CleanRooms

Ozonated water—Where the green choice is better

Research has demonstrated that ozone can offer a more environmentally friendly alternative to existing cleaning processes and, in many instances, can outperform them.

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In 1857, Werner Siemens developed the first dielectric barrier discharge technique for the reliable generation of ozone.[1-3] Since then, such electrical discharge techniques have become standard in equipment for the production of industrial quantities of ozone for water treatment and in other types of commercial ozone generators for a number of other applications, including semiconductor processing.[4] Ozone has a number of industrial uses beyond the disinfection of drinking water and treatment of wastewater. Medical sterilization, odor control, swimming pool water treatment, fish hatcheries, shrimp farms, and low concentrations of ozone in the air to prevent fruit ripening during storage are only some examples.

One of the key advantages for ozone is that its usage provides a safe and environmentally friendly alternative to toxic and corrosive chemical processes. The advent of stricter environmental enforcement made the semiconductor industry acutely aware of the need for environmentally benign chemistries in the different chemical processes associated with device fabrication. Under the heading of "Difficult Challenges," the 2003 International Technology Roadmap for Semiconductors (ITRS) section on Environmental Safety and Health specifically points out the need for improvements in Chemical Resource Management and Workplace Protection.[5] Research over the past decade has demonstrated that ozone can be effectively used in "greener" alternatives to existing cleaning processes and in many instances it actually provides superior process performance for advanced applications. Specifically, research in this area developed ozone alternatives for the wafer cleans based on SPM, H_2SO_4, and RCA SC-1 and SC-2 that are used for the most critical surface preparation steps in device fabrication processes. This work was greatly assisted by recent improvements to ozonated water delivery systems that provide exceptionally high ozone concentrations and throughputs at the wafer surface (see Figure 1). In the following, a survey of ozone applications in semiconductor device fabrication is given.


Figure 1. LIQUOZON® ozonated water delivery system. Source: MKS Instruments Inc.

Safer and greener alternatives for wafer cleans

Traditionally, the removal of contaminants from a wafer surface requires a sequence of cleaning steps. A typical cleaning cycle might include a Piranha etch (organic contaminant removal), followed by a dilute aqueous HF etch (sacrificial oxide removal), then an RCA SC-1 clean (particle removal and re-oxidation 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 percent H_2SO_4/30 percent H_2O_2 at ratios of from 2:1 to 8:1 and temperatures of approximately 100°C or higher. Beyond safety issues, cleaning cycles, as described, have a significant impact on economic and environmental costs. This is due to the fact that the water for dilution and rinsing in these multi-step cleaning cycles results in equally large quantities of wastewater having to be decontaminated. It is estimated[6] that up to 80 percent of the water requirements of the semiconductor industry (225 billion liters in 1999)[7] are due to cleaning process rinse cycles. Currently, the ITRS is requesting an 84 percent reduction in water usage by 2014 relative to the 1999 figure.

Surface organic contaminant removal

DI water/ozone solutions (DIO_3) provide an effective replacement for Piranha and RCA SC-1 and SC-2 cleans. The fundamental chemistry of ozone-based cleaning is due to both direct reactions of the contaminants with molecular O_3 (especially certain organics) and indirect reactions within oxygen radicals. Research into the purification of drinking and wastewater[8] has developed the knowledge base for understanding the mechanism by which DIO_3 removes organic contaminants from wafer surfaces (see Figure 2).

The exact reaction pathway is strongly dependent upon the reaction conditions. Radical reactions require an initiator such as high pH, the presence of hydrogen peroxide or UV irradiation. It should be noted that, while the high rate of radical reactions is a

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Figure 2. Ozone reaction schematic

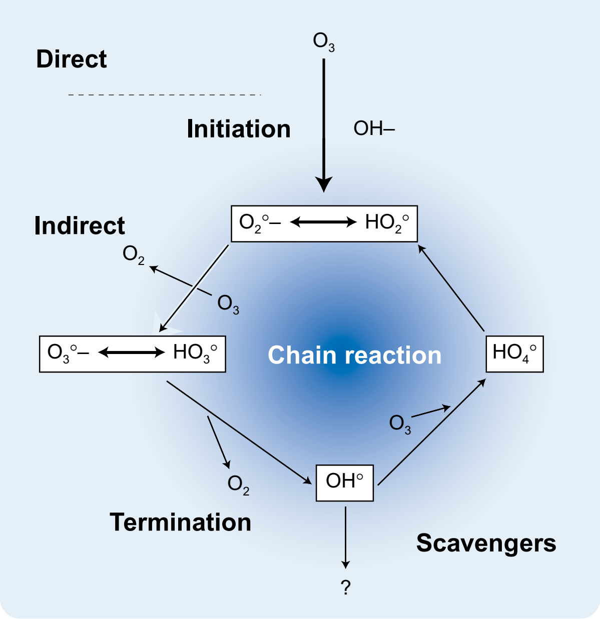

Figure 2. Ozone reaction schematic.[8]

desirable trait for surface cleans, conditions that promote only radical chemistries can be problematic. Radical species are highly reactive and have very short half-lives. As a consequence, radicals that are generated too far away from the wafer surface react out of the system before they can reach that surface and interact with the contaminants. This characteristic has obvious consequences for reactant depletion and probably loss of uniformity in the cleaning process.

Photoresist removal

Processes for the removal of photoresist residues are closely related to those for the removal of organic surface contamination. Traditionally, wet chemical processes for photoresist removal are based on Piranha-like solutions of sulfuric acid with either hydrogen peroxide (SPM) or ozone (SOM). Recent emphasis on reduced cost of ownership and improved performance has engendered interest in the development of ozonated DI water-based processes to replace these processes. Studies have shown that DIO_3 solutions are effective for photoresist strip, albeit with certain limitations. Photoresist removal rates are proportional to the ozone concentration and to the process temperature. Elevated temperatures enhance the strip rate but the solubility and stability of ozone decreases rapidly with temperature causing a fast decay of dissolved ozone concentrations at higher temperatures. Studies have shown that the rate-limiting step of DIO_3 photoresist stripping is mass transfer of molecular ozone to the wafer surface.[9] Thus, techniques that overcome boundary layer limitations can enhance strip rates (e.g., megasonic agitation or the use of vapor phase ozone-water vapor mixtures).[10, 11] 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 optimum process temperature.

Cleaning metal and particle contamination

DIO_3 by itself is not chemically suited to clean metals or particles directly from a wafer surface except in the case of particles that are organic in nature (Fe, Ni, Al, Mg, Ca, etc., are typically present on wafer surfaces as oxides or hydroxides). Conventionally, metals and inorganic particles are removed by directly etching an underlying silicon dioxide layer to "lift" the particles away from the surface, typically using dilute HF (dHF), followed by rapid removal of the freed particle from the vicinity of the surface. DIO_3 can remove particulates in a similar fashion through its ability to oxidize the wafer surface and produce a layer that is suitable for HF etching. The thickness of the oxide layer formed by DIO_3 is self-limited, typically about 1 nm thick. Parameters like ozone concentration and pH have been shown to influence the oxide growth rate.[15] The sequential applications of aqueous acid and ozone solutions can be very effective in cleaning metals and particulates from wafer surfaces.[11, 12-15, 19] Single wafer Spin Cleaning with Repetitive use of Ozonated water and Dilute HF (SCROD), developed by workers at Sony, alternately dispenses dHF and DIO_3 on a spinning wafer.[16] A typical one-minute, three-cycle SCROD clean can remove 87 percent of Al_2O_3 particles, 97 percent of Si_3N_4 particles and 99.5 percent of polystyrene latex particles[19] without significant surface roughening.

Figure 3. Cleaning and drying system

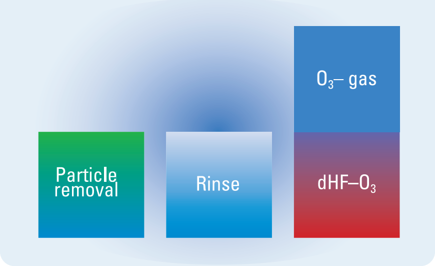

Figure 3. A schematic drawing showing the ASTEC dHF/O_3 cleaning and drying system.

Advanced Cleaning and Drying (ACD), developed by ASTEC in Germany, uses a similar sequential approach (see Figure 3). ACD gives results comparable to a standard RCA clean, but with significantly reduced chemicals consumption (up to 60 percent less chemical usage). The wafer can be easily re-oxidized in the atmosphere above the dHF/O_3 bath. A comparison of metal contamination on an Si (100) surface after a) one HF/O_3 cycle, b) a modified RCA clean, and c) an alkaline etch shows that metal contamination levels < 1 x 10^9 can be achieved using dHF/O_3.[17] These applications have been successful with non-structured and lightly structured wafers.[18]

Advanced reticle cleaning

Advanced reticles use phase shifting to increase resolution without reducing the wavelength of the light used to produce the lithographic image. Traditionally, reticles have been cleaned using conventional Piranha and RCA approaches. Recently, reports have shown that repeated application of these cleaning methods produces unacceptable variation in phase shift angle and transmittance in advanced masks.[20] Studies at the 180 nm technology node showed that reticles could only be cleaned two to eight times before unacceptable degradation in the optical properties occurred.[21] Optical degradation is directly related to the degree to which the mask is etched and its surface roughened. As was noted in previous sections, ozone-based etch chemistries result in very little surface roughening. These chemistries are therefore becoming preferred for reticle cleaning. It is also noteworthy that for heavy polymer removal, such as in photoresist strip, the most efficient processes are only realized at high ozone throughputs. Processes such as these therefore require high flow ozone systems.

DIO_3 etch processes and new equipment configurations

Single wafer processing has three main goals:

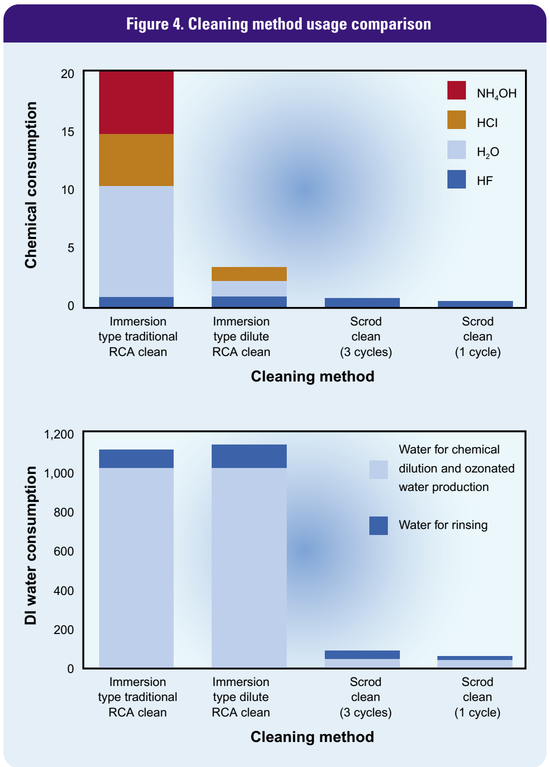
Figure 4. Cleaning method usage comparison

Figure 4. Chemical and DI-water usage of different cleaning methods. Source: T. Hattori, 2003

better process control; cost reduction; and reduced environmental impact. The control of reagent flows and purities, as well as more effective effluent handling, improves as the rapid removal of reaction products from near the wafer surface becomes possible. Single wafer configurations generally yield improvements in etch uniformities within wafer, wafer-to-wafer and lot-to-lot. Finally, fab economics and fab line flexibility are aided by the reduced footprint of single wafer systems vs. immersion systems. The use of ozonated water in single wafer processes requires relative low flow rates per chamber (1 to 2 L/min) and a very controlled dissolved ozone concentration to ensure repeatable process results. Workers at Sony[19] have shown that SCROD cleaning in a single wafer spin cleaning tool uses far less cleaning chemicals and rinse water than immersion RCA cleans (see Figure 4).

The need to replace Piranha and RCA cleans in device fabrication is driven by enhanced process requirements, economics, environmental impact and safety aspects. Various green alternatives to these processes have emerged in recent years, all based on the replacement of the oxidizers with ozone. O_3-based processes have been shown to improve performance while involving fewer steps, reduced chemical consumption, and lower costs. ■■■

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References

1. W. Siemens, *Poggendorff's Annalen der Physik Chemie*, 102, 66 (1857); cited in ref. 2.
2. U. Kogelschatz, "Dielectric-barrier discharges: Their history, discharge physics, and industrial applications," *Plasma Chemistry and Plasma Processing*, Vol. 23, No. 1, March 2003.
3. U. Kogelschatz, B. Eliasson and W. Egli, "From ozone generators to flat television screens: History and future potential of dielectric-barrier discharges," *Pure and Applied Chemistry*, Vol. 71, No. 10, 1999:1819-1828.
4. ASTeX® Ozone Product Line, MKS Instruments Inc., Wilmington, MA, http://www.mksinst.com/PRG3.html.
5. Semiconductor Industry Association, *The International Technology Roadmap for Semiconductors*, San Jose, 2003; available at http://public.itrs.net/Files/2003ITRS/Home2003.htm.
6. P. H. Gleick, D. Haasz, C. Henges-Jeck, V. Srinivasan, G. Wolff, K. Kao Cushing, and A. Mann, *Waste Not, Want Not: The Potential for Urban Water Conservation in California*, The Pacific Institute, San Jose, November 2003; available at http://www.pacinst.org/reports/urban_usage/waste_not_want_not_full_report.pdf.
7. P. Burggraaf, "A Closer Look at the Most Difficult Process Challenges," *Solid State Technology*, September 2000.
8. C. Gottschalk, A. Libra and A. Saupe, *Ozonation of Water and Waste Water—A Practical Guide to Understanding Ozone and Its Applications*, Weinheim Germany: Wiley-VCH, 2000.
9. S. De Gendt, J. Wauters and M. Heyns, "A Novel Resist and Post-Etch Residue Removal Process Using Ozonated Chemistry," *Solid State Technology*, Vol. 41, No. 12, 1998: 57-60.
10. H. Abe, H. Iwamoto, T. Toshima, T. Iino and G. W. Gale, " Novel photoresist stripping technology using ozone/vaporized water mixture," *IEEE Transactions on Semiconductor Manufacturing*, Vol. 16, No. 3, August 2003: 401-408.
11. S. De Gendt et al., "A Novel Resist and Post-Etch Residue Removal Process Using Ozonated Chemistry," *Solid State Phenomena*, Vol. 65-66, 1999: 165-168.
12. E. D. Olson et al., "Alternatives to Standard Wet Cleans," *Semiconductor International*, Vol. 23, No. 9, 2000: 70-76.
13. E. Bergman and S. Lagrange, "HF-Ozone Cleaning Chemistry," *Solid State Technology*, Vol. 46, No. 7, 2001: 115-124.
14. M. Alessandri et al., "Particle Removal Efficiency and Silicon Roughness in HF-DIW/O_3/Megasonics Cleaning," *Solid State Phenomena*, Vol. 65-66, 1999: 27-30.
15. T. Ohmi, "Total Room Temperature Wet Cleaning of Silicon Surfaces," *Semiconductor International*, Vol. 19, No. 8, 1996: 323-338.
16. T. Hattori, T. Osaka, A. Okamoto, K. Saga and H. Kuniyasu, "Contamination Removal by Single-Wafer Cleaning with Repetitive Use of Ozonated Wafer and Dilute HF," *J. Electrochem. Soc.*, Vol. 145, No. 9, 1998: 3278-3284.
17. C. Gottschalk, J. Schweckendiek, "Using dissolved ozone in semiconductor cleaning applications," *Micro*, March 2004: 81.
18. C.V. Ciufia, K.G. Knoch, J. Osterkamp, "Metal Removal and Drying by HF/O_3," abstract. Technical paper presented at Semiconductor Wet Processing Conference, 2004, available at: http://www.spwcc.com/abstracts_list.htm.
19. T. Hattori, "Implementing a Single-Wafer Cleaning Technology Suitable for Minifab Operations,"*Micro*, Vol. 21, No. 1, 2003: 49-57.
20. I. Kashkoush, G. Chen and R. Novak, "Today's binary and EAPSMs need advanced mask cleaning methods," *Solid State Technology*, Vol. 47, No. 2, February 2004.
21. A. Hand, "Getting Masks Clean With Minimal Optical Degradation," *Semiconductor International*, Vol. 26, No. 11, October 2003.

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