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ELECTRONICS FABRICATION WITH DISSOLVED O_3: AN ENVIRONMENTALLY FRIENDLY SOLUTION

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OZONE

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Ozone (from the Greek word *ozon*, neuter present participle of *ozein, to smell*) was first identified by chemist Christian Werner Schönbein in 1839 as a by-product of the electrolysis of water. The first ozone generator was built by Werner von Siemens 18 years later. Since then, ozone has found broad industrial application, especially for the treatment of drinking water and wastewater. In the 1990s, the semiconductor industry found applications for ozone and ozone/water mixtures in its process technology. Dissolved ozonated water (DIO_3), in particular, has been developed as an environmentally friendly alternative to sulfuric acid and ammonia-based mixtures that have historically been used in the traditional RCA surface cleaning process for semiconductor device fabrication.

DIO_3-based surface cleaning chemistries have highly desirable characteristics that include improved performance, fewer cleaning steps, and reduced chemical consumption as well as reduced temperature and costs. This article reviews the equipment requirements for the generation of DIO_3 and surveys the wet cleaning applications of ozonated water in semiconductor device fabrication.

Ozone Generating Equipment

In order to produce ozonated water effectively, close attention must be paid to equipment configuration and on the nature of the wetted materials used within the equipment. Typically, an ozone/water system consists of: an ozone generator, a contactor, an ozone gas destruct unit, and at least one ambient ozone monitor. Additional on-line ozone analyzers may be required, depending on the process requirements (e.g., for mass balances), the influent and effluent ozone gas concentrations as well as the dissolved ozone concentrations that must be measured (Figure 1).

Safety considerations. Safety and environmental considerations are critical in ozone generating equipment, as ozone has toxic properties. Effluent gaseous ozone must be re-converted to oxygen before leaving the DIO_3 generating system and this is usually done with an ozone-destruct unit based on either catalytic or thermal principles. An ambient ozone safety monitor for continuous monitoring of a potential ozone leak within the system should be provided in areas where equipment operators could face possible exposure, and should additionally be coupled with an automatic ozone generator shut-off. Typically, UV-photometers are preferred for the measurement of both low ambient and high process ozone concentrations, since other measurement techniques, based on electrochemical or semiconductor principles, are less reliable. Different concentration ranges (low ambient levels versus high process concentrations) will require different detector configurations (different cuvette lengths) for effective measurement. Certain UV photometers can also be used for the direct measurement of ozone dissolved in high-purity water.

Materials in contact with ozone. Ozone is a very strong oxidant, and therefore, all component materials within a system that come into contact with ozone must be highly corrosion resistant. Table A provides an overview of specific material compatibilities for use with ozone. Note that some purity and process requirements may preclude the use of certain materials with DIO_3, despite the fact that they are ozone resistant. For example, high quality stainless steel, while resistant to gaseous ozone, may produce unacceptable metal contamination levels when used with ozonated water. Great care must therefore be taken in screening all wetted compo-

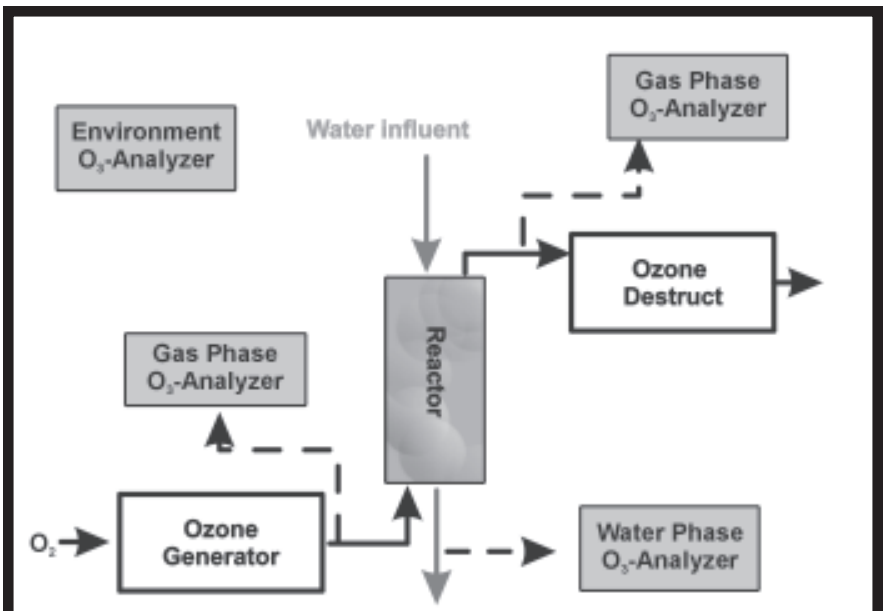

Figure 1. Components for dissolved ozone system.

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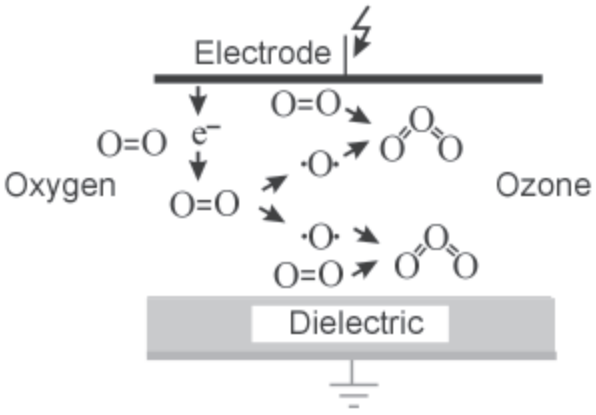

Figure 2. Silent electric discharge.

Figure 3. An example of a static mixer.

nents for material compatibility with respect to ozone.

For instance, silver, especially in the oxide form, cannot be used in ozone systems, since it will catalytically decompose ozone, producing particle and metal contamination. If conventional VCR fittings are used in equipment configured for ozone generation then problems will arise, since standard VCR gaskets are silver-plated. Thus, in ozone systems, non-plated stainless steel gaskets must be specified in order to avoid this effect. Other oxides (e.g., manganese [Mn] or palladium [Pd]), will also lead to the catalytic decay of ozone and may be used for the efficient destruction of ozone.

Polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF), while less expensive than polytetrafluoroethylene (PTFE)/polyfluoroalkoxy (PFA), are also less stable over time. PVC can be used for drain lines but it is not recommended for process lines. Polypropylene (PP) and polyethylene (PE) must to be avoided in all cases since they will be immediately destroyed, producing dangerous ozone leaks.

Ozone gas generation. Ozone is an unstable gas and must therefore be generated on-site. Clean ozone gas for use in semiconductor applications is produced from pure oxygen and electrical energy using a silent electrical discharge (also known as a dielectric barrier discharge or DBD) in an ozone generator. Oxygen is passed between two electrodes separated by a solid dielectric. An alternating high voltage field is applied to the one electrode, producing a discharge in the gap. Impact events between higher energy electrons in the discharge and molecular oxygen present in the gap initiate reactions that lead to the dissociation of the molecular oxygen into atomic O; ozone is then produced through recombination of these oxygen atoms with molecular oxygen (Figure 2). Semiconductor applications require a minimum oxygen purity of 99.995% with low levels of total organic carbon (TOC) and humidity.

Ozone generators based on the silent discharge principle require small quantities of a dopant with the oxygen feed. Typically, these dopants are nitrogen (N_2) and carbon dioxide (CO_2). The use of noble gases as dopants, such as helium (He), neon (Ne), and argon (Ar), has also been proposed (1). The presence of the dopant helps to produce long-term stability in the ozone-generation process. The dopant concentration in the feed may range from 10 parts per million (ppm) to 10%, which is dependant upon the ozone generator design and the quality of the feed gas. Some ozone generators can operate without the addition of a dopant gas, providing that the oxygen feed is not “too clean” (i.e., the oxygen already contains small amounts of impurities such as nitrogen).

Ozone production is an endothermic process ($\Delta H = +143$ kilojoule per mole [kJ/mol]) (2). Also, the process is relatively inefficient, as only 4% to 12% of the electrical energy supplied to the DBD goes into the formation of ozone; the rest of the input energy is transformed into heat (3). Since the ozone molecule decays quickly at elevated temperatures, efficient cooling is necessary for the efficient production of ozone. This balance between energy input and the need for low process temperatures typically results in maximum concentrations of 20 $\%_{weight}$ (approximately 300 g/Nm^3) ozone in oxygen, for DBD ozone generation systems.

Two additional methods for ozone production should be mentioned. Ozone can be produced either through the electrolysis of water, or by UV irradiation of an oxygen containing gas at wavelengths below 200 nanometers (nm), which is similar to the natural process occurring in the atmospheric stratosphere. These methods have capacity limitations and the cost and size of the generation equipment are high compared to that used in the silent discharge method.

Dissolved ozone. The ozone gas produced in a silent discharge can be used directly for certain dry applications. Wet (aqueous) applications require an additional process step to transfer the ozone gas into the fluid. This can be done by injection into water within an application tool, or with a separate contacting system to produce dissolved ozone at the necessary concentrations upstream of the application tool. Intimate contact of the ozone gas with the fluids can be achieved through a variety of different configurations of gas diffusers so long as they are constructed of materials resistant to ozone. The injection of ozone into solution can be accomplished using fine porous plates immersed in the fluid baths, membranes, injector nozzles, static mixers, or bubble columns.

PTFE membrane mixers direct the liquid phase through a bundle of microporous tubing that is housed in an appropriate shell. The gas is passed through the outer shell countercurrent to the liquid and diffuses through the

porous tube into the liquid. To avoid bubbles, the pressure on the gas side must always be lower than on the fluid side.

Static mixers (Figure 3) consist of several mixing elements arranged in a series within a pipe. Such systems are small and easy to handle. The hydrodynamic conditions provide for a uniform distribution of small bubbles of dissolved ozone over the entire cross section in which the fluid is contained. The ozone gas does not completely dissolve in the fluid in static mixers. The surplus gas appears as bubbles in the outlet of the mixer. If gas bubbles are undesirable in a particular process, a debubbler must be installed downstream of a static mixer.

Bubble columns are a very simple type of contactor, but have relatively low transfer efficiency. Modifications that increase gas/fluid contacting surfaces are known to enhance the efficiency of ozone dissolution, but are seldom reported.

Each type of contactor has unique hydrodynamic behavior and mass transfer characteristics and it is important to take these factors into consideration when evaluating experimental results and optimizing processes that require dissolved ozone.

Current developments in contacting technology provide ozone concentrations of 30 ppm (parts per million) dissolved in DI water at flowrates of 30 liters per minute (L/min) and over 90 ppm at 5 L/min at ambient temperature (5).

Applications

Surface cleaning is a critical and often repeated step throughout the manufacture process for semiconductor devices. Flat panel display (FPD) manufacture also requires critical surface cleaning, albeit with fewer cleaning steps in the process and much larger substrate size. Wet techniques offer greater efficiencies for surface cleaning and therefore dominate over dry cleaning.

The standard RCA cleaning sequence is by far the predominant technique. In this method, the surface is first cleaned using a sulfuric acid (H_2SO_4)/hydrogen peroxide (H_2O_2) mixture at 120 to 150°C to remove organics, followed by treatment with dilute HF for oxide removal. The surface is then subjected to an ammonium hydroxide (NH_4OH)/H_2O_2 mixture to eliminate particles and a hydrochloric acid (HCl)/H_2O_2 mixture to remove soluble metal contamination,

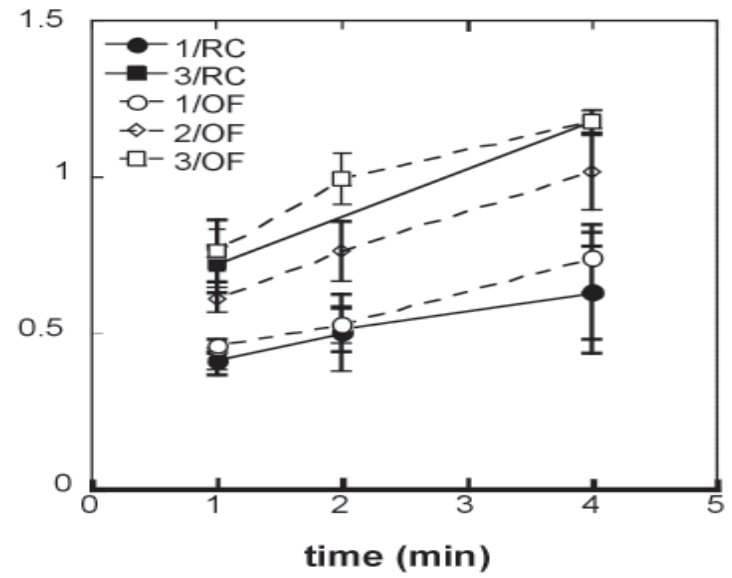

Figure 4. Oxide thickness as a function of ozone concentration and dip time (RC: recirculation mode, OF: overflow mode), 10 Å =1 nm.

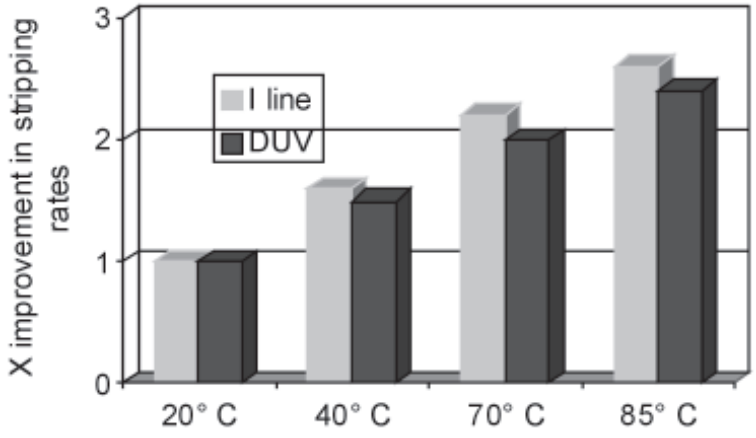

Figure 5. Stripping rates with ozonated DI water as a function of temperature (after 9).

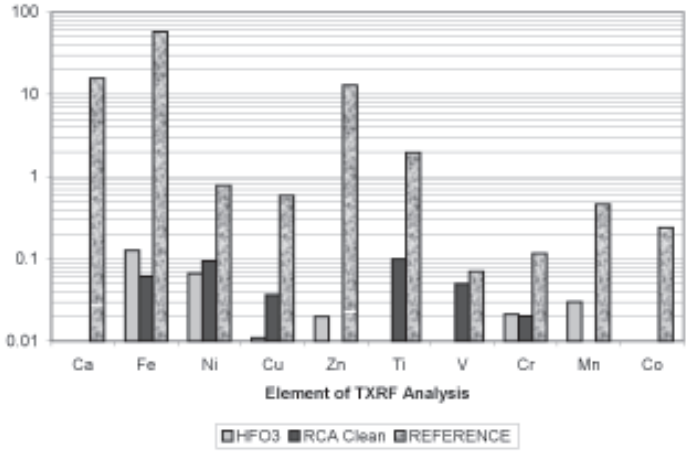

Figure 6. Metal surface concentration after three types of clean (after 11). Reference: after alkaline etch, RCA clean: modified RCA > 35 min, Spin Drying HF/O3: < 15 min

TABLE A
Material Compatibility (*: material compatible, X: material not compatible)

Material	*O_3 gas*	*O_3 dissolved*	*Comment*
Metals			metals can suffer severe corrosion
Stainless steel	*	X	
Silver	X	X	silver and other metals can destroy ozone catalytically
Inorganic oxides			
Glass, quartz	*	*	
Alumina oxide	*	X	
Fe-, Cu, Mn- oxide	X	X	efficient catalyst
Organics			Most organics are severely attacked
PTFE, PFA	*	*	
PVDF, PVC	X	(*)	PVDF/PVC are attacked in gas phase, used in drain lines
PP, PE	X	X	
Kalrez, chemraz	*	*	sealing

both at 80 to 90°C. Alternative processes that can accomplish all of the functions of the RCA cleaning sequence, while either reducing or replacing the usage of these highly corrosive and environmentally unfriendly chemicals, are being vigorously pursued within the semiconductor industry. Any new cleaning processes must address the current challenges in sub-micron particle removal as well as the environmental impact from the high consumption of water and chemicals and increasing costs.

Ozone-based chemistries have been developed that can replace RCA cleaning sequences and fulfill the environmental, economic and process requirements of advanced device fabrication. Ozone is of high interest for semiconductor applications because of its fast reaction rate, a direct consequence of its high oxidation potential combined with low activation energy of its cleaning reactions. The following section gives some examples of the application of ozone in semiconductor device fabrication.

Oxide growth. Silicon surfaces that are treated with ozone or DIO_3 solutions exhibit self-limiting oxide growth and a hydrophilic state in the resultant surface. Silicon dioxide growth in DIO_3 at room temperature self-limits at 10 to 11Å (Angstrom), a relatively thick layer as compared with other chemical oxidations. For example, oxide growth with hydrogen peroxide self-limits at a thickness of about 7Å. The addition of platinum (Pt) to H_2O_2 enhances the oxidation characteristic through the generation of radical species, increasing the self-limited oxide thickness 10 to 11Å (6). The maximum observed oxide thickness of SC1 is around 8Å (7). The main parameters influencing oxide growth rate in DIO_3 are the dissolved ozone concentration, the process time, pH, temperature, and the presence and type of additives coupled with equipment configuration (8).

Figure 4 indicates the influence of dissolved ozone, dip time, and process configuration on the thickness of an oxide layer grown on a silicon surface in DIO_3. The process configurations include either recirculation mode (RC) or overflow mode (OF). In the RC mode, ozone gas is brought into the bath by a diffuser (solid markers and lines). While processing the wafer, the gas flow is stopped to avoid bubbles. In the OF mode (open markers and dotted lines), ozonated water (DIO_3) is delivered continuously by a stand-alone DIO_3 system. The RC and OF modes yield comparable results in terms of oxide thickness. The continuous supply of ozonated DI water used in OF mode was observed to result in superior oxide thickness uniformities.

The thickness of the oxide grown in DIO_3 can be effectively controlled by exposure time and ozone concentration. This is a desirable attribute in the process since the full self-limited oxide thickness is not always advantageous in device construction. For example, establishing high quality electrical characteristics of the interface between a high-k oxide film (higher dielectric constant than silicon oxide) and a silicon substrate requires the presence of a well-defined, extremely thin, and uniform layer of silicon dioxide at that interface. This can be produced by saturating the surface with oxygen and subsequently performing an etch-back using dHF, or by a more easily controlled oxide growth process that adjusts, for example, the exposure time in a DIO_3 bath to yield the required thickness.

Photoresist stripping. Photoresists can be removed by either dry (e.g., plasma ashing) or by wet chemical processes. Wet chemical processes commonly use sulfuric acid (H_2SO_4), often combined with H_2O_2, (SPM) or O_3 (SOM). LCD panel processing differs somewhat in that the photoresist is stripped using a mixture of organic solvents such as dimethylsulfoxide (DMSO) and mono ethanol amine (MEA). Both the sulfuric acid-based and organic solvent-based processes are performed at elevated temperatures.

Ozonated water processes have been used for photoresist stripping, albeit within certain limitations. Higher strip rates can be achieved by increasing the dissolved ozone concentration as well as the process temperature. However, the instability of ozone and its decreased solubility at moderately elevated temperatures has hindered process optimization for resist stripping. Figure 5 shows the stripping performance for I line and DUV resist normalized at 20°C (9). A rate enhancement factor of up to 2.5 was observed when going to 85°C.

It is noteworthy during ozonated water stripping processes that the photoresist is not completely degraded to CO_2 and H_2O. Low molecular weight fragments with high oxygen content and high sol-

ubility such as acetic acid and oxalic acid are also produced (10).

Metal and particle removal. Particulate and metal contamination levels will continue to play a critical and potentially negative impact on device yields as feature sizes move into the nanometer regime. Sources of metallic contamination include metal leached from tools and tubing, as well as pre-existing contamination in chemicals and even DI water. Particle contaminations, both organic and inorganic, come from the clean room, process tools, and occasionally from chemical reactions.

Particle and metal contaminants are currently removed by the use of a two-step cleaning process. SC1 (standard clean) cleans are used to remove particles and SC2 cleans to remove metal contamination from wafer surfaces.

Ozonated water cleaning can effectively remove both particulate and metal contamination, and similarly requires the use of a two-chemical process. The sequential use of ozonated water with acid (e.g., HF and/or HCl) yields excellent results in the removal of particulate and metal contaminants. Metals are oxidized by ozonated water to form metal oxides and hydroxides. These oxides/hydroxides can be incorporated into the self- layer or bond to the Si-surface. Acids can then act as ion exchangers to yield soluble and thus removable metal species or, in the case of soluble oxides with hydrofluoric acid HF, they can simply dissolve the particle. Ozone alone may be sufficient to remove organic particulate contaminants.

The advanced cleaning and drying (ACD) method, developed by ASTEC (Berg, Germany), employs a mixture of dilute HF and ozone, and combines metal removal and drying into one process. Figure 6 shows a comparison of metal contamination on a Si <100> surface after a single HF/O_3 clean, a modified RCA clean, and an alkaline etch. Contamination levels of 1 E9 atoms per square centimeter (atoms/cm^2) or less were achieved.

Insoluble particles can also be removed from a wafer surface by the sequential use of ozone and dilute HF. As previously noted, ozone creates an oxide layer that can incorporate these particles. Once formed, this layer is easily removed using dHF. Care must be taken in the choice of process for dHF cleaning since re-deposition and roughening must be avoided. The process can be enhanced by the use of megasonics.

Starflinger et al. (12) reported the use of this sequence in a single wafer tool with an improved micro roughness compared to a typical RCA clean.

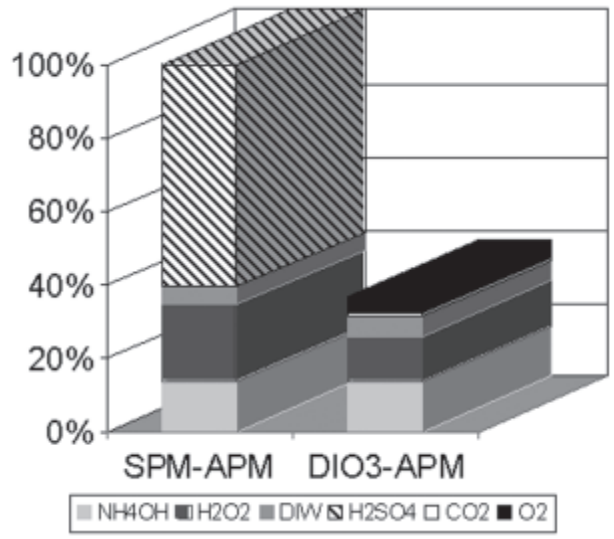

Figure 7. Detailed chemical cost per run for PR strip in a spray tool (after 9).

Disinfection. The higher oxidation potential of ozone makes it a more powerful disinfectant than either hydrogen peroxide or chlorine. In comparison to chlorine, ozone attacks a bacterium by directly destroying the cell membrane, whereas chlorine must first diffuse through the cell wall to the cytoplasm, where it then oxidizes the enzymes destroying the bacterium.

Ozone effectively controls bacteria in storage tanks and piping. Dosage levels are calculated as a function of time *t* and the dissolved ozone concentration *c*. A *ct* value of 1.6 to 2.0 milligrams per liter per minute (mg/L/min) (e.g., 0.4 mg/L of ozone for 5 minutes) is considered sufficient for disinfection, corresponding to ozone concentrations that are much lower than for wafer cleaning. Residual ozone is easily decomposed using UV irradiation.

Summary

Ozone is a strong oxidizing agent suitable for advanced wafer cleaning. Ozone-based processes have been shown to be effective replacements for traditional wet cleaning processes with the following additional benefits:

- Ozone is generated at the point of use, avoiding storage and transportation costs.
- Ozone can reduce chemical and high-purity water consumption.
- Low disposal costs.
- Benign by-products: oxygen and water.

Figure 7 shows a cost comparison for chemicals (including all process gases) between a standard SPM-SC1 clean and a DIO_3-SC1 photoresist stripping process. The comparison shows that the ozone-based process results in a cost savings of 63%. Ozone-based processes thus provide better, or at least comparable, performance to standard technologies with the additional benefits of environmentally friendly chemistries and substantial reduction in process costs.■

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