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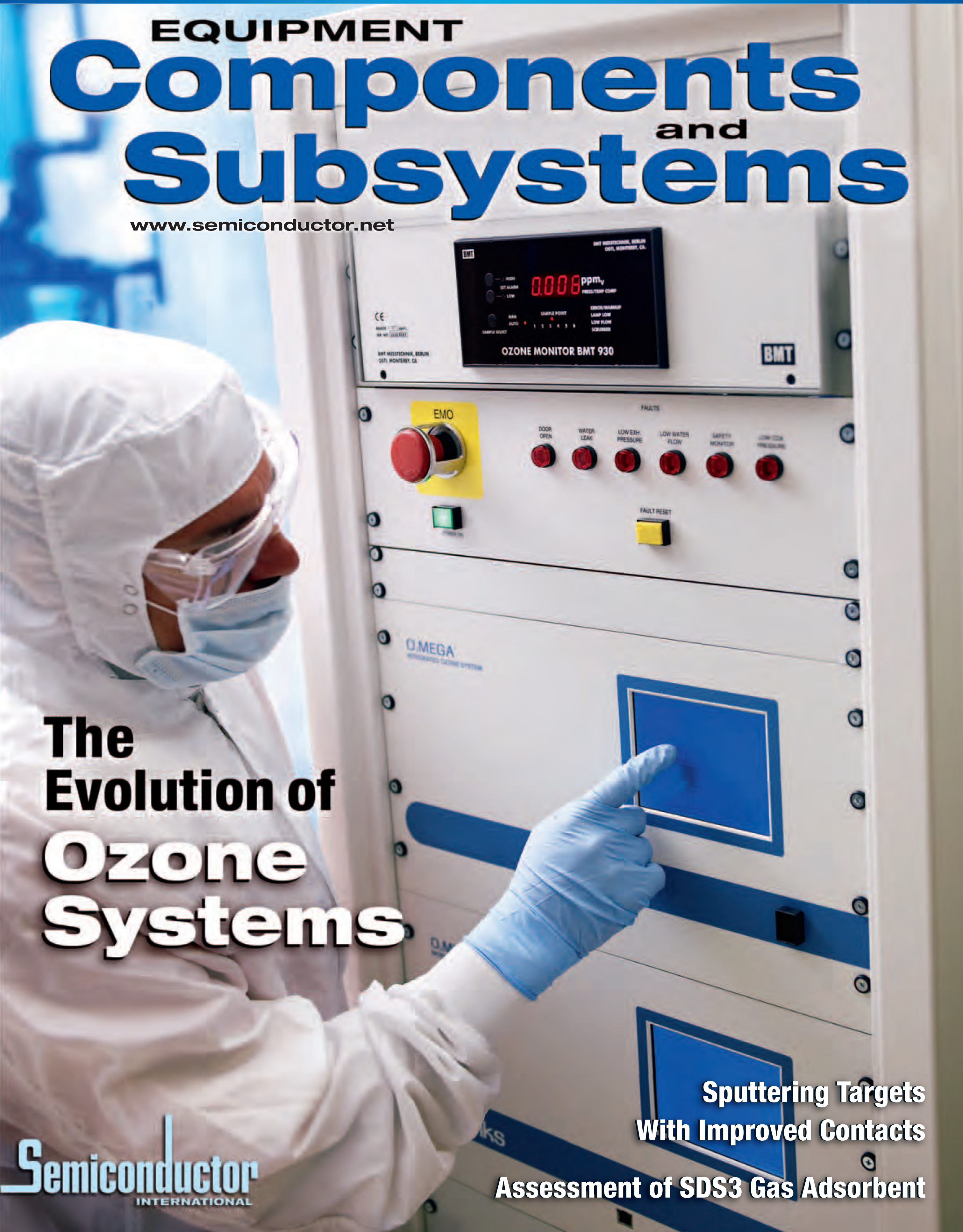

The Evolution of Ozone Systems

Sputtering Targets With Improved Contacts

Assessment of SDS3 Gas Adsorbent

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The Evolution of Ozone Subsystems

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AT A GLANCE

Ozone is a versatile oxidizer used in a variety of applications, including CVD, ALD, surface cleaning/ conditioning, and resist stripping.

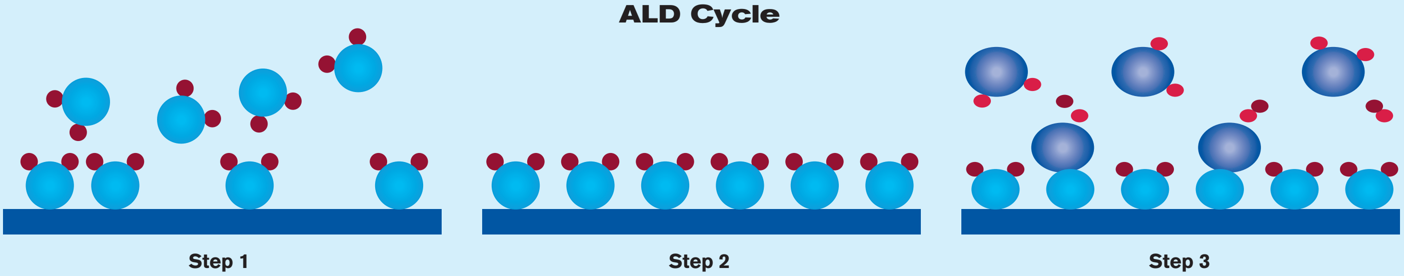
Since the late 1800s when reliable ozone (O_3) generators were first developed,[1] ozone has found broad use as an excellent oxidizer for industrial applications such as water treatment and medical disinfection, as well as the preservation of agricultural products during prolonged periods of storage.[2,3] Today, ozone continues to find additional industrial uses and is replacing traditional, more toxic chemicals as a highly effective, safer and more environmentally friendly alternative to more corrosive oxidants.

The general characteristics of ozone, as well as its high redox potential, make it particularly suitable for semiconductor processing applications. There are two types of ozone delivery systems commonly used in semiconductor manufacturing: ozone gas delivery systems and DIO_3 (ozone dissolved in deionized water) delivery systems. Ozone gas systems are used widely in chemical vapor deposition (CVD) processes such as TEOS/O_3 CVD SiO_2 deposition,[4-6] as well as in advanced processes such as atomic layer deposition (ALD).[7] Today, DIO_3 delivery systems are used in photoresist stripping,[8] wafer cleaning and surface conditioning applications,[9] as well as for ultrathin oxide growth.[10] The unique chemistry and ease of abatement of ozone also have made compliance with increasingly stricter environmental guidelines within the semiconductor industry possible for many applications.[11] As a result, there is a growing need for flexible, more advanced ozone delivery systems that can accommodate the wide selection of equipment and emerging processing needs.

Ozone gas subsystems for ALD

A major driving requirement for the development of new gas ozone delivery systems has been the emergence of ALD as a production-worthy solution for the deposition of advanced films in semiconductor manufacturing. ALD (Fig. 1) is a critical new process that offers distinct and unique advantages over conventional CVD.[12-14] It enables precise control of the deposited material thickness and composition over the large areas and aggressive topologies typically found in advanced device fabrication. ALD processing is particularly effective in the formation of DRAM capacitor structures offering unprecedented control of film thickness and stoichiometry. The aspect ratios in these structures have become so severe that conventional CVD cannot provide the step coverage needed. As ALD is inherently 100% conformal, it provides a good solution to this problem.

The formation of ALD gate oxide and advanced dielectric films requires the use of a precursor capable of supplying reactive oxygen radicals at the film surface. Precursors that fulfill this requirement include O_3, O_2, H_2O_2, H_2O, and $^{\bullet}OH$ (hydroxyl radical).[15] Ozone has distinct advantages over the other oxidants when compared with these and other precursors for ALD. It has a high electrochemical potential, resulting in higher reaction rates (e.g., 2.08 eV for ozone vs. 1.23 eV for the oxygen molecule). It also has a higher volatility compared with alternate common choices, giving it a significant advantage for improving process throughput in most ALD applications (ozone is more easily purged between deposition cycles than hydro-



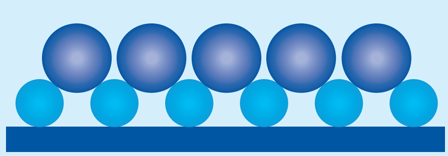
1. In a typical ALD cycle, steps 1 and 2 depict the creation of the initial film generated by the reaction between the primary precursor and the substrate material, and steps 3 and 4 depict the generation of the final film created by the reaction between the initial film and a reactant precursor material.

gen peroxide or water). Furthermore, because ozone contains no hydrogen, it results in lower hydrogen and hydroxyl residuals in the oxide films, reducing problems such as film delamination during anneal.[16] Ozone also offers additional advantages over alternate precursors. Transportation and storage are major sources of contamination in process reagents. Because ozone is generated at the point of use, it minimizes the potential for contaminants caused by prolonged storage and reduces both storage and transportation costs associated with alternate oxidizers. Ozone is easily decomposed back to oxygen by a simple catalytic or thermal destruct unit, making ozone a safe and eco-friendly "green" precursor, as there is no need for disposal of the spent oxidizer.

Several years ago when ALD processes were first being developed and precursor requirements were first being discussed, it was apparent that ozone, because of its advantages, was being considered as the prime oxidizer candidate. However, the industry had not yet settled on single-wafer, batch or mini-batch platforms, and many OEMs had different process needs, requiring different ozone concentrations at various flow regimes. It was clear that, as processes were being developed, both process engineers and equipment manufacturers needed ozone delivery systems that were flexible, highly customizable, and operable within a wide range in order to conduct experiments and finalize production process parameters. This gave rise to compact and standalone ozone delivery systems that were quickly and easily tailored to meet most development and processing needs. Configurable and flexible systems such as these were easily integrated into new and existing tool platforms by providing ozone-generating technology along with user-defined options for flow, concentration, control requirements, and number of output channels (process chambers). Figure 2 shows the typical equipment topology for ozone-based ALD processing. Next-generation ozone generator systems can supply ozone concentrations of up to 20 wt% (300 g/m^3) at flow rates of 0.5-20 slm.

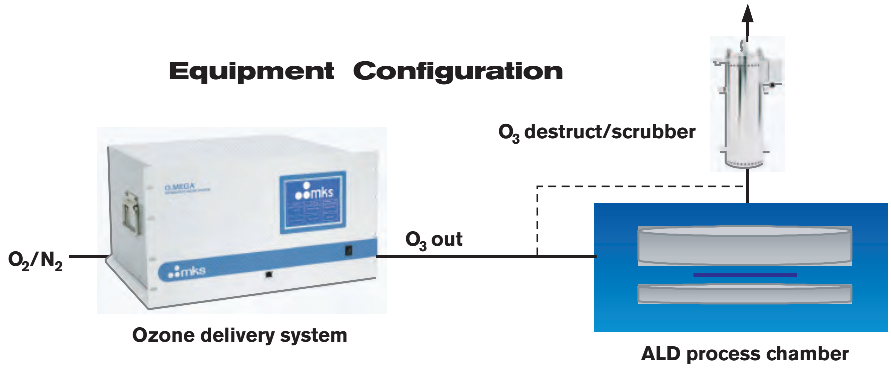
ALD processing continues to be viewed as the technology of choice for thin-film deposition for advanced device structures, as is attested by the rapid growth in the ALD tool market. The application of ozone as an oxidizing precursor in ALD processing — with inherent advantages for wafer throughput, process/film properties, safety, and chemical handling and disposal costs — will be a major factor in the continued growth of this market. Subsystems such as the O_3MEGA

Advanced ozone delivery subsystems minimize space requirements and maximize flexibility in processes that range from wafer surface cleaning to ALD. An operator is seen adjusting ozone flow and concentration settings prior to ALD processing.



Step 4

compact ozone delivery system provide significant advantages in performance, size, flexibility, integration and control, while minimizing tool space requirements and maximizing productivity.



2. Typical equipment configuration for the use of an ozone delivery system in an ALD tool.

DIO_3 in wet processing and wafer cleaning

Traditionally, a sequence of cleaning steps is required to remove contaminants from a wafer surface. The sequence may include Piranha etch (organic contaminant removal), followed by a dilute aqueous HF etch (sacrificial oxide removal), an RCA SC-1 clean (particle removal and reoxidation of the surface), an RCA SC-2 (metals clean) and, depending on the application, oxide removal using a final dilute aqueous HF etch.

Piranha solutions use 98% H_2SO_4/30% H_2O_2 at ratios of 2-8:1 and temperatures of 100°C or higher. Handling these solutions present distinct safety hazards. Also, the use of these cleaning cycles has a significant impact on economic and environmental costs because of the fact that the water needed for dilution and rinsing results in equally large quantities of waste water that must be decontaminated. Studies suggest that up to 80% of the water requirements of the semiconductor industry (225 billion liters in 1999) are because of cleaning process rinse cycles.[17,18] The International Technology Roadmap for Semiconductors (ITRS) is requesting an 84% reduction in water usage by 2014 relative to 1999.

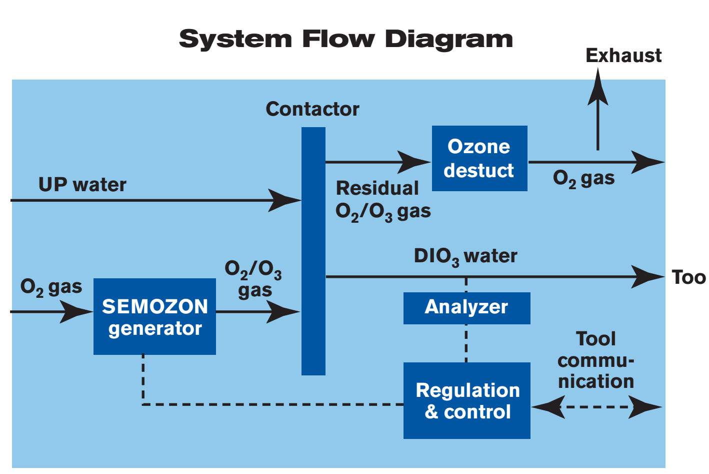
Recent research has shown that ozone provides a "green" chemistry alternative that is both safer and less costly in terms of waste handling than those reagents that have historically been used for wafer surface cleaning in the semiconductor industry. DI water/ozone solutions, collectively known as DIO_3, are thus good replacements for Piranha and RCA SC-1 and SC-2 cleans in a variety of applications.

Surface organic and photoresist removal

DIO_3 has been found to be very effective for the removal of trace organic contaminants from wafer surfaces. The fundamental chemistry of the ozone-based removal of surface organic species from wafer surfaces involves both direct reactions of molecular O_3 with the contaminants (especially certain organics) and indirect reactions via oxygen radicals.[19] The removal of photoresist residues is chemically similar to the removal of trace organic contamination, and DIO_3 solutions are effective for photoresist strip, albeit with certain limitations. Photoresist removal rates are directly proportional to the ozone concentration and exhibit an inverse relationship to the process temperature. Although elevated temperatures enhance the strip rate, the solubility and stability of ozone rapidly decreases with temperature, and this causes a fast decay of dissolved ozone concentrations at higher temperatures. The rate-limiting step of DIO_3 photoresist stripping is thus mass transfer of molecular ozone to the wafer surface.[20] The best process results for photoresist strip are achieved through the use of physical optimization of ozone mass transport mechanisms coupled with the highest possible ozone concentrations and an optimum process temperature. DIO_3 photoresist removal processes, therefore, require high-concentration, high-flow ozone systems. Figure 3 shows a schematic of one such system, suitable for deployment in conventional batch-style photoresist removal cleaning equipment. Such systems deliver high concentrations (up to 114 ppm) of dissolved ozone at very high flow rates (up to 80 lpm).

Metal and particle removal

DIO_3 alone is not chemically effective in the removal of metals or particulates from a wafer surface (iron, nickel, aluminum, magnesium, calcium, etc. are typically present as oxides/hydroxides). Metals and inorganic particles must be cleaned by an HF etch of a sacrificial oxide layer, followed by the rapid removal of the freed particles from the region near the wafer surface. DIO_3 particle cleans remove particulates through the action of oxidation of the wafer surface to produce a layer suitable for subsequent HF etching. The thickness of the oxide formed by DIO_3 is self-limiting, typically about 1 nm. Ozone concentration and pH influence the oxide growth rate.[21] Single-wafer spin cleaning with repetitive use of ozonated water and dilute HF (SCROD), developed by workers at Sony, alternatively dispenses dHF and DIO_3 on a spinning wafer.[22] A typical one-minute,



3. A schematic showing a typical equipment subsystem for the delivery of DIO_3 to batch wafer cleaning tools.

three-cycle SCROD clean can remove 87% of Al_2O_3 particles, 97% of Si_3N_4 particles, and 99.5% of polystyrene latex particles without significant surface roughening.[23] Advanced cleaning and drying (ACD), developed by Astec, uses a similar sequential approach. ACD gives results comparable to a standard RCA clean, but with significantly reduced chemical consumption (up to 60% less chemical usage). The wafer can easily be reoxidized in the atmosphere above the dHF/O_3 bath. A comparison of metal contamination on a silicon (100) surface after one HF/O_3 cycle; a modified RCA clean; and an alkaline etch shows that metal contamination levels $<1 \times 10^9$ atoms/cm^2 can be achieved using dHF/O_3.[24]

Reduced reagent/DI water use

Single-wafer DIO_3-based wafer cleaning systems require relatively low flow rates per chamber (1-2 lpm) and strictly controlled dissolved ozone concentrations. Configurations that employ SCROD cleaning, as described above, are desirable in production environments since they have been proven to use far less cleaning chemicals and rinse water than do immersion RCA cleans (Fig. 4). Ozone delivery systems that are suitable for single-wafer cleaning systems using SCROD or ACD approaches are commercially available.

It is possible to achieve tight control of reagent flows and purities, as well as effective effluent handling, when the rapid mass transport of reaction byproducts away from the vicinity of the wafer surface is possible. Single-wafer equipment configurations accomplish this removal very effectively and yield significant improvements in etch uniformities, within wafer, wafer-to-wafer and lot-to-lot. These factors are strong contributors to the increased deployment of DIO_3 cleaning approaches in single-wafer cleaning equipment.

As semiconductor processes and requirements continue to evolve, so does the need for more flexible systems.

Conclusion

Ozone is a versatile oxidizer used in semiconductor applications, exhibiting many advantages for advanced manufacturing processes. In the gas phase, it is widely used in TEOS CVD, as well as other CVD and furnace oxidation applications, and is also being implemented as the oxidizer of choice for ALD processes used in advanced oxide film deposition. In addition, it is being used as a liquid-phase oxidant in ultrathin DIO_3/SiO_2 film processes, DIO_3-based silicon surface cleaning/conditioning, and photoresist stripping processes. As semiconductor processes and requirements continue to evolve, so does the need for more flexible systems that can deliver gaseous ozone or DIO_3 tailored to specific processes. **SI**

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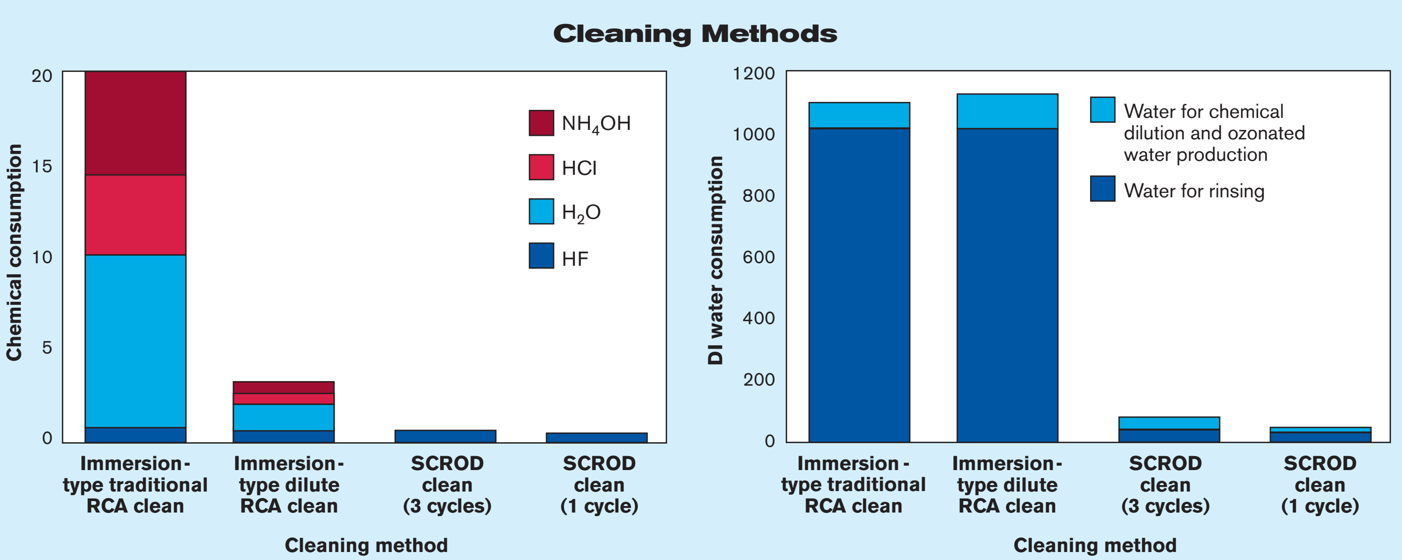

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