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Using dissolved ozone in semiconductor cleaning applications

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A survey of several wafer-cleaning techniques highlights the advantages of dissolved ozone over traditional sulfuric acid–peroxide methods and RCA cleans using SC-1 and SC-2 mixtures.

Ozone (O_3), an allotrope of oxygen, is a highly reactive gaseous oxidizing agent that absorbs harmful ultraviolet (UV) radiation, thus enabling life on earth. The first ozone generator was developed by Werner von Siemens in Germany in 1857. In 1896, Nikola Tesla obtained the first U.S. patent for an ozone generator based on electric discharge in an oxygen-containing gas, which is the primary method of ozone generation used today.

The number and diversity of ozone applications have increased enormously since ozone's first full-scale use as a disinfectant for drinking water in Nice, France, in 1906. It is widely used to treat and purify ground and surface water as well as domestic and industrial wastewater, to disinfect swimming pools, and to prevent the growth of microorganisms in cooling-tower systems. This article surveys ozone applications in the semiconductor manufacturing industry and provides sample data from users and researchers.

Ozone Uses in the IC Industry

For more than 20 years, semiconductor industry researchers have investigated the use of ozone for wafer-cleaning and resist-stripping applications. To lower chemical consumption and disposal costs as well as to improve cleaning efficiency, ozone has been studied during the past decade as an alternative to traditional sulfuric acid–peroxide and RCA cleans using basic (SC-1) and acidic (SC-2) hydrogen peroxide mixtures. It is effective because of the multiple influences exerted by the disinfecting activity of O_3 and O_3-derived oxidizing species such as OH radicals.

In chip fabrication processes, ozone is

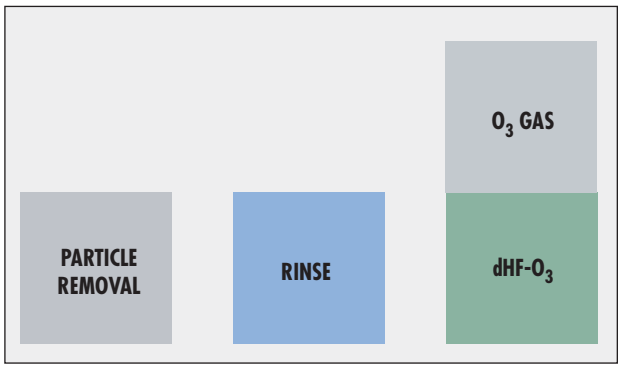

Figure 1: Schematic diagram of three-step ACD cleaning system configuration.

principally used to clean wafers; eliminate organics, metals, and particles; remove photoresist; and disinfect DI-water facilities. Cleaning with ozone always involves oxidation. Process differentiation depends on the primary purpose of the cleaning step.

Removing Organics. Much information on the ability of ozone to remove organics has been derived from research on the treatment of drinking water and wastewater.[1] Ozonated DI water (DIO_3) has a high oxidation potential and can degrade organic contamination. Its removal efficiency depends on the type of organic species, the ozone concentration, and the reaction regime.

Ozone dissolved in ultrapure water generates an OH active radical during self-decomposition. While the ozone decomposes the organics directly, the active radical decomposes them indirectly. The different reaction pathways lead to different oxidation products. The direct ozone reaction

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pathway is selective, with normally slow reaction-rate constants. The indirect OH reaction is fast and nonselective, but it must be activated by initiators such as a high pH, hydrogen peroxide, or UV radiation. Although a fast reaction is desirable, a reaction by radicals alone should be avoided. In many cases, active species must act directly on a surface, since species that are generated too far away from the surface become deactivated and lost.

Removing Metal and Particles. DIO_3 alone cannot effectively remove such metals as iron, nickel, aluminum, magnesium, and calcium, which deposit on silicon surfaces such as metal hydroxides or metal oxides. Depending on their nature, the metals may be incorporated into the oxide layer or reside at the Si-SiO_2 interface. They can be removed with acids acting as ion exchangers, or the oxide can be dissolved using hydrofluoric acid (HF), enabling metal removal.

DIO_3 alone may be sufficient for the removal of adhered particles if they are of an organic nature. However, particles on silicon dioxide are generally removed by etching the oxide beneath the particle with dilute hydrofluoric acid (dHF) and avoiding particle redeposition. If the bulk of the particle is not dissolved by dHF, O_3 as an oxidant can create a new layer that is etchable by HF. This is true for silicon particles and silicon surfaces.

The formation of an oxide layer on silicon is a self-limiting process. At room temperature, the oxidation of the silicon surface creates an oxide layer that can measure up to approximately 1 nm thick. The quality of the thin oxide layer depends on other parameters, such as humidity. In tests involving spray and immersion tools, the initial oxide growth rate was a function of ozone concentration.[2] In immersion tools, final oxide thickness was dependent on the initial ozone concentration and pH value, indicating a reaction-limited process.[3] However, since a static system was used in these tests, the decay and consumption of ozone may have influenced the results.

Several research studies have been published on cleaning processes that combine ozone with HF, hydrochloric acid (HCl), or both. In these studies, the chemicals were applied in sequence or as mixtures in spray, immersion bath, or single-wafer processes.[4–9]

The single-wafer spin cleaning with repetitive use of ozonated water and dilute hydrogen fluoride (SCROD) method alternately dispenses dilute dHF and DIO_3 on a spinning wafer.[9] Depending on the desired final condition of the surface, the process ends with either a dHF/rinse or DIO_3/rinse followed by spin drying in nitrogen. A one-minute, three-cycle process can remove 87% of Al_2O_3 particles, 97% of Si_3N_4 particles, and 99.5% of polystyrene latex particles. In contrast to methods that apply dHF and DIO_3 simultaneously, repetitive SCROD cleaning does not increase surface roughness.

The advanced cleaning and drying (ACD) method developed by ASTEC (Berg, Germany) uses a mixture of dHF and O_3, combining metal removal and drying into one process. In combination with a particle-removal step using either a traditional SC-1 clean or a surfactant, the ACD process consumes up to 60% less chemicals than the classical RCA process. The result is a hydrophobic wafer that, if necessary, can be reoxidized in the gaseous ozone directly above the dHF/O_3 bath, as shown in Figure 1.

Figure 2 presents typical metal contamination levels on <100> silicon wafers after an HF/O_3 clean, a modified RCA clean, and alkaline etch. After only one HF/O_3 cycle, contamination levels were reduced to $\sim 1 \times 10^9$ atoms/cm^2 or less for all measured metals. The metal removal/drying step can be performed without changing the number of particles on the wafer surface and without a significant increase in the number or size of crystal-originated particles.

Photoresist Removal. Traditional wet chemical processes used to remove photoresist rely on concentrated sulfuric acid combined with hydrogen peroxide (SPM) or ozone

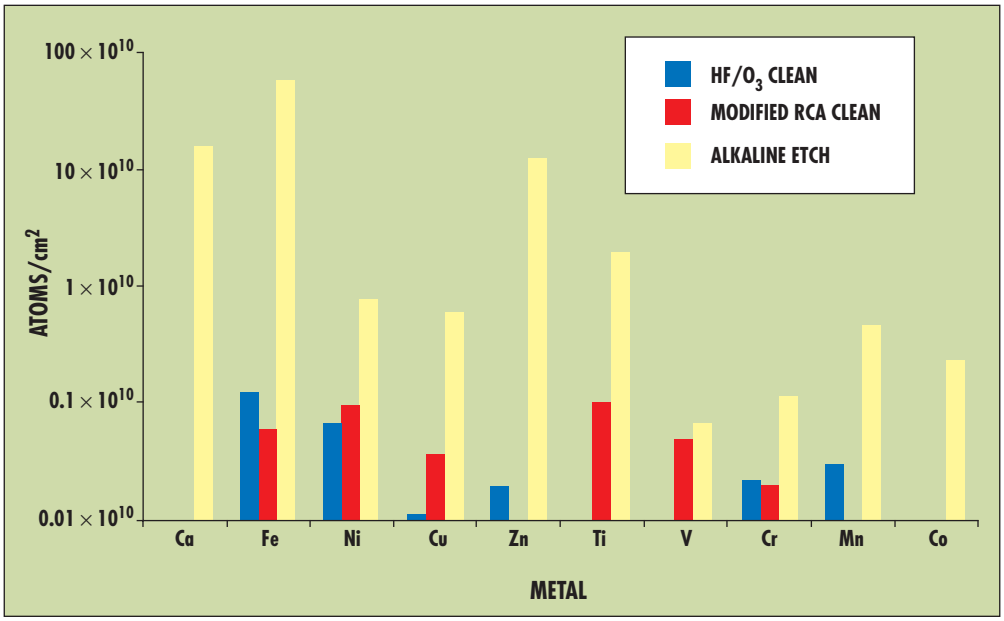

Figure 2: Typical residual-metal surface concentrations after three types of clean processes on <100> silicon wafers: a one-step process in an HF/O_3 dryer, a modified RCA clean, and an alkaline etch.

(SOM). An alternative process using ozone dissolved in DI water provides environmental benefits and lower costs.

Photoresist-strip rates in DIO_3 increase with increasing ozone concentration or temperature (at a constant ozone concentration). Unfortunately, with increasing temperature, the saturation ozone concentration in water decreases while the rate of ozone decay increases. The ozone-delivery process must be carefully optimized to achieve the maximum photoresist removal rate.

Several attempts to use ozone in resist-strip processes are reported in the literature. For example, ozone has been mixed with hot DI water at the point of use in an effort to achieve a high ozone concentration, and scavengers have been added to prevent ozone decay.[10–13] It has been found that strip rates are influenced by the mass transfer rate of dissolved ozone from the bulk liquid into the boundary layer at the wafer surface.[14] Diffusion limitations can be reduced by employing megasonic agitation or by reducing the thickness of the boundary layer—for example, by increasing the wafer rotation speed in a spin tool. To overcome the influence of the boundary-layer barrier, researchers have mixed ozone gas with water vapor at elevated temperatures.[12] The addition of scavengers and the increase in temperature have improved strip rates. However, photoresist removal using a wet clean process remains a challenge that depends on the type of resist and postexposure processing used.

Disinfection. The introduction of ozone into water treatment systems about a century ago was directed at the disinfection of microbiologically polluted water. In the semiconductor world, ozone is used to disinfect water purification systems. However, chemicals such as chlorine or chlorine dioxide, which are used to purify drinking water, are not acceptable in the IC industry. An advantage of ozone is that it decays back to oxygen. However, in a closed water-purification system, the oxygen concentration can accumulate to levels that are higher than specified in *The International Technology Roadmap for Semiconductors*.[15]

An International Sematech study on high-purity water disinfection reported that reduced dissolved-oxygen concentrations were achieved by combining a Gore-Tex membrane contact system from W. L. Gore & Associates (Newark, DE) with a high-capacity ozone generator from ASTeX (Berlin, Germany).[16] An oxygen concentration of ~240 ppb was obtained.

The ozone concentrations required for water disinfection are much lower than those required for wafer cleaning. A key parameter is the free disinfectant concentration c multiplied by the available contact time t (CT value).[17] A CT value of 1.6–2.0 mg/L/min is considered to be sufficient for effective disinfection. Table I provides examples of disinfection dosages reported in the literature.[18]

Pathogen	Ozone Dose
Bacillus anthracis	Ozone susceptible
Escherichia coli bacteria	Destroyed by 0.2 mg/L within 30 seconds
Encephalomyocarditis virus	Destroyed to 0 level in less than 30 seconds with 0.1 to 0.8 mg/L
Poliomyelitis virus	99.99% killed with 0.3 to 0.4 mg/L in 3–4 minutes
Streptococcus bacteria	Destroyed by 0.2 mg/L within 30 seconds

Table I: Ozone dose for disinfection of certain bacteria and viruses.

Seeking an Alternative to RCA Cleans

Studies have been conducted to find an alternative to RCA cleans that offers

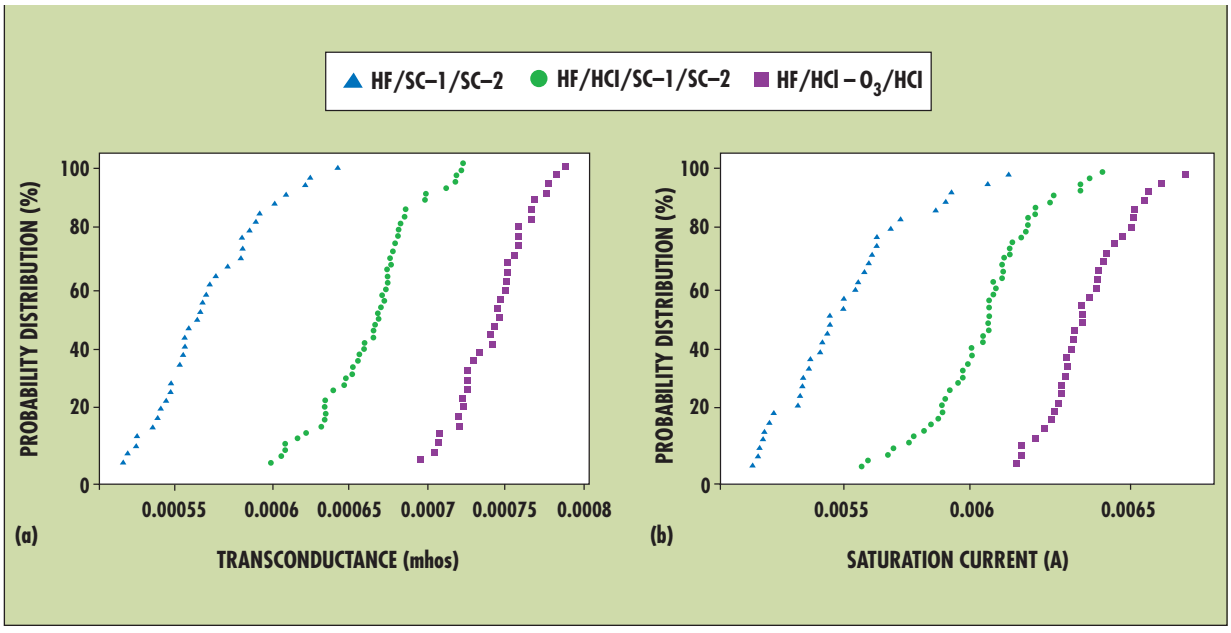

Figure 3: Transconductance data (a) and saturation-current data (b) from CMOS devices for three types of pregate oxide cleans. (Oxide thickness = 21 Å, gate length = 0.15 µm.)[21]

equivalent or improved performance while involving fewer steps, reduced chemical consumption, and lower costs. Examples of such alternatives are the ACD process, the SCROD method, IMEC cleans, diluted dynamic cleans, and Ohmi ultraclean technology.[6,9,19,20] In terms of particle and metal removal efficiency, environmental impact, cost, wafer-surface characteristics, and final device electrical performance, all of these processes perform as well as or better than RCA cleans.

A study by International Sematech evaluated different pregate oxidation cleaning chemistries for devices having 21-Å-thick SiO_2 gate dielectrics, including anhydrous HF vapor, HF/SC-1/SC-2 without HF last, HF/HCl-O_3/HCl, and HF/SC-1/SC-2/SC-1.[21] Experiments performed using an FC-821L advanced wet bench cleaning tool from DNS Electronics (Sunnyvale, CA) and an ASTeX Liquozon ozonated water delivery system showed that the use of ozone instead of an SC-1/SC-2 chemistry led to an increase in transconductance and saturation current, as illustrated in Figure 3. Moreover, the ozone method resulted in the lowest levels of surface roughness and interface scattering.

Conclusion

Wafer wet cleaning processes will continue to play an important role in semiconductor manufacturing as the complexity of wafer structures increases. Developments in reliable ozone-generation systems make ozone an attractive alternative to traditional wet cleaning and photoresist removal methods. Ozone/water cleaning processes are less expensive and more environmentally benign than RCA cleaning techniques. Ozone is no longer merely of scientific interest in semiconductor applications; it can provide practical benefits in wafer and IC manufacturing processes.

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