

CVD: CLEANING

Advances in Remote Plasma Sources For Cleaning 300 mm and Flat Panel CVD Systems

By Xing Chen, William Holber, Paul Loomis, Evelio Sevillano and Shou-Qian Shao, MKS Instruments, and Scott Bailey and Michael Goulding, STMicroelectronics

SEMICONDUCTOR EQUIPMENT COMPONENT suppliers are now required to develop and provide application-specific subsystems that involve more and more process expertise and equipment engineering know-how [1]. In this article, we describe the evolution and operating characteristics of a compact integrated subsystem for cleaning chemical vapor deposition chambers used in processing 300 mm integrated circuit wafers and flat panel display substrates.

INTRODUCTION

A key to high productivity for many chemical vapor deposition (CVD) processes is the cleaning step that keeps the chamber and tooling free of unwanted deposits. Over the past 20 years, the industry has moved from periodic manual (wet) cleaning of the chamber interior to routine *in situ* plasma cleaning and, finally, to remote plasma cleaning. Each evolutionary step has brought increased throughput, decreased tool maintenance and lowered the overall cost of ownership.

The first major evolutionary step was the replacement of manual cleaning of the process chamber by an *in situ* radio frequency (RF) plasma clean. However in many cases, the length of time it took to do *in situ* RF plasma cleaning limited throughput. In addition, the technique did not clean chamber parts shielded from the plasma, and the chamber and tooling surfaces were damaged by ion bombardment, requiring periodic process kit changes.

The next evolution was the first generation of “remote” plasma cleaning systems using a microwave plasma generator external to the process chamber. Today, new high-efficiency RF remote plasma cleaning sources efficiently dissociate perfluorocompound (PFC) input gases, an important attribute in light of the semiconductor industry’s commitment to reduce atmospheric emissions that contribute to global warming [2].

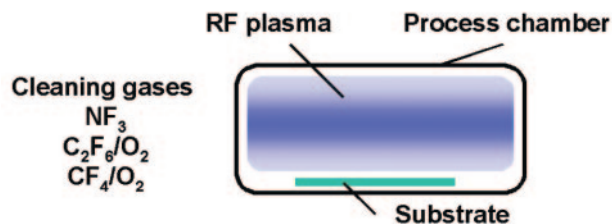
EVOLUTION OF CVD CHAMBER CLEANING METHODS

For many CVD processes, the task of keeping the chamber and tooling free of unwanted deposits occupies much of the avail-

able tool time, limiting wafer throughput. The first CVD chamber cleaning methods used labor- and time-intensive wet cleaning with acids and solvents. This was supplanted by *in situ* RF plasma cleaning using reactive gases (Figure 1). If the tool was used for a plasma-assisted deposition, the RF generator and electrodes were already present. In other cases, such as thermal low-pressure CVD deposition, the hardware for RF clean had to be added.

Although faster and more efficient than manual wet-cleaning procedures, *in situ* RF plasma cleaning suffered from a number of deficiencies: it was slow, did not clean chamber parts that were not directly exposed to the plasma, and the ion bombardment sputter eroded the chamber and tooling surfaces. This required expensive and time-consuming process kit changes. In addition, the PFC gases used for the cleaning steps were, in most cases, not completely dissociated, leading to undesirable exhaust gas emissions. To remedy the disadvantages of traditional RF plasma cleaning, so-called “remote” plasma cleaning was evaluated as an alternative to direct plasma cleaning. ➔

FIGURE 1



In situ plasma cleaning requires chamber RF to be operating. All portions of the process chamber are bombarded by reactive gas ions. Thermal CVD systems require an added RF power supply.

REMOTE PLASMA CLEANING: THE SCIENCE

In contrast to *in situ* RF cleaning methods where the cleaning occurs from a combination of ion bombardment-induced and chemically induced reactions, remote chamber cleaning involves a purely chemical reaction. The key factors in this chemical process are the production, transport and reaction rates of the active species.

PRODUCTION OF THE ACTIVE SPECIES

Feed gas is supplied to the remote plasma source, which dissociates the input gas into its constituent atoms. In many cases, the dissociation fraction can exceed 95 percent. When NF_3 is used as an input gas, the plasma in the remote plasma source will dissociate nearly 100 percent of the gas, resulting in a mixture of atomic fluorine (F), atomic nitrogen (N), molecular fluorine (F_2) and molecular nitrogen (N_2) leaving the plasma source. Important issues relative to the plasma source itself are range of operation (flow rate and pressure), dissociation efficiency, and resistance to erosion from chemical attack and ion bombardment.

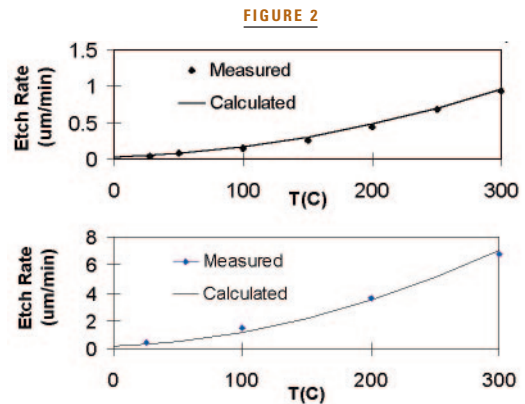
Transport of the active species

The atomic species must pass from the plasma source to the interior of the process chamber. The transport region may, for example, consist of a short connecting tube and the shower-head of the process chamber. In this region, no new atomic species are created, only lost. It is advantageous to make the transport space as short as possible to minimize the residence time and the opportunity for loss of the active species through recombination or reaction with surfaces and other gaseous species. Important issues relative to the transport region are the construction materials (which impact both recombination of the active species and potential for contamination), the length and diameter of the region (which impacts residence time) and the cooling of the transport region, since considerable thermal energy can be deposited into the transport region by recombining neutral species (particularly atomic nitrogen).

Reaction rates

In the process chamber, the active species react with wall deposits, converting them to volatile compounds through a chemical-etching process. The wall surface temperature is critical, as both the reaction rate and volatilization are thermally activated. The construction materials used for the chamber's internal parts are also very important, as they must be resistant to attack by the reactive species. Common construction materials for both the transport region and the chamber's internal parts include aluminum, anodized aluminum and ceramics.

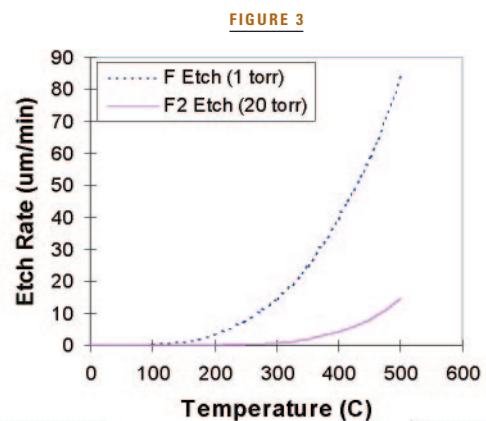
Atomic fluorine, a common example of chamber-cleaning reactant species, can be used to clean a variety of films. The reaction rate for the film removal depends on both the local concentration of atomic fluorine and the temperature of the surface being cleaned. As long as the atomic fluorine concen-



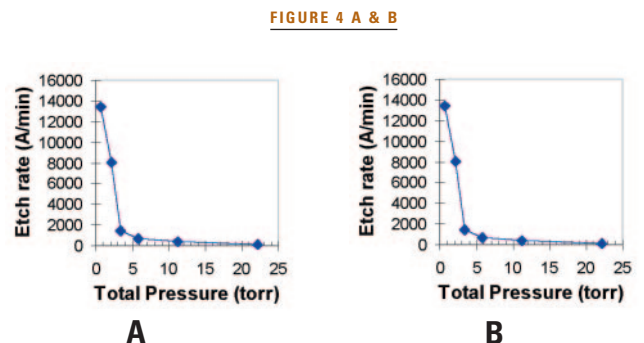
Predicted and experimental results for etching of thermal SiO_2 samples using remote etching by F generated from NF_3 using a high-efficiency RF plasma source. Pressures measured prior to plasma ignition.

Top: NF_3 flow rate 0.19 slm, Ar flow rate 0.19 slm, total pressure 0.95 Torr. Bottom: NF_3 flow rate 2 slm, Ar flow rate 2 slm, total pressure 5.5 Torr.

Note that the rates shown are higher than what would be obtained in a typical CVD chamber, since the etch rate measurements were taken under idealized conditions (see text).



Predicted etch rates of W by F and F_2 . Modeling parameters from Rossner, et al. [5]



Measured etch rate of W films in a test chamber using a high-efficiency plasma source.

A. Sample temperature 150°C, flow rates 150 sccm NF_3 , 750 sccm Ar.

B. Sample temperature 400°C, flow rates 150 sccm NF_3 , 300-900 sccm Ar.

tration is not rate limiting, the reaction rate will generally be exponentially dependent on the surface temperature.

Etching of silicon dioxide

The etch rate of silicon dioxide (SiO_2) films etched by F atoms has been experimentally determined to be [3]:

$$\text{Rate (microns/min)} = 6.14 \times 10^{-17} N_F T^{1/2} e^{-1892/T},$$

where N_F is the concentration of fluorine atoms per cm^3 and T is the temperature in Kelvin.

The etch rate is directly proportional to the local concentration of fluorine atoms, and the temperature dependence is somewhat faster than exponential. The study also showed that over the temperature range examined, there is negligible etching of SiO_2 due to F_2 .

MKS Instruments conducted a set of etching experiments using thermal SiO_2 samples under conditions similar to those found in a CVD remote chamber-clean application. A high-efficiency plasma source was used to dissociate the NF_3 input gas [4]. Previous measurements showed the NF_3 dissociation under these conditions to be nearly 100 percent. The results (etch rate vs. temperature) are shown in Figure 2 for two conditions of flow rate and pressure.

The etch rates are higher than those found in a typical chamber-clean application, since the output of the plasma source is directed toward the etch sample with no intervening showerhead or gas baffle to spread the flow of atomic fluorine and reduce its concentration by surface recombination. We found a close correlation between the measured rate and the rates predicted by the above equation.

An important parameter is the NF_3 flow rate. For example, the results indicate that at 200°C , the ability to increase the NF_3 flow rate by a factor of 10 also increases the etch rate by 10 times.

Etching of tungsten

Rosner, et al. measured etching of tungsten (W) films due to both F and F_2 [5]. They found, in contrast to the SiO_2 case, that there was measurable etching of W by F_2 , although at a much lower rate than by F, as the activation energy for F_2 etching of W films is much greater than for F etching. The etch rates that they determined were:

• for F etching:

$$\text{Rate (microns/min)} = 2.92 \times 10^{-14} T^{1/2} N_F e^{-3900/T}$$

• for F_2 etching:

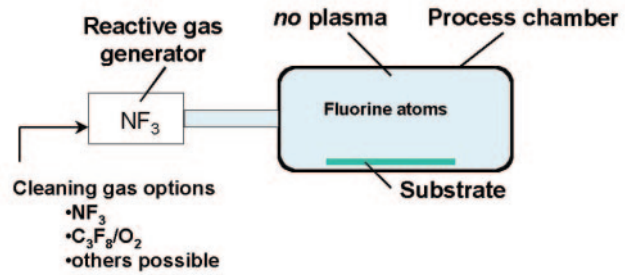
$$\text{Rate (microns/min)} = 6.6 \times 10^{-15} T^{1/2} N_{\text{F}_2} e^{-6432/T},$$

where N_F is the concentration of fluorine atoms per cm^3 , N_{F_2} is the concentration of fluorine molecules per cm^3 and T is the temperature in Kelvin.

Figure 3 plots the etch rates of W vs. temperature expected from the above relationships. The partial pressures of F and F_2 were selected as examples of possible cleaning conditions. The relation predicts that for a given temperature, the etching due to F_2 will be about one-fifth to one-tenth that due to F, and that significant etching by F_2 requires a temperature above 300°C .

We also conducted etching experiments using W film samples under conditions similar to those found in a CVD

FIGURE 5



Remote reactive radical cleaning. No plasma within the process chamber and no ion-bombardment erosion of reaction chamber. The selective chemical reaction of atomic fluorine radicals with the chamber coating is thermally driven.

FIGURE 6



Example of first-generation remote plasma cleaning source. The equipment utilizes a microwave discharge at 2.45 GHz.

FIGURE 7



Second-generation CVD chamber clean subsystem incorporating a remote plasma source.

remote chamber-clean application, using the same high-efficiency plasma source as in the SiO_2 experiments. For these experiments, a baffle plate was introduced between the entrances of the gaseous species into the process chamber and the W film sample to better simulate the etch rates expected in an actual process chamber. The results (etch rate in $\text{\AA}/\text{min}$ vs. total pressure) are shown in Figure 4 for two temperatures (150°C and 400°C), using argon/ NF_3 mixtures. For the 400°C experiments, the Ar/ NF_3 flow ratio was increased with higher total pressures. The NF_3 dissociation under these conditions was found to be nearly 100 percent. The peak in the etch rate near one torr pressure is due to the atomic fluorine (F) that is lost at higher pressures due to recombination effects. The gradual increase in etch rate at the higher pressures shown in Figure 4B is attributed to molecular fluorine (F_2), which does not decrease in concentration as the pressure is increased.

APPLICATION OF REMOTE PLASMA CLEANING

The first application of the results of our experimental research on remote plasma cleaning was the use of a separate plasma discharge upstream of the deposition chamber to dissociate fluorine-bearing cleaning gases. As the atoms diffuse into the deposition chamber, they react with the deposits to produce volatile fluorides (Figure 5). As there is no direct ion-bombardment, there is minimal erosion of chamber walls and tooling.

This first generation of remote plasma-clean hardware used microwave-based discharges [6]. While the microwave-based sources were generally technologically successful and were implemented across a range of 200 mm deposition chambers, their flow-rate capability was generally limited and required a fairly complex and bulky set of supporting microwave hardware (Figure 6).

Extending plasma-clean technology to systems requiring a smaller footprint and higher gas flow rates, such as process tools for 300 mm wafers and flat panel substrates, required the development of a radically new technique for generating the remote plasma discharge. The second generation of remote chamber clean plasma sources required a technology that could supply the advantages of the microwave-based techniques (wide range of operation and acceptable lifetime of the plasma discharge chamber) while also reducing cost, size and complexity and allowing for extendibility to larger process chambers and higher flow rates.

The technique pioneered by MKS Instruments uses a compact, inductively coupled toroidal plasma chamber operating at 400 kHz (Figure 7). More than 3,000 such units are in use for applications involving chamber cleaning using NF_3 . These second-generation reactive gas generators were two to five times smaller in footprint, weight and cost as compared to their microwave plasma predecessors. Unlike microwave-based systems that required several individual components to be assembled into a single subsystem, all components were within a single, compact enclosure. The high-efficiency plasma source had an integrated electronic control, power supply and cooling system, and was rated for continuous

FIGURE 8

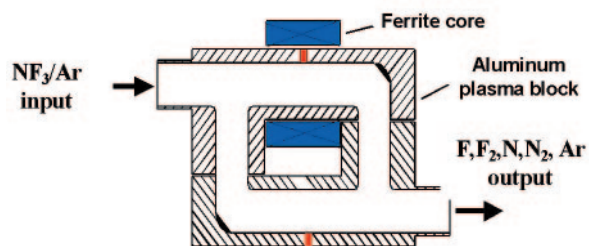


Diagram of high-efficiency toroidal plasma source.

FIGURE 9

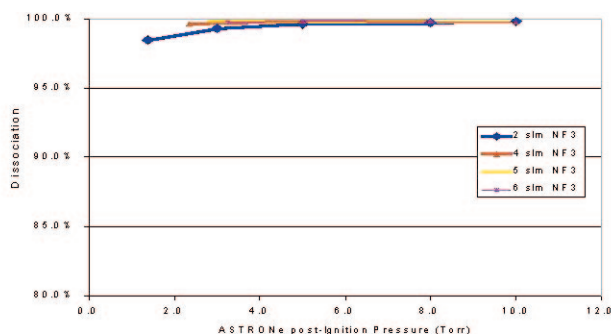


Examples of third-generation CVD chamber clean subsystems.

Left: ASTRONe remote plasma source. Right: ASTRONi remote plasma source.



FIGURE 10



Percent NF_3 dissociation vs. exit port pressure and NF_3 flow rate (without argon) for MKS ASTRONe toroidal plasma reactive gas generator.

operation. The unit was small enough to be mounted directly on the process chamber lid, thus eliminating the need for remote mounting.

Figure 8 is a diagram of the basic functional element of the first ASTRON Series products. A built-in control unit handles I/O from the process tool to sequence the cleaning operation and automatically controls the power level and monitors for abnormal operation. RF power is supplied by 400 kHz switching power supply technology with feedback control from the plasma current. The plasma itself acts as a closed-current-loop secondary of a transformer circuit that couples electromagnetic energy directly into the source reaction chamber. An on-board RF generator drives the primary of the transformer circuit. The plasma is contained within a 2.5 cm-diameter cylindrical channel that is machined into a conductively cooled block of aluminum. The electric fields within the plasma are kept low (~ 4 V/cm) to minimize sputtering of the plasma chamber walls.

INCREASING FLOW CAPACITY AND PROCESS FLEXIBILITY

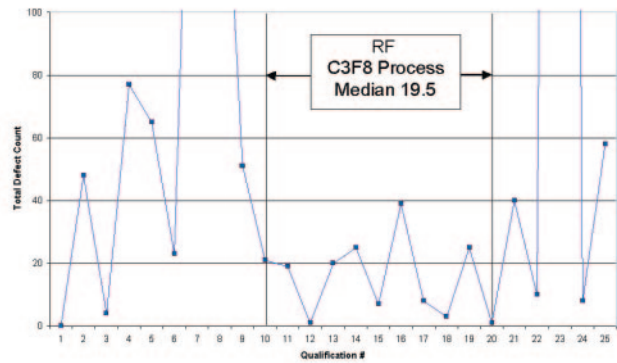
The first designs of these high-efficiency plasma sources limited the maximum gas flow rate to two standard liters per minute (slm) for NF_3 . Argon was typically required both for ignition of the plasma and for operation. Cleaning gases other than NF_3 could be used only in low flow-rate applications. Larger process chambers for 300 mm wafers and flat panels required using higher-cleaning gas flow rates to obtain acceptable cleaning rates. To meet these needs, we developed a third generation of atomic fluorine sources with a higher flow-rate capability, an extended operating pressure range with high-dissociation efficiency, and the possibility of operating with gases other than NF_3 (Figure 9). The operating characteristics of the extended flow-range product, when operated with 100 percent NF_3 as the input gas are shown in Figure 10. The dissociation fraction of NF_3 is near 100 percent over a wide pressure range.

A further advantage of these third-generation sources is that they can operate with gases such as CF_4 , C_2F_6 , and C_3F_8 at flow rates up to two slm. With these fluorocarbon gases, oxygen (O_2) must be added to scavenge carbon from the gas stream. This offers the user increased flexibility to optimize production processes for throughput, gas costs and facilitization expenses. Table I lists representative data for the relative etch rates of thermal SiO_2 samples using various flow rates for NF_3 and $\text{C}_3\text{F}_8/\text{O}_2$ gas mixtures. These data were measured in a test chamber using the ASTRONe remote plasma source, and while the absolute etch rates may or may not represent what will be obtained cleaning a CVD deposition system, the results indicate that a $\text{C}_3\text{F}_8/\text{O}_2/\text{Ar}$ mixture can achieve etch rates similar to that obtained using one slm of NF_3 .

EVALUATION OF REMOTE RF CLEANING IN PRODUCTION

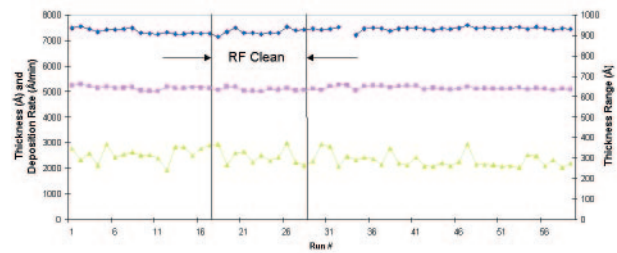
An evaluation was done on a commercial plasma-enhanced CVD (PECVD) SiO_2 reactor in which the second-generation remote NF_3 plasma source was replaced with a third-generation

FIGURE 11



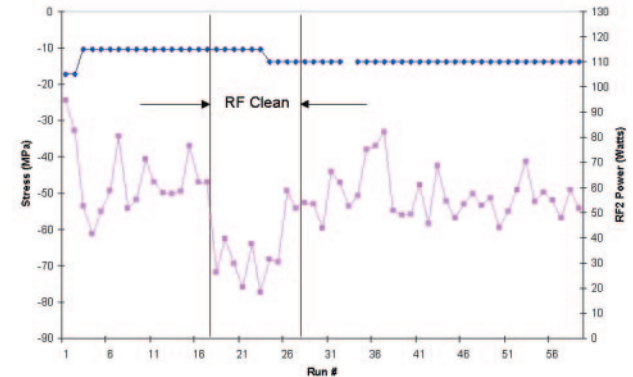
Trend chart for defects $>0.2 \mu\text{m}$ for an SiO_2 PECVD process. Chamber is cleaned with an optimized remote plasma $\text{C}_3\text{F}_8/\text{O}_2$ clean. (from Ref. 7).

FIGURE 12



Trend chart of thickness (purple), deposition rate (blue), and thickness range (green) for a 5-kÅ-thick TEOS PECVD-deposited SiO_2 film. Chamber is cleaned with an optimized remote plasma $\text{C}_3\text{F}_8/\text{O}_2$ clean (from Ref. 7).

FIGURE 13



Trend chart of RF power setting during deposition (RF2, blue) and as-deposited film stress (purple) in 5-kÅ-thick TEOS PECVD-deposited SiO_2 film. Chamber is cleaned with an optimized remote plasma $\text{C}_3\text{F}_8/\text{O}_2$ clean (from Ref. 7)

TABLE 1

Etch rates obtained in test chamber using thermal SiO₂ samples and input gases of NF₃ and C₃F₈/O₂/Ar, operated with an ASTRONe remote plasma source. Sample temperature was 100°C in all cases.

Gas Flow Rates (slm)	Pressure (torr)	Average Etch Rate (nm/min)
Ar – 1 NF ₃ – 1	3	156
Ar – 2 NF ₃ – 2	4	209
Ar – 4 O ₂ – 1.5 C ₃ F ₈ – 0.75	5.6	118
Ar – 4 O ₂ – 1.5 C ₃ F ₈ – 0.75	6.1	129
Ar – 4 O ₂ – 1.5 C ₃ F ₈ – 0.75	6.6	122
Ar – 4 O ₂ – 1.88 C ₃ F ₈ – 0.75	5.6	122
Ar – 4 O ₂ – 2 C ₃ F ₈ – 0.75	6.8	155


ASTRON high-efficiency, high-flow source. The cleaning results obtained using C₃F₈/O₂/Ar gas mixtures were compared to the NF₃ results obtained using the original plasma source [7].

The clean process was optimized using a design-of-experiment matrix of the key variables: C₃F₈ flow rate, oxygen/C₃F₈ ratio, and pressure. The outcomes optimized were cleaning etch rate; emissions of SiF₄, C₃F₈, and other gaseous byproducts; film uniformity and particle adders. Extractive Fourier Transform Infrared (FTIR) spectroscopy was used to measure the effects of process variables on the mass of SiF₄ removed and the net PFC emissions at the vacuum pump exhaust. When the RF plasma clean unit was operating with C₃F₈/O₂, there was no C₃F₈ detected in the pump exhaust. This suggests that the destruction efficiency is greater than 99.9 percent during operation with the optimized process.

The results are shown in Figures 11 to 13 as trend charts for particle adders, thicknesses, stresses and power settings. The

positive effects were the reduction in particle count and deposition power (RF₂) required when the remote plasma C₃F₈/O₂ clean was used, compared to the remote NF₃ clean. The other effects were neutral to the cleaning method.

SUMMARY

Remote plasma cleaning of the CVD deposition systems employed in manufacturing semiconductors and flat panel displays has been widely accepted and implemented. The first-generation technology for remote plasma cleaning used microwave plasma sources. The second generation of equipment used a toroidal high-efficiency RF plasma source that provided significant process flexibility and greatly reduced the size, weight, complexity and cost compared to microwave technology. The current third generation of equipment, also based on toroidal plasma technology, offers significant expansion in process flow rate and pressure operating ranges, including the capability to operate with cleaning gases other than NF₃, thus allowing more flexibility for process and cost optimization. 

ACKNOWLEDGEMENTS

ASTRON is a registered trademark of MKS Instruments, Inc.

The authors would like to thank International SEMATECH for its evaluation of the ASTRON remote plasma source in the study of cleaning methods comparing C₃F₈/O₂/Ar mixtures to NF₃.

REFERENCES

1. P. Blackborow, "Everybody Has to Be a Process Expert Now," Semiconductor International 24(2), Supplement: Equipment Components and Subsystems, Feb. 2001, p. 2.
2. Proceeding of the Global Semiconductor Industry Conference on Perfluorocompound Emission Control, Monterey, Calif., 7-8 April 1998.
3. D.I. Flamm, "Plasma Etching: An Introduction," D.M. Manos and D.L. Flamm, eds., Academic Press (1989), p. 118.
4. MKS Instruments ASTeX ASTRON series of remote plasma sources.
5. Daniel E. Rosner and H. Donald Allendorf, "Kinetics of the Attack of Refractory Solids by Atomic and Molecular Fluorine," The Journal of Physical Chemistry, 75(5), 1971, p. 308-317.
6. See for example, S. Raoux, et al., "Remote microwave plasma source for reducing chemical vapor deposition chambers: Technology for reducing global warming gas emissions," J. Vac. Sci. Technol. B 17(2), pp. 477-485 (March/April 1999).
7. S. Bailey, M. Goulding, L. Tousignant, L. Zazzera and S. Shao, "Evaluation of an MKS ASTRONex and C₃F₈ for Remote Plasma Chamber Clean," presented at SEMICON West Technical Symposium (2002), ISBN #1-892568-75-6/02.

Reprinted with permission from Semiconductor Magazine, August 2003.



Six Shattuck Road
Andover, MA 01810-2449
Tel: (978) 975.2350
Tel: (800) 227.8766 within U.S.A.
Web: www.mksinst.com