that are closer together, so the gas molecules get very hot. In the case of Litmas' atmospheric abatement source, a plasma is formed from the effluent stream using a microwave chamber. Using similar mixing gas arrangements, oxidising or reducing environments can be used to shape the chemical profile of the exhaust stream. A picture of the Litmas Red™ atmospheric system (with the cover removed) is shown in Figure 4. This type of system is useful for CVD applications such as the nitride process discussed earlier in this article.

Plasma treatment systems offer advantages over flame or catalytic-based systems not only in the variety of possible operating chemistries, but also in cost. Both the hardware and the running costs are lower than for burner or catalytic systems. Plasma devices deposit their energy directly in the gas stream, while flame or catalytic systems only indirectly deposit energy. A plasma system consuming 5 kW total power can create the same oxidising chemistry as a methane burner using more than 105 kW of fuel. Further, all of the energy that goes into a system must come out again, usually in the house cooling water. Lower energy use in the plasma translates to lower load on the cooling water, and overall energy savings for the factory. Figure 5 shows a per-chamber cost analysis of foreline plasma, post-pump plasma, thermal, and catalytic abatement systems.

### CONCLUSION

Long the favoured environment for preparing thin films on wafers, now plasma tools offer facilities personnel greater flexibility in the sub-fab as well. These tools use no sub-fab floor space, save energy, save cost, yet still manage to beat foreseeable emissions standards for the next decade. A facilities engineer can choose a treatment chemistry most suitable for existing or new equipment, thus minimising the emissions profile of the plant—reducing its environmental footprint.

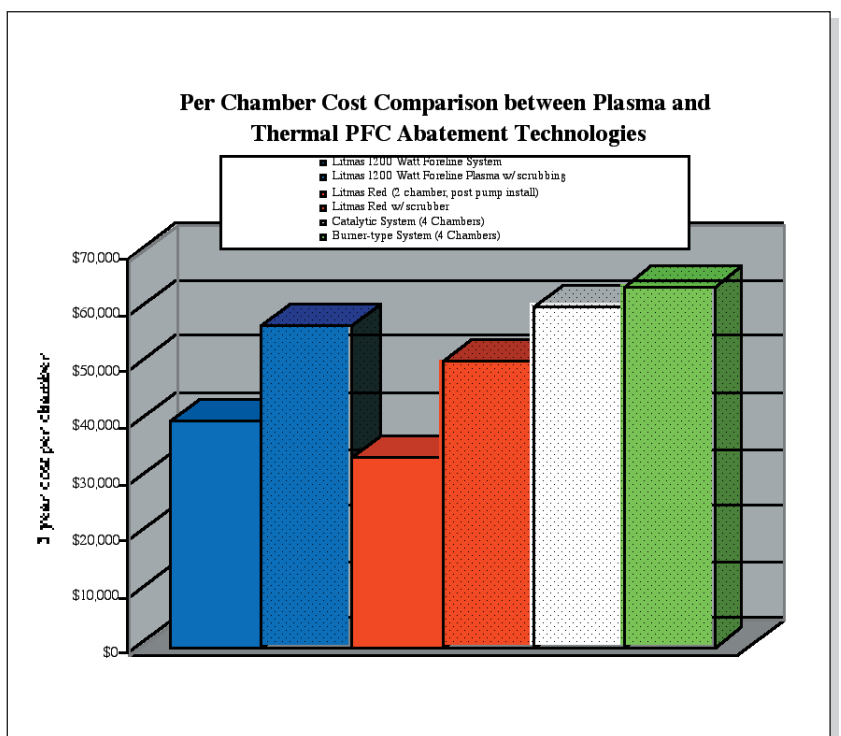
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- [1] SI2.04: "Plasma Boosted Hydrogen Generation for Vehicle Pollution Reduction", Daniel R. Cohn (Massachusetts Institute of Technology Plasma Science and Fusion Center), 41st Annual Meeting of the Division of Plasma Physics, American Physical Society, November 18, 1999
- [2] <http://www.dryscrub.com/>
- [3] <http://www.astex.com/>



Figure 4  
The plasma source in the Litmas Red™ atmospheric pressure abatement system, with its protective covers removed. The plasma plume shown is formed from 100% nitrogen, using only electricity as fuel. The diameter of the plasma region is 5 cm

Figure 5 (below)  
A comparison of the 5-year costs of thermal- and plasma-based treatment systems. The low energy usage of the plasma systems makes them very cost efficient. Costs were modelled with a 5-year capital cost amortisation, including installation and direct utilities cost. The model does not include indirect costs such as the heat load on the factory



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**ABOUT THE AUTHORS**

Rusty Jewett is one of the founders of Litmas, Inc. and is currently serving as its President. His work is focused on high performance plasma sources, with emphasis on environmental remediation. The first product from Litmas was designed to use plasmas to treat perfluorinated compounds. Prior to Litmas, he was a member of the corporate research staff at Lam Research Corporation, where he has several semiconductor hardware-related patents. His work there included improved impedance matching algorithms and new methods for exciting plasmas for thin film applications.

Dr. Eric Tonnis is a senior applications engineer at Litmas. He recently received his PhD degree in chemical engineering at the University of California at Berkeley under the direction of Prof. David Graves. His PhD dissertation studied the application and mechanisms of point-of-use plasma abatement for destruction of FCs from semiconductor etch processes. Contact e-mail: [tonnis@litmas.com](mailto:tonnis@litmas.com).

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