SPECIAL APPS
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MATERIALS INTEGRATION
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EXCLUSIVE INTERVIEW
Applied Materials’ Mike Splinter
Using dissolved ozone in semiconductor cleaning applications

Christiane Gottschalk, MKS Instruments, ASTeX;
and Juergen Schweckendiek, ASTEC

Ozone (O₃), 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 waste-water, 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 O₃ and O₃-derived oxidizing species such as OH radicals.

In chip fabrication processes, ozone is
Much information on the ability of DIO₃ alone cannot efficiently remove contaminants to levels of 1 atom/cm² or less. The removal efficiency depends on the type of organic species, the ozone concentration, and the reaction regime.

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. 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.

DIO₃ can degrade organic contamination. Its removal efficiency depends on the organic species, ozone concentration, and reaction regime.

The advanced cleaning and drying (ACD) method developed by ASTEC (Berg, Germany) uses a mixture of dHF and O₃, 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/O₃ bath, as shown in Figure 1.

Figure 2 presents typical metal contamination levels on <100> silicon wafers after an HF/O₃ clean, a modified RCA clean, and alkaline etch. After only one HF/O₃ cycle, contamination levels were reduced to ~1 x 10⁶ atoms/cm² 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.
An alternative process using ozone dissolved in DI water provides environmental benefits and lower costs. Photoresist-strip rates in DIO3 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. 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. 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. 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. 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). 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). 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.

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

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

### Seeking an Alternative to RCA Cleans

Studies have been conducted to find an alternative to RCA cleans that offers...
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.\textsuperscript{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.\textsuperscript{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.

**References**


![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.)\textsuperscript{21}](image)


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