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The Increasing Importance of the Use of Ozone in the Microelectronics Industry

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Abstract

Recently the microelectronics industry is investigating the application of ozonated solutions in the cleaning of semiconductor devices as an alternative for the frequently used H₂SO₄-mixtures. The use of ozone would result in more environmentally friendly and cost-saving cleaning concepts. To optimize this new wet chemical cleaning processes, fundamental understanding of the behavior of ozone in ultrapure water is required. The decomposition and the solubility of ozone in ultrapure water were investigated as a function of pH, temperature and various additives. Some applications will also be discussed, namely the oxidation of silicon and the mechanistic aspects of the removal of organic contamination.

Key Words

Ozone; Microelectronics Industry; Ultrapure Water; Ozone Decomposition; Semiconductor Applications;

Introduction

The use of ozone in practical systems is mainly related to the field of drinking water treatment where it is used for disinfection purposes (1), inorganic (2,3) and organic pollutant oxidation (4). More recently other applications of ozone become an important issue, for example in the field of the manufacturing of semiconductor devices.

The performance of integrated circuits (IC) has increased enormously during the last decade and this is mainly due to a decreased size of their components. In order to achieve a better performance for these smaller semiconductor devices the quality and the purity of the main material, in particularly silicon, and the chemicals used during the fabrication process need to increase as well. The purity required puts stringent demands

on the levels of contamination that can be tolerated during the entire fabrication process. The type of contamination which can be present in or on silicon surfaces can be divided in various types which are illustrated in Figure 1.

One of the main concerns in micro-electronics industry is the cleaning of silicon wafers prior to the fabrication of semiconductor devices. This cleaning is a combination of wet and dry cleaning steps whereby different aqueous solutions or gases are used. Cleaning steps account for more than 30 % of the steps in the production process, indicating their great importance. Therein are wet cleaning methods responsible for more than 80 % (5). Various wet cleaning concepts exist with the RCA-clean (6) and the IMEC-clean (7) as the two most widely used ones. A brief description of the IMEC-clean will be given below: see Figure 2.

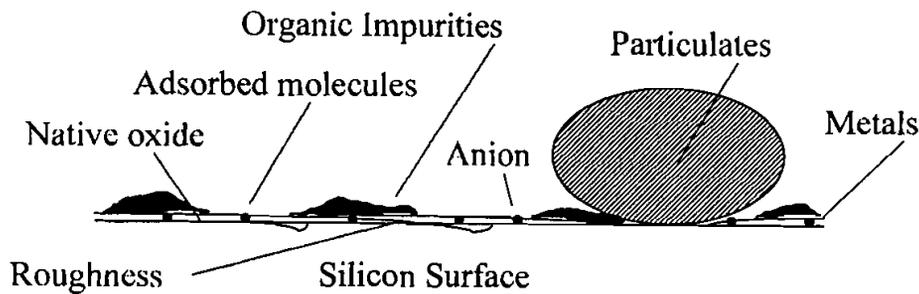


Figure 1. Illustration of the various types of contamination in or on silicon surfaces (8).

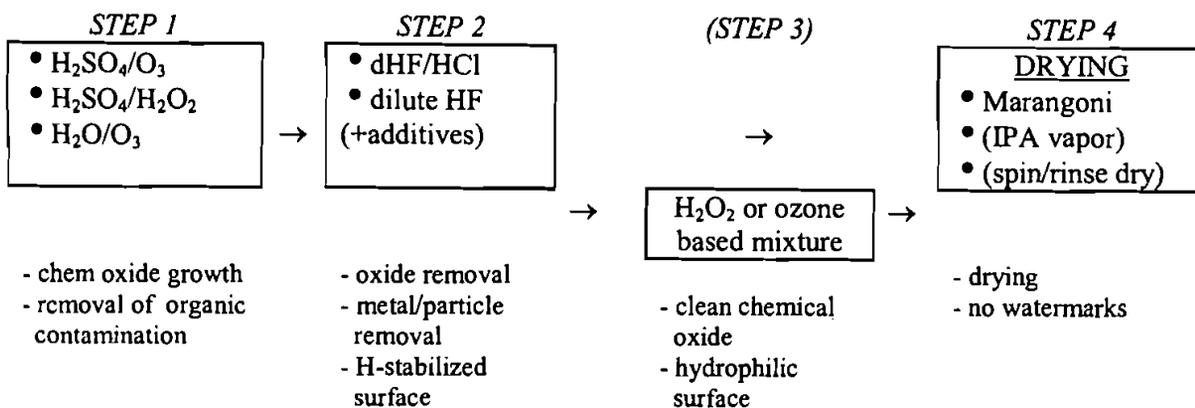


Figure 2: Schematic representation of the IMEC-clean concept (7).

In contrast to the RCA-clean, the IMEC-clean consists mainly of acidic solutions in order to avoid (re)deposition of metals, especially iron. Moreover it involves less steps than the RCA-clean, leading to a reduced consumption of chemicals, a better process robustness and a short cycle time. It is at least as effective and certainly more cost-effective and environmentally friendly than the RCA-cleaning concept.

The IMEC-clean essentially consists out of three steps with an optional fourth step. In step 1 an oxide layer is grown after the removal of the organic contamination by using a H₂SO₄/H₂O₂-mixture (Sulfuric acid Peroxide Mixture, SPM). Alternatively this SPM-step can be replaced by ozonated solutions in H₂SO₄ or deionized water (DI-water). In contrast to the RCA-cleaning concept where oxidation and etching occur at the same moment, the IMEC-clean separates these two actions. The oxide layer is etched away in the second step by dilute HF (d-HF) and mixtures with HCl and other additives. In this step the required etch depth for optimal particle removal efficiency is achieved.

Only acidic solutions are used and thus no more silicon surface roughening occurs because no etchant is present during the oxidation. The use of only acidic solutions results in a simplified design of the cleaning tools and a decreased metal (re)deposition.

Depending on the possible applications of the IC components, a third step is optional where a chemical oxide is grown with H₂O₂ or O₃ to achieve a hydrophilic surface. The final step involves the drying of the wafer surface, but this topic will not be discussed in the frame of this paper.

The first and important step uses the SPM-mixture (H₂SO₄/H₂O₂) as cleaning agent. It is used for the removal of organic contamination on the silicon wafer surface, for the stripping of photoresist material and for growing a thin oxide layer. Because of the large quantity of rinse water required by the SPM-step and in view of the safety hazard implied by the use of H₂SO₄, one of the main objectives of current research is to find other, less aggressive and more environmentally friendly mixtures with the same or even a better cleaning efficiency. An

interesting alternative is the use of ozone in aqueous solutions and therefore the use of ozonated solutions is currently an important research topic. The effective use of O₃/DI-water processes in the production of semiconductor devices leads to a decreased volume of rinse and waste water.

For example, compared to the conventional RCA-clean the IMEC-clean only uses two chemical baths instead of four and it has been shown that two rinse baths instead of five and only 8.7 10⁶ L DI-water/year instead of 26 10⁶ L/year were needed (9). Concerning the chemical waste per year, the IMEC-clean produces 2 10⁴ liters whereas the RCA-clean 3.3 10⁵ liters. Globally the IMEC-clean reduces the consumable cost by more than a factor of two.

Figure 3 demonstrates the cost reduction that is achieved by using O₃-based cleaning processes for organic contamination removal. Less chemicals are used and less rinse water is needed, thus leading to a cheaper cleaning process.

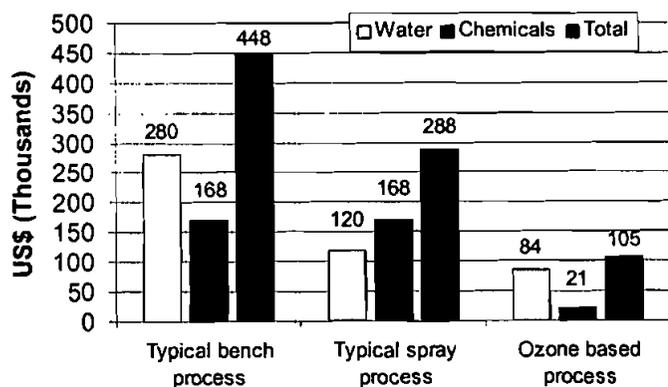


Figure 3: Example of the annual water and chemical costs for removing photoresist material (assumption of 20.000 wafers per month with six passes per wafer; cost of deionized water is one cent per liter, cleaning chemicals \$2 per liter and acid resist strip chemicals \$3 per liter) (10).

From the above it is clear that the micro-electronics industry is very interested in the application of ozone chemistry because ozone based cleaning technologies are more cost-effective and more environmentally friendly. Possible applications are: the oxidation of silicon to form thin SiO₂-layers, the oxidative degradation of organic contamination on

silicon surfaces (both monolayers and photoresist residues) and the re-use of rinse water after an ozone treatment.

In order to be able to optimize these applications, the physico-chemical behavior of ozone in DI-water needs to be clarified. Therefore fundamental knowledge on the solubility and the decomposition kinetics of ozone in aqueous solutions is needed. Also the mechanism of the oxidation of silicon by ozonated solutions needs to be understood. While a complete description of the topics mentioned above is given elsewhere (11), a summary of the results will be presented below.

Results

Generation of Contamination by the Production of Ozone.

As purity requirements are very stringent in cleaning processes applied in IC manufacturing, contamination levels need to be controlled, especially metallic and organic contamination.

Currently ozone is generated by an electrical discharge in pure oxygen whereby ozone is formed in the following reaction sequence requiring an energy of about 144.4 kJoule/mole in the first step, Equation [1]:



A problem is that the production of ozone by electrical discharges leads to the formation of both metallic and organic contaminants.

Since for wet chemical cleaning processes, ozone is introduced in DI-water, the metals K, Ca, Fe, Mg, Al, Ti, Cr and Zn were detected at concentration levels between 10 and 1000 µg/L after 3 hours of ozonation with a Fischer type ozone generator (11). These levels of metallic contamination are detrimental for the device performance and therefore cleaning baths need to be refreshed regularly. It must be noted that recently new O₃ generators are built which produce far less metallic contaminants and which are almost metal-free (11).

Besides metals, organic species are also introduced in the aqueous solution (12): acetate, formate and

oxalate. These species are believed to originate from the slow degradation of the Teflon tubing used, namely FEP (Fluorinated Ethylene Propylene) and PFA (Per Fluoro Alkoxy). Although the presence of these organic species is less detrimental than metals, the cleaning solutions need to be refreshed often to avoid a build-up of these organics.

Ozone In Ultrapure Water: Fundamental Aspects.

The Decomposition of Ozone in Ultrapure Water.

Ozone is not a stable species in aqueous solutions. Literature data on the ozone decomposition are easy to find, especially at relatively high pH-values ($\text{pH} > 7$) in waste and natural waters. However the wet methods for cleaning semiconductor devices involve ultrapure aqueous solutions, mostly at low pH to avoid (re)deposition of metals. These conditions are not so common and therefore experiments on the ozone decomposition in DI-water at low pH were performed (11,13).

The ozone decomposition rate r_{O_3} is formally described by Equation [3]:

$$r_{\text{O}_3} = \frac{d[\text{O}_3]}{dt} = -k_{\text{exp}} \cdot [\text{M}]^m \cdot [\text{O}_3]^n \quad [3]$$

where n and m are apparent reaction orders of respectively the ozone concentration and the concentration of a yet unknown reaction partner M and k is the apparent rate constant for the ozone decomposition.

The ozone decomposition rate was determined as a function of pH, temperature and nature of the additive. Various acids were used to achieve low pH-values, for example nitric acid, Figure 4:

When $\ln[\text{O}_3]$ is plotted versus time one observes linear decays indicating a first-order decomposition reaction: $r_{\text{O}_3} \sim [\text{O}_3]^1$. From the slopes one sees that the decomposition rate is a function of pH: r_{O_3} increases at higher pH. However when the pH becomes larger than 5, r_{O_3} does not follow anymore the first-order decomposition kinetics. A mathematical analysis from the kinetic rate expression indicates that the apparent reaction order

n becomes equal to 1.5. This is shown by a plot of the inverse of $[\text{O}_3]^{0.5}$ as a function of time, resulting in a straight line.

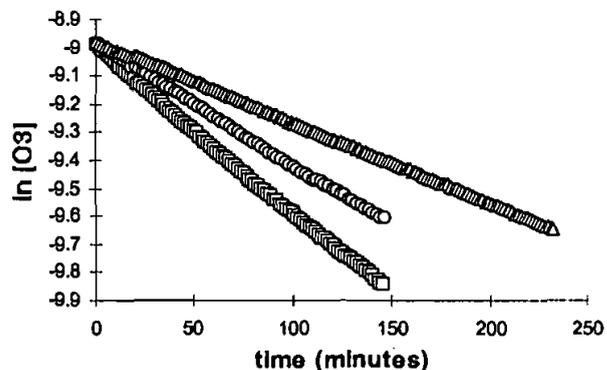


Figure 4: Pseudo first-order decays of the ozone concentration as a function of time at room temperature in DI-water with nitric acid as additive : pH = 3.87 (□); pH = 2.97 (○); pH = 1.83 (Δ).

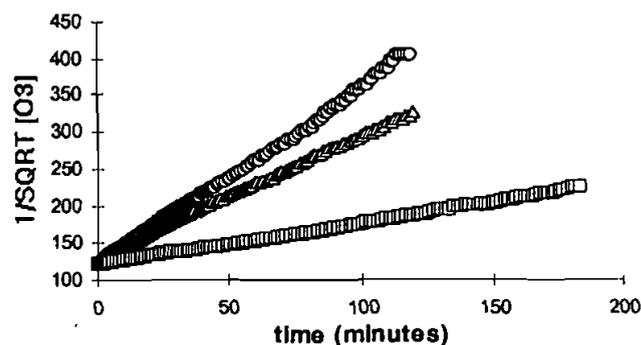


Figure 5: Pseudo order 1.5 decays of the ozone concentration as a function of time at room temperature in DI-water with NaOH as additive : pH = 7.13 (○); pH = 6.96 (Δ); pH = 5.41 (□).

This is illustrated in Figure 5 for the pH-values of 7.13, 6.96 and 5.41. When exposed to atmospheric conditions, ultrapure water has a pH of about 5.6 due to the carbonic acid equilibria. In order to increase the pH, NaOH was used as additive in these experiments. Since it is well known that OH^- ions destroy ozone in solution (14) (Equation [4]) it is logical to assign OH^- as the reaction partner M in Equation [3]. The quantitative results are shown in Table I where a summary is presented of the values of the parameters k , m and n in various experimental conditions at room temperature with the additives

HNO₃, NaOH, CH₃COOH, H₂SO₄, HCl and CH₃COONa.

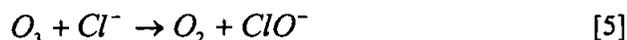


At near-neutral pH-values, the order n shifts from 1 to 1.5 and the order m goes from 0.112 to 0.296, thus the ozone decomposition rate becomes more dependent on the pH. Adding sodium acetate leads to an inhibiting effect on the decomposition rate which is due to the scavenging of radical intermediates of the ozone decomposition process by acetate/acetic acid.

Table I: Kinetic expressions for the ozone decomposition rate (r_{O_3}) in aqueous solutions at room temperature as a function of pH and additive (11).

pH-range	Additive	r_{O_3}
1.8 < pH < 4.4	HNO ₃	$1.0 \cdot 10^{-3} [OH^-]^{0.112} [O_3]^1$
5.4 < pH < 7.2	NaOH	$1.93 [OH^-]^{0.296} [O_3]^{1.5}$
pH < 4.5	CH ₃ COOH	$3.6 \cdot 10^{-4} [OH^-]^{0.072} [O_3]^1$
2.12 < pH < 3.2	H ₂ SO ₄	$2.1 \cdot 10^{-4} [OH^-]^{0.044} [O_3]^1$
1.2 < pH < 2.8	HCl	$4.2 \cdot 10^{-3} [Cl^-] [O_3]^1$
5.7 < pH < 7.5	CH ₃ COONa	$0.531 [OH^-]^{0.447} [O_3]^1$

A specific case is the ozone decomposition in hydrochloric acid where r_{O_3} is higher than in nitric acid below a pH of 2. This can be explained by the well-known reaction of the chloride anion with ozone (15), Equation [5]:



From our data a rate constant for this reaction equal to $(0.0042 \pm 0.0020) M^{-1}s^{-1}$ at room temperature could be derived (11).

The ozone decomposition rate depends besides the pH also on the temperature. The expression is given in Equation [6] where $k_{exp,T}$ is the experimental rate constant at a temperature T (expressed in Kelvin), R the universal gas constant and E_d the activation energy.

$$k_{exp,T} = k_{exp,T_{ref}} \cdot e^{-\frac{E_d}{R \cdot T}} \quad [6]$$

From our experiments in the temperature range from 19 to 67°C we could determine the value of $E_d = (39.6 \pm 4.1) kJ/mole$ at pH 1.8 in nitric acid (11). This value is in fairly good agreement with the literature values in the range of 41.23 to 46.4 kJ/mole (16).

For the application of ozone in cleaning processes, it is important to carefully select the appropriate working conditions like pH and temperature. A very interesting parameter to be considered when confronted with decomposition processes is the half-lifetime $t_{1/2}$. In this context $t_{1/2}(O_3)$ is defined as the time needed to reduce the initial ozone concentration with a factor two. The results are shown at room temperature with various additives in Figure 6.

From Figure 6 one sees that half-lifetimes of ozone of the order of 3 to 4 hours can be achieved under acidic conditions in the pH-range between 1.8 and 3. Only when HCl is used as additive much lower half-lifetimes are obtained due to the interference of the Cl⁻ reaction (Equation [5]).

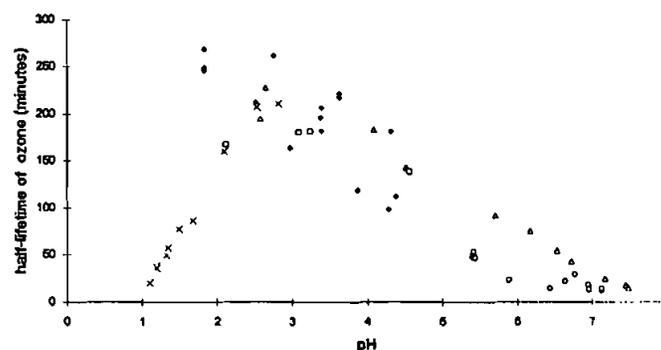


Figure 6: $t_{1/2}(O_3)$ at room temperature as a function of pH and additive (X) HCl, (O) NaOH (initial ozone concentration 10 mg/L), (□) H₂SO₄, (Δ) HAc/Ac⁻, (◆) HNO₃

The Solubility of Ozone in Ultrapure Water.

For many applications in IC-manufacturing the ozone concentration in the solution needs to be maximized. To achieve this goal one needs to have information of its solubility in water. When the solubility of gases is considered one has to take into account the gas/Liquid equilibrium which is governed by Henry's Law with an equilibrium

constant, the Henry's Law coefficient H^T_X , Equation [7]:

$$H^T_X = \frac{[X]_{liq} \text{ (mol/l)}}{[X]_{gas} \text{ (atm)}} \quad [7]$$

$[X]_{liq}$ is the concentration of X in the liquid phase (expressed in mole/L) and $[X]_{gas}$ is the partial pressure of X in the gas phase (expressed in atmosphere).

An increase of $[X]_{gas}$ leads to an increase of the concentration of the gas X in the solution and thus the solubility of a component depends on its concentration in the gas phase in equilibrium with the solution.

Normally Henry's Law is perfectly applicable for inert gases which do not react in the solution and which solubility is only temperature dependent. But as ozone decomposes in the solution (see the previous section), this ideal situation is not met. Therefore a pseudo-Henry's Law coefficient *H is defined at a given temperature T and pH, Equation [8]:

$$^*H^T_{O_3} = \frac{[O_3]_{liq,ss} \text{ (mol/l)}}{[O_3]_{gas} \text{ (atm)}} \quad [8]$$

*H is not only temperature dependent, but also pH-dependent due to the ozone decomposition. The mathematical expression for $H^T_{O_3}$ is given by Equation [9] (17):

$$\begin{aligned} ^*H^T_{O_3} &= \frac{[O_3]_{liq,ss}}{[O_3]_{gas}} = \frac{[O_3]_{liq}^* - \frac{r_{O_3}}{k_L a}}{[O_3]_{gas}} \\ &= H^T_{O_3} - \frac{r_{O_3}}{[O_3]_{gas} \cdot k_L a} \end{aligned} \quad [9]$$

with $[O_3]_{liq,ss}$ the steady state concentration of ozone, $[O_3]_{liq}^*$ the maximum ozone concentration at low pH, r_{O_3} the ozone decomposition rate, $k_L a$ the mass transfer coefficient and $H^T_{O_3}$ the Henry's Law coefficient at low pH where the ozone decay is negligible.

In a whole series of experiments we have determined $^*H^T_{O_3}$ as a function of temperature and pH. At low pH HNO_3 was used as additive while for the neutral-alkaline pH-values $NaOH$ was the additive. The results are shown in Figure 7.

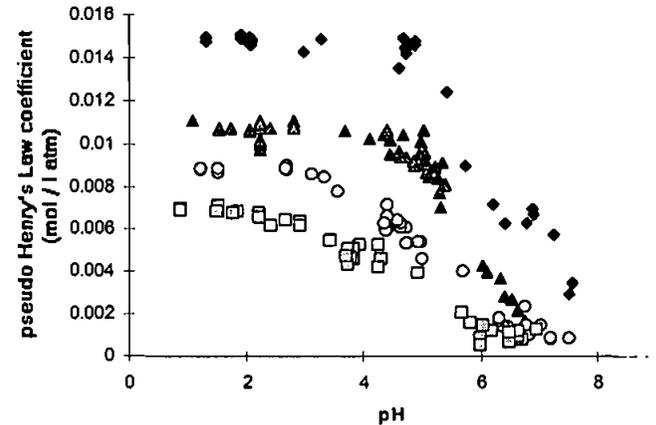


Figure 7: Pseudo Henry's Law coefficient $^*H^T$ of O_3 as a function of pH with $HNO_3/NaOH$ as additive (temperature = $16^\circ C$ (\blacklozenge); $26^\circ C$ (\blacktriangle); $35^\circ C$ (\circ) and $44.5^\circ C$ (\square)) (17).

At low pH-values between 1 and 4 the pseudo Henry's Law coefficient is nearly constant, but from pH 5 to 6 and higher, $^*H^T_{O_3}$ starts to decrease and the ozone solubility becomes very low at $pH > 8$. As it is logical, the plateau value of the pseudo Henry's Law coefficient at low pH decreases with increasing temperature.

When hydrochloric acid is used as additive for acidification, another behavior is seen: Figure 8.

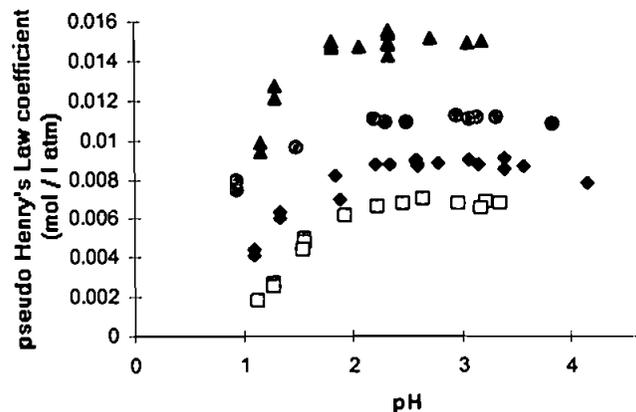


Figure 8: Pseudo Henry's Law coefficient of O_3 as a function of pH with hydrochloric acid as additive (temperature = $16^\circ C$ (\blacktriangle); $26^\circ C$ (\circ); $35^\circ C$ (\blacklozenge) and $44.5^\circ C$ (\square)) (17).

Between pH 2 and 4 the pseudo Henry's Law coefficient remains also constant, but now a lowering of the pH below 2 leads to a decrease of $\overset{\circ}{H}$. This is caused by the destruction reaction (Equation [5]) leading to an increase of r_{O_3} . Adding acetate/acetic acid however increases $\overset{\circ}{H}^T_{O_3}$ due to the acetate scavenging reactions leading to a lower value of r_{O_3} .

For practical uses Table II gives a few examples of ozone solubilities that can be achieved in the liquid phase as a function of pH, temperature and the concentration of ozone in the gas phase.

Table II: Solubility of ozone in solution (mg/L) as a function of temperature T (°C), pH and ozone concentration in the gas phase $[O_3]_{gas}$.

T (°C)	pH	$[O_3]_g = 50 \text{ g/m}^3$	$[O_3]_g = 200 \text{ g/m}^3$
16	2.1	16.7	66.8
	6.9	7.7	30.8
26	1.4	12.0	48.0
	6.7	1.9	7.6
35	2.7	9.9	39.6
	6.8	1.7	6.8
45	1.0	7.8	31.2
	6.6	1.4	5.6
68	1.0	3.9	15.6

Ozone generators can produce up to 300 gram ozone per m^3 (which is almost 15 % v/v) and thus the ozone solubilities given in Table II can easily be reached. The pH-issue is most of the time also no problem as most cleaning concepts are based on acidified solutions in order to avoid metal (re)deposition.

A problem might arise at high temperatures at which a number of cleaning processes are run. For example photoresist removal occurs by spraying hot water of approximately 85°C on the silicon surface in an ozone saturated reaction chamber (18). In that case it is difficult to obtain high ozone concentrations in the liquid phase, even when radical scavengers are present to suppress the ozone decomposition rate.

The solubility of ozone $[O_3]_{liq}$ (mg/L) at a temperature T and low pH (< 3) can be represented by the following empirical equation derived from our experiments, Equation [10]:

$$[O_3]_{liq} = 1.12 \cdot 10^3 \cdot [O_3]_{gas} \cdot e^{-0.028 \cdot T} \quad [10]$$

with $[O_3]_{gas}$ the gas phase concentration (g/m^3), T the temperature of the solution (Kelvin) and the factor $1.12 \cdot 10^3$ a proportionality constant with the units of $(mg/L)(g/m^3)^{-1}$. The exponent -0.028 has the units K^{-1} .

Once the solubility of ozone as a function of the various parameters has been determined, the experimental conditions have to be established for each specific application as will be illustrated in the next section.

Applications

The Oxidation of Silicon by Ozone in Solutions.

Besides the silicon oxidation process in the gaseous phase, in the past years the use of ozone in the liquid phase has gained interest for growing thin passivating oxides in wet cleaning processes (7,8,19). As the device scale reduces rapidly, the growth of good quality ultra-thin oxide layers on silicon wafers is becoming very important, e.g. the formation of gate oxides between 1.5 and 3 nanometer (20). A general tendency is to lower the temperature of the oxidation process while maintaining the same gate oxide characteristics. Since the oxidation process with ozone was not yet well characterized on the mechanistic level, the oxidation by means of ozone/DI-water needed to be better investigated (11,21,22).

The effect of several parameters on the oxide growth such as the pH of the solution, the ozone concentration and the nature of the additive has been systematically investigated. Finally an appropriate oxidation model for the oxide growth kinetics was selected. When hydrophobic silicon wafers are immersed in ozonated solutions, a parabolic oxide growth profile is observed as is illustrated in Figure 9 at pH 4.6 for various ozone concentrations.

The silicon dioxide layer t_{ox} shows a fast initial growth whereas the oxide growth levels off at longer reaction time. An analogous growth profile has also been seen in other studies (23). A few experiments were performed at oxidation times for 40 minutes but the oxide layer thickness t_{ox} remained nearly constant. Higher ozone concentrations result in thicker oxide layers. Above 20 mg/L ozone no

further increase of $t_{ox,max}$ was observed, not even with 40 mg/L of ozone (11).

At a lower pH of 1.2 with nitric acid as additive, analogous growth profiles have been measured (11). Approximately the same $t_{ox,max}$ were obtained for equal initial ozone concentrations, thus no

pronounced pH-effect is observed. Also with HCl as additive instead of HNO_3 , almost no change in the oxide growth profile has been noticed. The growth of SiO_2 by ozonated solutions is rather insensitive to pH-changes and the nature of the additive used. The effect of the temperature on $t_{ox,max}$ is also very small in the range between 20 and 50°C (11).

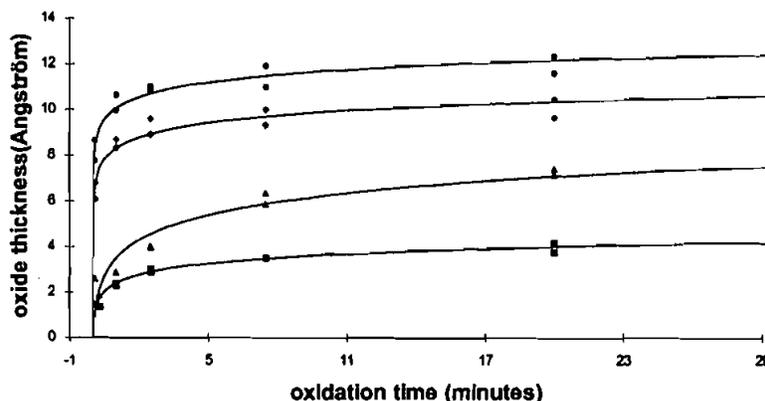


Figure 9: Growth profiles of SiO_2 as a function of the ozone concentration under the following experimental conditions: $T = 22^\circ C$ and $pH = 4.6$ (the ozone concentrations are $\blacksquare = 1$ mg/L; $\blacktriangle = 5$ mg/L; $\blacklozenge = 15$ mg/L; $\bullet = 17.6$ mg/L). The solid lines represent a fit based on the Fehner-expression.

Table III: Various oxidation models for the silicon dioxide growth. (with t_{ox} the oxide layer thickness, t the oxidation time, τ a shift in the time-axis due to the possible presence of an initial oxide layer and A, B, C, D, E, F fitting parameters)

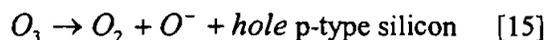
Deal-Grove (24)	$t_{ox}^2 + A \cdot t_{ox} = B \cdot (t + \tau)$	Eq. [11]	Thermal oxidation (700 – 1300°C).
Cabrera-Mott (25)	$\frac{1}{t_{ox}} = C - D \cdot \ln(t)$	Eq. [12]	Metal oxidation.
Fehner-Mott (26)	$t_{ox} = E \cdot \ln(1 + F \cdot t)$	Eq. [13]	Expansion of the CM-theory.

Concerning the mechanistic aspect of the SiO_2 -growth kinetics, various existing models were evaluated: the models of Deal-Grove (DG) (24), Cabrera-Mott (CM) (25) and Fehner-Mott (FM) (26). The mathematical expressions and experimental conditions are summarized in Table III.

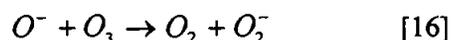
From our experimental results it was found that the Fehner-Mott equation provided by far the best fit to the experimental data (22) as is seen by the solid lines in Figure 8.

This FM-model implies that anions are the main oxidation precursors which migrate through the oxide layer under the influence of an electric field over the oxide. The oxidation precursor is thus a charged species which excludes molecular ozone. Experimental evidence strongly suggests that the bulk chemistry of ozone does not play a role in the silicon oxidation process. This leads to the exclusion of charged intermediates as oxidation precursors which are formed during the ozone decomposition process in the bulk solution.

The following possible pathway was proposed whereby O^- ions, formed directly at the $SiO_2/Liquid$ -interface, play a crucial role:



In this hypothesis a higher ozone concentration in the solution will result in a higher ozone concentration at the $SiO_2/Liquid$ -interface and this of course will enhance the O^- formation. However when the ozone concentration further increases the oxide thickness $t_{ox,max}$ becomes limited by the field-imposed drift as indicated by Fehner. O^- ions can also be lost by a mechanism which up to now remains uncertain but the reaction with ozone itself is a good possibility, Equation [16]:



In conclusion it can be stated that ozonated solutions can grow thin SiO_2 -layers of 5 to 12 Angstrom at room temperature within 5 to 10 minutes, even with only a few mg/L ozone in the solution. There is no need for higher ozone concentrations or elevated temperatures as the maximum achievable oxide thickness seems to be kinetically limited.

The Removal of Organic Contamination.

Organic contamination is one of the sources of device malfunction. Various types of organic contamination exist: contamination which is introduced on the silicon surface from the clean room environment (small organic molecules) and contamination which remains after certain process steps, e.g. photoresist residues. Sometimes organic layers of more than one micrometer thickness need to be removed, the so-called photoresist layers (19,27). As described in the introduction the organic contamination is currently removed by H_2SO_4 -mixtures, but the micro-electronics industry looks for more environmentally friendly and cost-saving (alternative) cleaning processes.

One possibility is the use of ozone/DI-water processes as it is known that ozone reacts with organic molecules both in the gas as in the liquid phase. Due to its high oxidizing potential of 2.08 V (28) and its oxidizing capability at low temperature,

ozone is considered a valid alternative in wet cleaning processes for the removal of organic contamination on wafer surfaces (29,30,31), resist strip and polymer removal (32).

For unsaturated compounds such as alkenes or aromatic molecules the reaction with ozone is fast and the application of ozone as cleaning agent is very promising. The reactivity of ozone with the saturated organic molecules however is too low to be applicable in the cleaning processes of semiconductor devices where times of the order of 10 minutes or less are required. In that case radical-based chemistries seem to be needed. These radicals are generated during the ozone decomposition and kinetic modeling is a very good tool to gain insight in the nature and concentration levels of these species in solution. The FACSIMILE software (33) is currently used to simulate the ozone decomposition processes and the generation of intermediate radicals and ions.

For simplification, all radical concentrations are summed up to form the Radical Pool (RP). RP, expressed in mole/Liter, is a measure for the relative importance of radical reaction pathways involved in the ozone decomposition process.

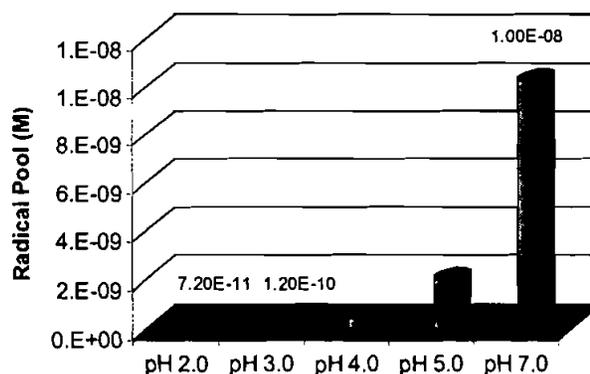


Figure 10: Radical Pool as a function of pH (modeled with FACSIMILE).

As is illustrated in Figure 10 the magnitude of RP is a very strong function of the pH. This leads to the conclusion that depending on the nature of the organic contaminant to be removed, the pH of the ozonated solutions has to be adjusted.

Table IV: Detected organic acids after photoresist degradation (I-line type) by O₃/DI-water.

$\text{H}-\text{COOH}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HOOC}-\text{C}-\text{COOH} \end{array}$	CH_3-COOH	$\text{HOOC}-\text{COOH}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{COOH} \end{array}$	$\text{OHC}-\text{COOH}$
Formic acid	Ketomalonic acid	Acetic acid	Oxalic acid	Pyruvic acid	Glyoxylic acid

Degradation of photoresist layers by ozonated solutions generates small carboxylic acids in the solution. For I-line type of photoresist 6 organic ions are detected by Ion Chromatography (IC): acetate, formate, pyruvate, glyoxalate, oxalate and ketomalonate (34): Table IV.

For another type of photoresist, namely DUV, the same reaction products are seen except for pyruvate which was not detected (34). Oxalate and acetate are present in the highest concentration whereas ketomalonate and glyoxalate are only present in trace concentrations. The former two compounds are known to react slow with ozone and therefore they are relatively stable in the solution. The other compounds undergo further degradation reactions in the presence of ozone.

Besides the application of ozonated solutions for the removal of organic contamination on the silicon surface, O₃/DI-water can also be applied for the treatment of process rinse waters (35). The objective here is to decrease the volume of rinse water needed through recycling. It has already be shown that mainly small carboxylic organic species are formed as reaction products of photoresist removal processes (34). These species are relatively stable against further ozonation and it will be further investigated at which concentration levels they are harmful for re-use of the rinse water.

Conclusions

Contamination control during IC fabrication is extremely important, especially since the device size decreases continuously. Micro-electronics industry always looks for better cleaning processes to achieve lower levels of contamination. Driven by the environmental concern and the cost-saving aspect, the micro-electronics industry is substituting H₂SO₄-based cleaning procedures by O₃/DI-water. The latter has proven to be a good alternative leading to less consumption of rinse and waste water.

First the generation of contamination from the ozone production has been discussed with the introduction of organic contamination and metals in the solution.

To optimize the various ozone-based cleaning concepts, fundamental understanding of the behavior of ozone in ultrapure water is needed. The ozone decomposition and solubility were investigated as a function of various parameters and it was found that pH, temperature and nature of the additive play an essential role.

Concerning the direct applications of O₃/DI-water systems, the silicon oxidation and the removal of organic contamination are two important issues. The oxidation of silicon is rather insensitive to pH, temperature and nature of the additive.

Future research includes the fundamental study of the degradation of organic contamination on silicon wafer surfaces by means of ozone-based chemistries. The simulation of the ozone destruction process and the organic degradation processes will be further investigated. The main aim of this research is to unravel the physico-chemical processes behind the ozone/organics interactions in order to optimize the ozone cleaning procedures for semiconductor devices.

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