Wafer Cleaning: Wet Methods Still Lead the Pack

As cleanliness and environmental demands grow, the industry standard RCA clean is slowly giving ground to a multiple choice list of alternate wafer cleaning options.

Ron Iscoff, West Coast Editor

As feature sizes continue their frantic descent into the sub-0.5 μm region, wafer cleaning is on its way toward becoming a true enabling technology.

Ridding wafers of their process chemicals is one of the most common steps in fabrication. It's also, often a dirty one, in terms of picking up contaminants. The heavy metals, alkali metals and light elements, all common to wafer processing, also threaten silicon devices (Table 1).

Wafer cleaning systems can be a major source of submicron particulates that are difficult to detect. One way to detect them, says Paul Paduano, diffusion section head of Micron Semiconductor, is with a deposited film to "decorate" the defects.

Key factors

The type of cleaning equipment, its age and its original cost are key factors in the amount of wafer contamination a user is likely to find, says Gary DePinto, a thin film section manager for Motorola.

"There is equipment available that addresses most contamination problems, for example, hoods and recirculation systems," says DePinto. "If you're willing to spend the money, it's available."

Heavy metal "dirt" looms large at Philips Semiconductors (Sunnyvale, Calif.). The company, formerly Signetics, processes 100 mm wafers for bipolar analog devices.

"Our first concern is removing heavy metals and making a chemically-clean surface," reports Alan Mertens, engineering manager for Fab 1. The second concern is to achieve a low particle count for optimum yield. Current systems are adequate, using the RCA clean and megasonic cleaning methods. "They give us clean wafers and only the driers cause problems," Mertens says.

"There is equipment available that addresses most contamination problems. . . "

There are two principal methods of cleaning wafers: gas-phase — dry cleaning — (Figs. 1 & 2) and liquid phase — wet cleaning — (Figs. 3 & 4.) Although the respected "standard clean," the RCA wet clean, continues its foothold, other technologies, including dry methods, are beckoning to users.

Two-step cleaning

Dr. Werner Kern, then at RCA Laboratories, devised the RCA clean for RCA's use in 1965. He detailed the process publicly five years later. (Table 2). This two-step clean is an oxidizing and complexing treatment. It employs aqueous H_2O_2 - NH_4OH and H_2O_2 - HCl mixtures at 75-80°C for 10 min.

Chemically, it works, says Kern, now a consultant, because H_2O_2 at a high pH is a powerful oxidant, that destroys organic contaminants, and decomposes to H_2O + O_2. NH_4OH is a strong complexant for many metals.

Furthermore, HCl in H_2O_2 forms soluble alkali and metal salts by dissolving and/or complexing. These mixtures also meet a chief criteria for wafer cleaning: they won't attack Si or SiO_2 when properly formulated.

Effective? Yes, but these mixtures employ chemicals that are potentially toxic and harmful to the environment.

The use of advanced wet-chemical cleaning for making ultrapure silicon wafers will persist for several more years, says Kern. The trend, however, is from liquid to gaseous reactants.

"Eventually and ideally," Kern adds, the entire cleaning sequence will be conducted *in situ* by a sequence of gas phase reactions at low or reduced pressure with elevated temperature. This will take place in a cluster tool integrated with other cluster modules for film deposition, annealing, dry etching and other fabrication steps.

Tightened parameters

Future wafer cleaning demands include further tightening of parameters. For instance, Kern notes, a 200 mm silicon wafer for 64Mb DRAMs needs particle

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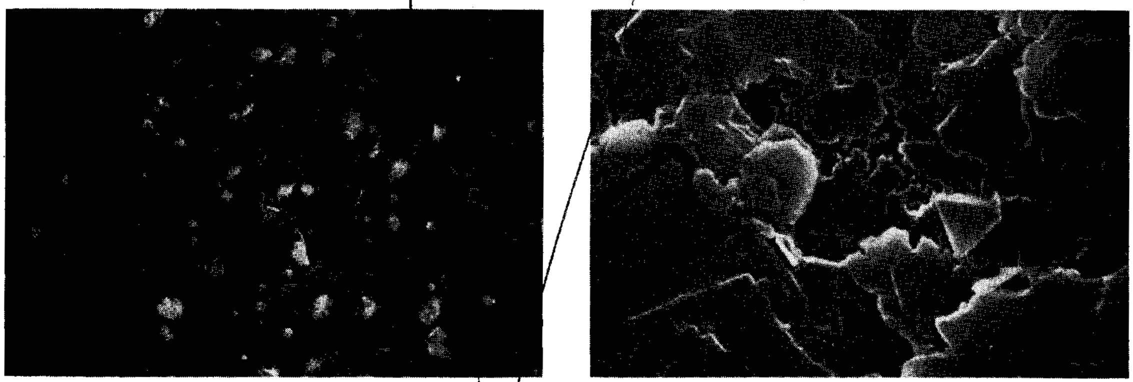

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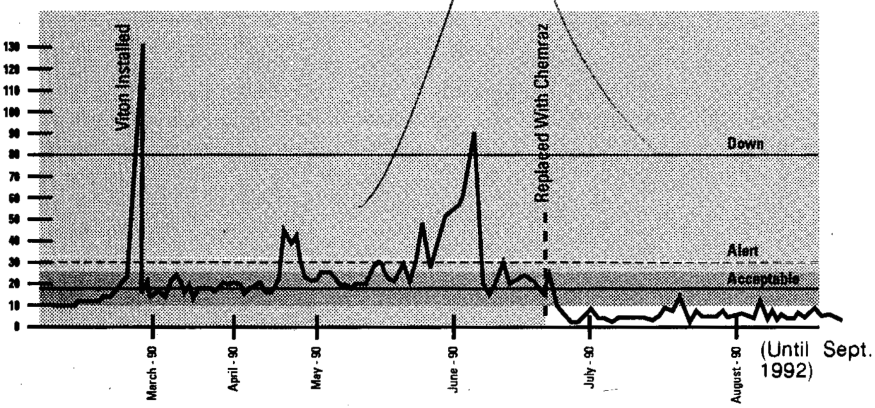

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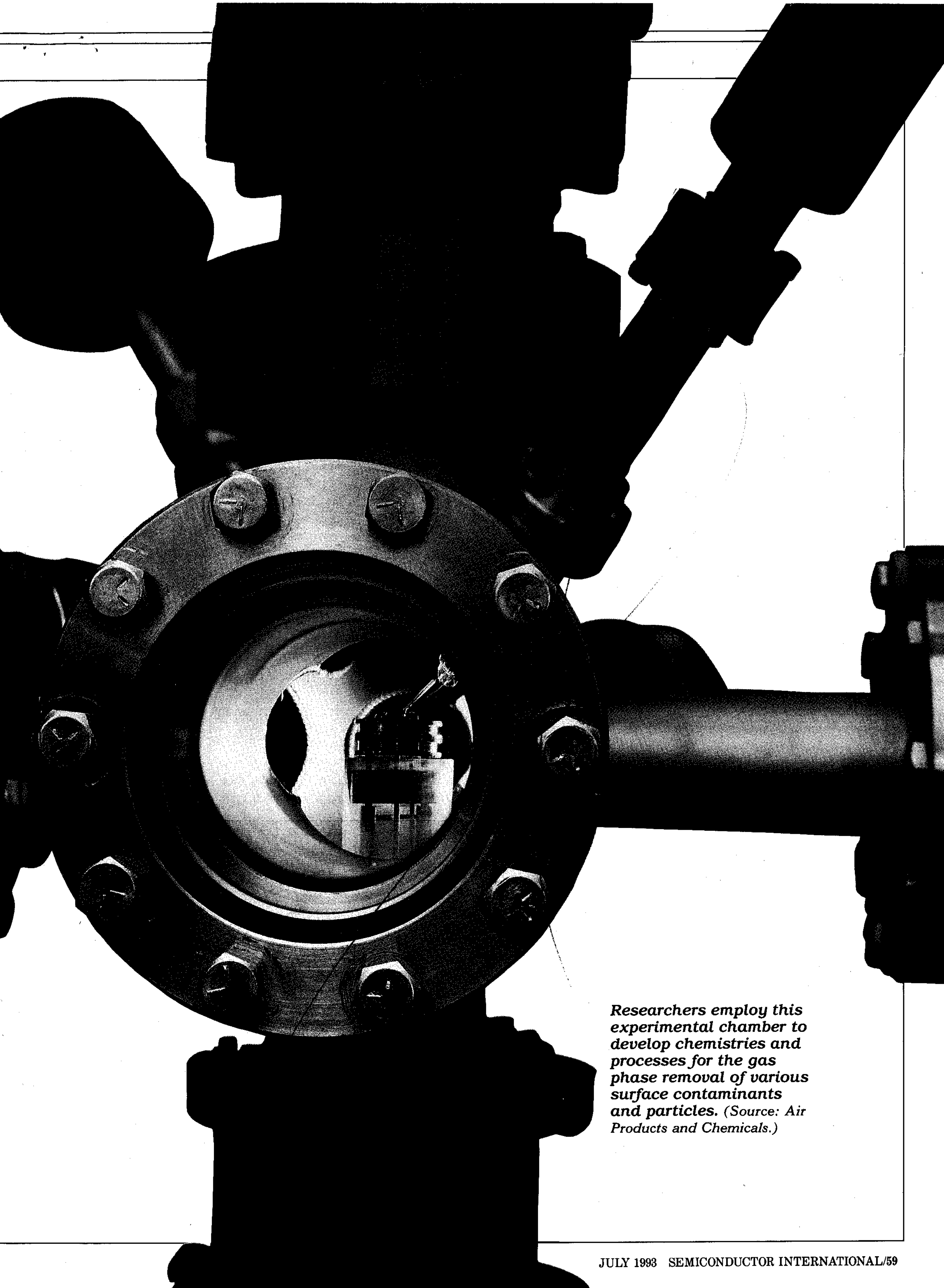


Researchers employ this experimental chamber to develop chemistries and processes for the gas phase removal of various surface contaminants and particles. *(Source: Air Products and Chemicals.)*

levels of ≥ 0.1 μm cut to >10/wafer. Alkali and heavy metal elements must be $>10^{10}$ per cm^2 surface. The light metal ion requirement will be $>10^9$ per cm^2.

Dr. Jerzy Ruzyllo of Pennsylvania State University, a wafer cleaning authority, contends that in time, the device fabrication process will become "cleaning-less."

He doesn't expect dry cleaning to replace wet cleaning, except in applications where wet cleans cannot be used.

Major trends

There are four major technology trends in wafer cleaning, says Bobby Greenberg of Prism Technologies. Prism represents Dainippon Screen, a major Japanese maker of cleaning equipment.

- 1. Decreased wafer contamination. "We think the goal for 1993 is x 10^{10} atoms/cm^2 metal contamination."
- 2. Particulate reduction to less than 10 particles of 0.3 μm or greater for a 200 mm wafer.
- 3. Reduced amounts and/or chemical concentrations used in cleaning wafers.
- 4. Control of the native oxide growth on the wafer's surface.

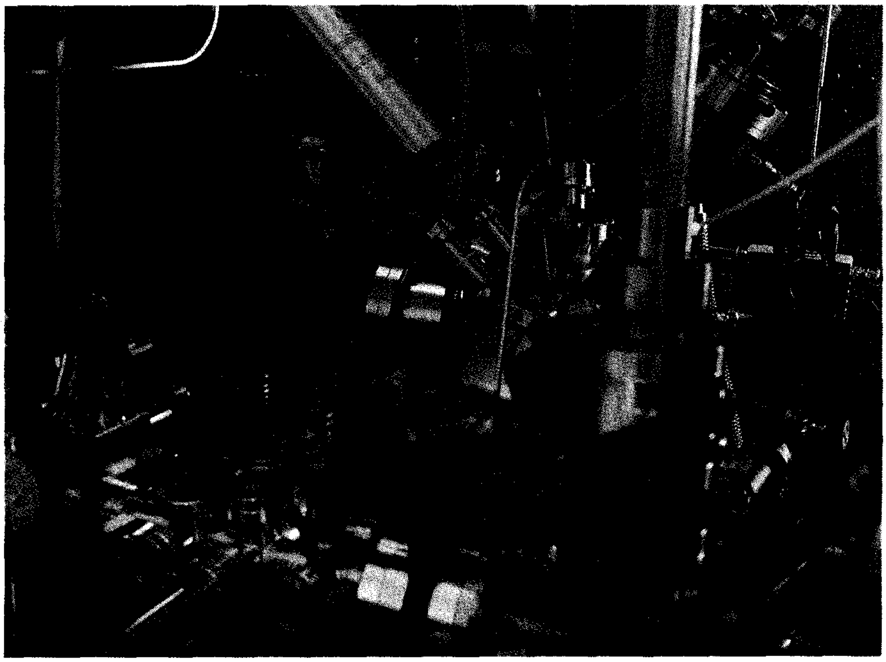
Spin scrub cleaning both sides of the wafer before chemical cleaning will cut particulate generation, Greenberg declares. In effect, the wafer scrubber becomes a pre-clean and the wet station is the final clean.

Tomorrow's problem, being generally recognized today, is the difficulty of removing smaller particles in the 0.1 μm (and smaller) range, adds Robert Donovan of Research Triangle Institute. Most of today's particle removal technology becomes less effective, Donovan adds, as particle size decreases.

The future of cleaning development will rely on application-specific uses, says Dr. Donald Deal, chief technologist for FSI International. Each clean, Deal adds, will have specific requirements dictated by the subsequent processing step. The variation in these requirements will cause a variation in the clean technology, sequencing and tool that the process engineer selects. This, Deal contends, will lead to variations in chemical sequence, chemical concentrations and changes to new chemistries. The bottom line: "All basic cleaning technologies, wet, vapor or dry, will be required and used either separately or in combination."

While the basic evaluation criteria for cleaning particles and metals will continue to be important, other factors — surface roughness, surface termination and oxide and growth characteristics — need to be completely understood, Deal says. Not only that, but cleaning success will increasingly be "based on electrical test as opposed to particles and metals."

In fact, Deal, whose firm is one of the largest suppliers of cleaning equipment, calls for a "holistic approach" to wafer cleaning needs. This means that the relationship between cleaning and the process steps prior and after must be understood and development completed together.



1. Brian Felker, an Air Products' senior research technician, performs surface analysis on a sample which has undergone a sodium ion removal process using chemical vapor cleaning.

Table 1. Technology Milestones

1950s	Early techniques (solvents, acids, brush cleaning, ultrasonics)
1970	RCA cleaning procedure published (Kern and Puotinen)
1972	First of over 30 papers verifying effectiveness of RCA cleaning (Henderson)
1974	General UV-O_2 cleaning described (Sowell, et al; Vig)
1975	First automatic spray machine for corrosives (FSI Corp.)
1976	Choline cleaning described (Asano, Cho and Muraoka)
1979	Megasonic system discussed (Mayer and Shwartzman)
1985	Megasonics for wafer cleaning (Shwartzman, Kern and Mayer)
1986	Closed system cleaning introduced (CFM Technology)
1987	UV-O_2 for preoxidation post-RCA cleaning (Ruzyllo) Anhydrous HF gas phase etching (FSI Corp.)
1988	Wafer dry cleaning feasibility considered (Ruzyllo)
1989	Replace RCA SC-1 with UV-O_2 (Ruzyllo) First international conference on wafer cleaning technology

Source: Werner Kern Associates

Dr. Fred Hiatt, also with FSI International, says the use of surfactants helps to overcome the inherent problems in wetting submicron features with cleaning chemicals.

Hiatt, project manager of new development, says spray cleaning is becoming a more realistic approach for smaller geometries. However, vapor-phase and dry gas-phase cleaning will be needed for the 256Mb devices with feature dimensions approaching 0.25 µm and smaller.

Compensating method

Many users, particularly those in Japan, are anxious to migrate to a more "HF-last" or "HF-only" process, claims Chris McConnell, chairman of CFM Technologies, West Chester, Pa., a cleaning equipment supplier.

The reason, says McConnell, is that the RCA clean is being recognized as a method designed to compensate for limitations in both chemical purity and wet processing techniques. The HF step is typically followed by the Standard Clean-1. This passivates the hydrophobic wafer surface before drying. Standard Clean-2, which follows, then works to remove surface metals that may be plated out onto wafers during SC-1 treatment.

"For many applications, SC-1 and SC-2 treatments are unnecessary if the wafer can be dried cleanly without adding particles following HF exposure," McConnell insists. With the advent of advanced IPA drying techniques, HF only processing has become a viable alternative to many conventional cleaning recipes, McConnell says.

HF-only cleaning offers several attractive advantages, he says. First, it's possible to produce a very hydrophobic, hydrogen-terminated surface. This surface will be virtually free of native oxide. Many users believe that this type of surface provides a superior foundation for downstream process steps, McConnell notes.

Reducing waste

Also, by moving to a more streamlined cleaning process, it's possible to realize substantial reductions in chemical use and waste generation. The shortened process also boasts a significant increase, McConnell adds, in equipment throughput. "Both of these benefits can be obtained without an increase in capital cost. In many cases, the initial cost of equipment may actually be lower," according to McConnell.

Carbon dioxide

Carbon dioxide snow is one method that stirred considerable interest in the past, RTI's Donovan notes. This method works by directing high-pressure carbon dioxide gas, expanded through a nozzle. The pressure drop, which accompanies the expansion, reduces the temperature so that many solid carbon dioxide particles are formed.

These particles bombard the wafer surface. The problem is that the purity of the CO_2 seems to be incompatible with silicon wafers. As a result, says Donovan, it has been largely abandoned for cleaning silicon wafers.

Air Products and Chemicals is among many firms exploring dry replacements

Cleaning Equipment Market Poised for Strong Growth

The global market for semiconductor cleaning equipment will grow dramatically over the next five years, according to a Mountain View, Calif.- based research firm.

Market Intelligence (MI) forecasts that this market will grow from revenues of an estimated $284.3 million this year to $506.4 million by 1998.

MI couples the growth to an expanding number of fabrication sites in Asia, along with growth in the domestic flash memory market. The compound annual growth rate between 1988-1998 is pegged at 10.7 percent.

Acceptance of larger wafer sizes is also expected to help in growing the cleaning equipment market. Many new systems able to handle larger 200 mm and up wafers will be needed to replace those currently in the field.

Costs of this equipment have been escalating, too, according to MI. A weighted average unit price of semiconductor cleaning equipment rose during the late 1980s by about 3 percent each year.

By 1991, MI placed the average unit price at about $34,000. In 1998, MI forecasts that cleaning equipment, on average, will cost more than $42,000 per unit.

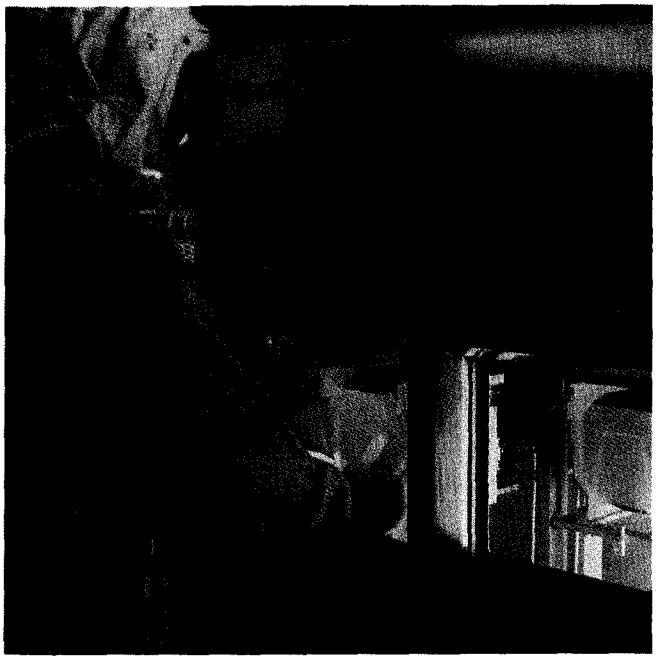
Projected revenues by geographic region are shown in the table. Asia/ROW was the leader, with Japan the main consumer.

By the end of the forecast period, Asia/ROW will decline slightly, with Europe gaining. After a decline beginning in 1989, the U.S. will fractionally exceed its 1988 level.

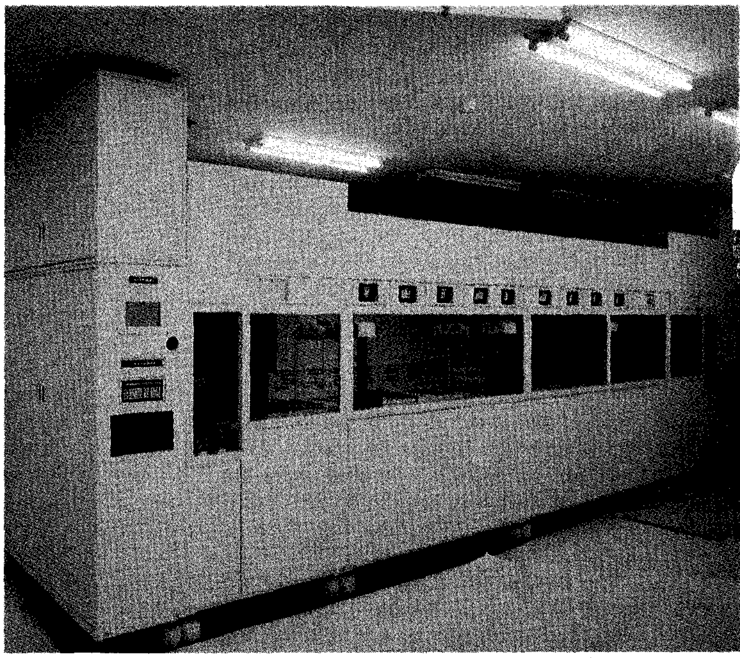
Total Semiconductor Cleaning Equipment Market: Percent of Revenues by Geographic Region (World) 1988-1998

Year	U.S. (%)	Europe (%)	Asia/ROW (%)
1988	45.0	9.0	46.0
1989	44.1	9.2	46.7
1990	43.7	9.5	46.8
1991	43.1	9.8	47.1
1992	41.5	10.2	48.3
1993	41.4	10.4	48.2
1994	41.5	10.6	47.9
1995	41.8	10.7	47.5
1996	42.5	10.7	46.7
1997	43.6	10.9	45.5
1998	45.3	10.8	43.9

Key: ROW = Rest-of-World Note: All figures are rounded. *Source: Market Intelligence*



2. *Vapor processing represents an alternative to traditional peroxide-based wafer cleaning. This Excalibur II, developed by FSI International, can employ multiple chemistries.*



3. *This cassetteless wet cleaning system, developed by Dainippon Screen, is aimed at the stringent cleaning requirements of 200 mm wafers containing advanced DRAMs.*

for the RCA clean. The focus, says David Bohling, is in two areas: The first is particle removal using cryogenic argon systems. Air Products, jointly with IBM, has developed an argon aerosol technology.

Bohling, an R&D manager, believes argon offers many advantages over CO_2 chemistry. Argon's key feature is the level of purity compared to CO_2 that it offers.

The second area Air Products is researching involves the removal of trace metal contamination from surfaces using dry processing. Air Products has succeeded in removing metals such as, iron, chrome and copper, which could originate from piping systems. A separate process enabled the company to remove sodium from surfaces at temperatures under 300°C.

"The problem with dry cleaning, says Bohling, is that "the chemistries must be fairly complex. You also don't want to risk removing a lot of substrate."

A number of companies, Bohling points out, predict that by 1998-2001, 90 percent of their cleans will be dry, with feature sizes approaching 0.18 µm. "When you reach that level, it will be difficult to use wet processes. If the trench or via is only 0.3 µm across, it will be tough to get wet cleaning chemistries out."

Philips' Mertens believes wet cleaning alternatives have been slow to gain ground. "I guess that's because of the particle transfer properties of a liquid clean — it's very effective," he says. The question is, he says, "If you clean in a plasma, where do the particles go?"

New tools and techniques are being added all the time.

"Don't clean wafers at all"

The best alternative? Keep a super clean area and don't clean wafers at all! Mertens says Philips attempts this feat by using a direct-transfer approach between operations — and by keeping a effective cycle-time management. This cycle-time management is aimed at limiting wafer exposure to potential contamination accidents in the fab.

A plethora of wafer-cleaning systems and chemistries exist. New tools and techniques are being added all the time. Among the latest: chemical reprocessing.

Chemical reprocessing systems don't clean, per se. They attack the problem through high purity in the process chemicals. Athens, now the largest provider of HF reprocessing systems, says Texas Instruments credits its system for a five percent yield improvement because of cleaner wafer surfaces.

UV-light approach

Another recent technology uses nonreactive gas-phase wafer cleaning. Specifically the process employs UV light to photo-dissociate contaminants from surfaces. Contaminants are then conveyed in a trap or scrubber by an inert flowing gas.

Developed by Radiance Services Co., the technology addresses "current and future needs to remove thin film and particle contaminants smaller than 0.2 µm," reports Donna K. Fitzpatrick, Radiance president.

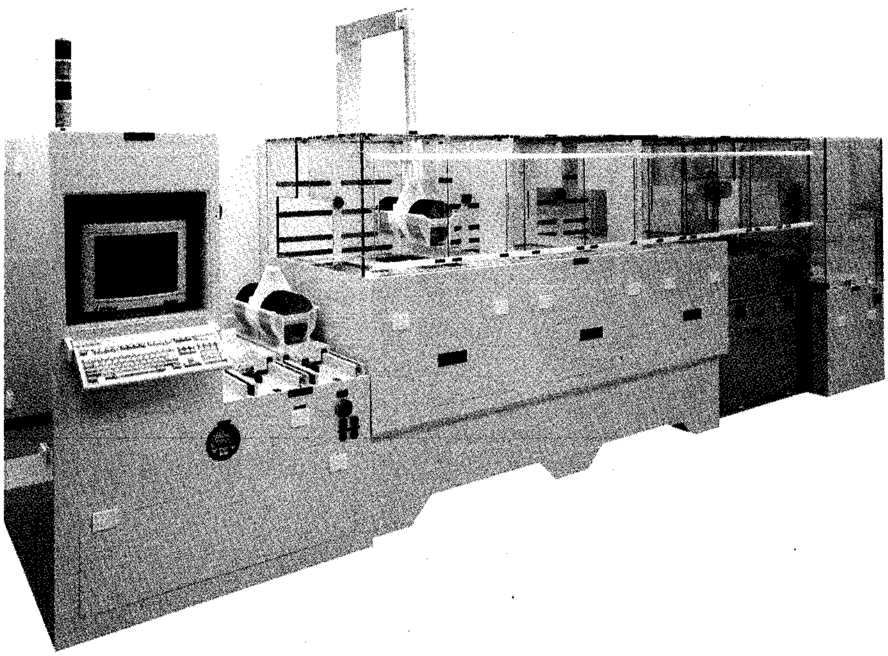
Storing wafers for long periods, he adds, to prepare for a furnace batch causes delays since the number of machines needed to support furnace loads can become quite costly.

Important items for cleaning systems on user wish lists: minimum floor space,

Table 2. Alternative Cleaning Methods

1.		Mechanical techniques
	a.	Brush scrubbing (hydroplaning)
	b.	High-pressure fluid jet (up to 4000 psi)
	c.	Ultrasonics (20 kHz and above)
2.		Wet chemical procedures
	a.	Surface-etching with HF-(HNO_3) or H_2O-H_2O_2-HF
	b.	Choline treatments ("Summa-Clean") mixture of H_2O, H_2O_2, surfactant, trimethyl-2-hydroxyethyl ammonium hydroxide
3.		Dry processes
	a.	UV-ozone (shortwave UV + O_2)
	b.	Dry ice snow (from liquid CO_2)
	c.	Anhydrous HF gas phase etching (of SiO_2 films)
	d.	Other advanced techniques (gas and plasma reactions)

Source: Werner Kern Associates



4. SubMicron Systems' Model 486 modular wet station claims tank-to-tank transfer ≤6 sec and 500 hrs MTBF for the entire system, including the IPA vapor dryer pictured here.

no operator intervention and self-cleaning. Plus, keep the hazardous chemicals safely stored outside the fab.

Conclusion

Wet cleans, based on the RCA clean, will not soon disappear, despite some hardy band pushing for their elimination. Dry cleaning techniques, as Motorola's DePinto notes, "are pretty application-specific."

Typically," says Micron's Paduano, "alternative cleaning methods have not been implemented where high throughput is needed." Look for the use of both wet and dry cleans to become quite application-specific and to work side-by-side.

Most of the action will be to reduce the need for cleaning, or to move it inside the cluster tool. While wet cleans will lose ground to dry, the former will be around for the long haul. □

Reference

Proceedings of "Semiconductor Wafer Cleaning Technology" course, February 23-24, 1993, Austin, Texas, Werner Kern Associates.

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