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The Application of Ozone in Semiconductor Cleaning Processes

The Solubility Issue

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The solubility of ozone in aqueous solutions expressed as a pseudo-Henry's law coefficient for ozone, ${}^*H_{O_3}^T$, is measured over a pH range of 1 to 8, and temperature range of 15 to 45°C in the presence of several additives: HCl, HNO₃, HAc (Ac is acetate), NaAc, and NaOH. The value of ${}^*H_{O_3}^T$ was found to be a function of temperature, pH, and nature of the anion. The pseudo-Henry's law coefficient is maximal at low pH and decreases with rising pH of the aqueous solution. The addition of chloride enhances the ozone decay rate and thus decreases the solubility below pH 2 while the addition of acetic acid/acetate results in an increase of ${}^*H_{O_3}^T$ for pH > 3. The solubility enthalpy ΔH_{sol}^0 for ozone is found to be equal to (-22.38 ± 0.79) kJ/mol. For applications of ozone in semiconductor cleaning processes, knowledge of the dependence of ${}^*H_{O_3}^T$ on pH, temperature, gas phase concentration, and additive is important in order to achieve optimized cleaning conditions.

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A major concern in the microelectronics industry is the cleaning of silicon wafers using different solutions or gases. Various cleaning procedures exist with the RCA clean¹ and the hydrophilic IMEC clean² as the two most widely used ones. One of these cleaning solutions is a mixture of sulfuric acid and hydrogen peroxide (SPM mixture) (H₂SO₄/H₂O₂). It is used for the removal of organic contamination on the wafer surface, for the stripping of photoresist material, and for growing a thin oxide layer on the silicon wafer surface. This layer, which contains the metallic contamination, is then etched away by HF resulting in the removal of the metals from the silicon surface. In this way, a clean surface is obtained on which a new (thin) oxide layer can be grown. Because of the large quantity of wastewater produced by this cleaning procedure and in view of the health hazard implied in the use of the SPM mixture, research is going on to find other, less aggressive, and more environmentally friendly mixtures with the same or even better cleaning and oxidizing efficiency. An interesting alternative is the use of ozone in aqueous solutions.

It is well known that ozone in the gas phase is able to react with organic molecules and substances and that it oxidizes silicon but at an extremely low reaction rate at room temperature.³⁻⁶ In view of its high oxidation potential (E_0) of 2.08 V⁷ in the liquid phase, ozonated solutions have been used over the past years to remove monolayers of organic contamination and resist layers in the micrometer thickness range.⁸⁻¹² In the latter case, the amount of ozone in the solution needs to be maximized in order to achieve sufficiently high strip rates.⁸ For the (re)oxidation of silicon wafers by means of ozonated solutions, the ozone concentration does not seem to be so critical.¹³⁻¹⁵ An important parameter when optimizing ozone cleaning or oxidation procedures is the solubility of ozone in aqueous solutions. The solubility can be treated quantitatively by the Henry's law coefficient H_X^T which is an equilibrium constant for a system where a gas, X_{gas}, is in equilibrium with a solution containing X_{liq} (Eq. 1)



In general, when X is not chemically reacting in the liquid phase, the following definition for H_X^T at a temperature, T, is used¹⁶ (Eq. 2)

$$H_X^T = \frac{[X]_{\text{liq}} \text{ (mol/L)}}{[X]_{\text{gas}} \text{ (atm)}} \quad [2]$$

$[X]_{\text{liq}}$ is the concentration of X in the liquid phase, expressed in mol/L, and $[X]_{\text{gas}}$ is the partial pressure of X in the gas phase expressed in atmosphere.

Equation 2 shows that the concentration of the gas X in the solution, and thus its solubility, is dependent on the ozone concentration in the gas phase: *e.g.*, as the gas phase concentration is increased, the concentration in the liquid phase must increase proportionally.

In this paper, the ozone solubility is investigated as a function of several parameters, such as the pH of the solution, the temperature, and the nature of some additives. These conditions have an influence on the ozone decay rate and thus the maximum achievable ozone concentration in the solution. Since the experiments will be performed in a dynamic system, also the mass transfer coefficient of ozone in the solution will be determined as a function of temperature and pH.

Experimental

In order to determine the solubility of ozone as a function of the various experimental parameters the following experimental setup (Fig. 1) was used.

A gas flow of oxygen was introduced from the gas cylinder (A) to the Fischer ozone generator (B) where ozone is generated by an electrical discharge. The tubing consists of fluorinated ethylene propylene Teflon. The oxygen flow in the range of 1 to 500 L/h was controlled by a rotameter (R), and the discharge current is variable between 0.1 and 2.4 A. The ozone concentration in the gas phase $[O_3]_{\text{gas}}$ was measured just upstream of the inlet of the reaction vessel using an ozone meter (F) of the type Anseros Ozomat GM. The technique is based on the UV absorbance of ozone in the gas phase at 254 nm and the instrument has a measuring range of 0-200 g/m³ with a precision of 0.1 g/m³. The oxygen/ozone gas mixture was then bubbled in the reaction vessel (D) through a circular ring with a radius of 15 cm containing 18 holes with a diam of 2 mm (E). Experiments can be performed at various temperatures in the reaction vessel by means of an external heater (C) and the temperature was checked by a thermometer (T). After leaving the reaction vessel, the ozone/oxygen gas stream was led through an O₃ scrubber (KI/water) (G), and subsequently, to the exhaust (H). The concentration of ozone in the liquid phase was measured by spectrophotometry. Samples of the solution were taken from the reaction vessel and the absorbance was measured directly at 260 nm with a Shimadzu UV-160A double beam spectrophotometer. The ozone concentration in the solution was determined by means of the Lambert-Beer relationship (Eq. 3)

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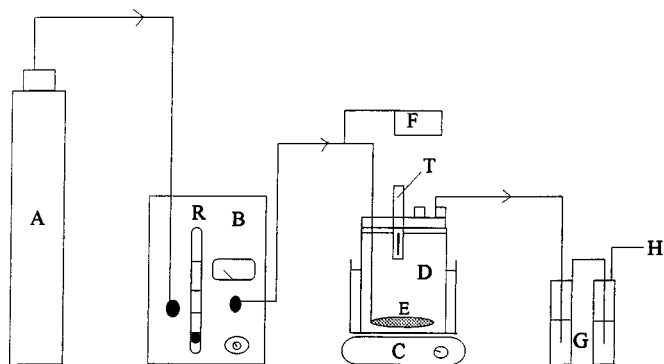


Figure 1. Schematic view of the experimental setup used for the determination of the Henry's law coefficient of ozone in aqueous solutions. A = oxygen gas cylinder; B = Fischer ozone generator; R = rotameter; F = Ozomat GM meter; D = reaction vessel; E = diffuser; G = KI destruction units, and H = exhaust.

$$A_{260\text{ nm}}^{O_3} = \varepsilon_{260\text{ nm}}^{O_3} cb \quad [3]$$

where $A_{260\text{ nm}}^{O_3}$ is the UV absorbance of ozone at a wavelength of 260 nm, $\varepsilon_{260\text{ nm}}^{O_3}$ is the molar extinction coefficient of ozone in the solution at 260 nm which is equal to $3300\text{ M}^{-1}\text{ cm}^{-1}$,¹⁷ c is the concentration of O_3 in the solution (mol/L), and b is the optical path length (in this case 1 cm).

Oxygen from Praxair had a purity of better than 99.995%. Milli-Q water with a resistivity of 18 M Ω cm was used in all the experiments. In order to change the pH, the following additives were used: HNO_3 Ultrex II, HCl (Ashland), and acetic acid (Riedel-Dehaën) for pH < 5 and NaOH pellets (AnalaR) for pH between 5 and 8.

Results

Determination of the ozone mass transfer coefficient $k_L a$.—Beside the fact that the ozone concentration in the liquid phase in a dynamic system is influenced by temperature, pH, and the kind of additive as shown later, it takes a certain period of time before the maximum ozone concentration was reached when ozone was bubbled through the solution. This time dependence is governed by the mass transfer coefficient $k_L a$, which is an empirical parameter characteristic for the reaction vessel and the type of ozone diffuser (E).

In order to determine $k_L a$, the ozone concentration in the liquid phase was followed as a function of the bubbling time until the steady state concentration was reached. This is illustrated in Fig. 2 at

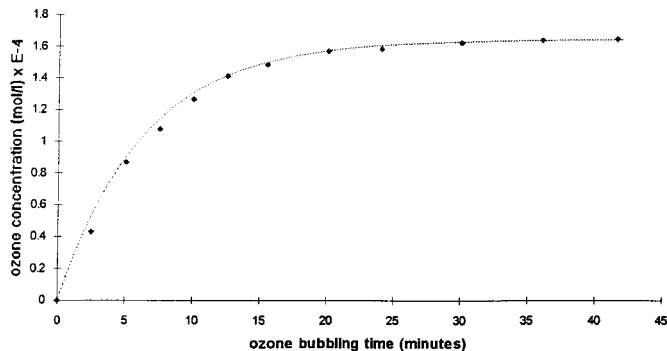


Figure 2. $[O_3]_{\text{liq}}$ as a function of the bubbling time at 44.4°C, pH 1.52 (HNO_3), and $[O_3]_{\text{gas}} = 0.0232\text{ atm}$ (49.7 g/m^3).

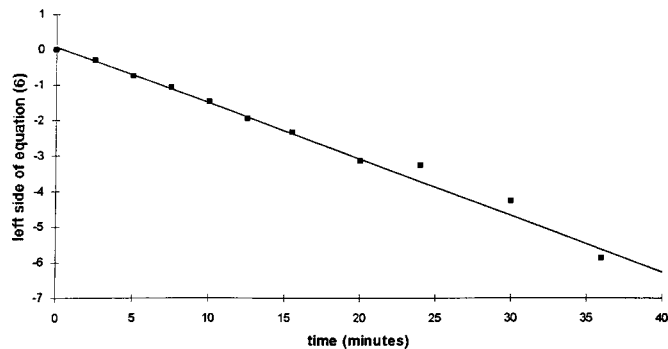


Figure 3. Plot of the left side of Eq. 6 vs. the ozone bubbling time at 44.4°C, pH 1.52 (nitric acid), and $[O_3]_{\text{gas}} = 0.0232\text{ atm}$.

pH 1.52 (HNO_3) and $T = 44.4^\circ\text{C}$ where a steady state concentration of $1.65 \cdot 10^{-4}\text{ M}$ or 7.9 mg/L ozone was reached at a gas phase concentration of 0.0232 atm or 49.7 g/m^3 .

Under these conditions of continuous ozone bubbling through the solution, Eq. 4 describes the evolution of the ozone concentration as a function of time¹⁸

$$\frac{d[O_3]_{\text{liq}}}{dt} = k_L a ([O_3]_{\text{liq}}^* - [O_3]_{\text{liq},t}) - r_{O_3} \quad [4]$$

The $k_L a$ is the product of a liquid mass transfer coefficient k_L (cm/s) and the specific mass transfer area a (cm^{-1}). The latter is among others a function of the size of the gas bubbles and thus of the design of the ozone diffuser. $[O_3]_{\text{liq}}^*$ is the saturation concentration of ozone in the liquid phase governed by the magnitude of Henry's law coefficient and the applied partial pressure of O_3 in the gas stream in contact with the solution. $[O_3]_{\text{liq},t}$ is the actual concentration at a certain time t and r_{O_3} is the ozone loss rate which is dependent on pH, temperature, and nature of the additive. In fact, the ozone decay rate in aqueous solutions is governed by a complex radical chain mechanism wherein the hydroxyl radical is an important chain carrier.^{19,20} It is also well known that the ozone decomposition rate increases with increasing pH and this from pH 4-5.²⁰ This pH dependence is caused by the OH^- catalyzed initiation reaction.²⁰ The ozone decomposition rate also increases with temperature and is sensitive to the presence of radical scavengers like carbonate, acetate, and phosphate ions which inhibit the ozone decay due to their reaction with the chain carriers active in a complex radical chain mechanism²⁰ (see further in this paper). At pH values below 4, the ozone loss rate becomes negligibly low and Eq. 4 can be approximated by Eq. 5

$$\frac{d[O_3]_{\text{liq}}}{dt} = k_L a ([O_3]_{\text{liq}}^* - [O_3]_{\text{liq},t}) \quad [5]$$

Under the experimental conditions of Fig. 2, the maximum concentration of ozone is reached at an ozone bubbling time of about 25 min. This maximum ozone concentration is equal to $[O_3]_{\text{liq}}^*$ and this for a given set of fixed reaction parameters like pH and temperature. The value of $k_L a$ can be derived after integration of Eq. 5 to the following expression

$$\ln \frac{[O_3]_{\text{liq}}^* - [O_3]_{\text{liq},t}}{[O_3]_{\text{liq}}^* - [O_3]_{\text{liq},0}} \approx - (k_L a) t \quad [6]$$

where $[O_3]_{\text{liq},0}$ is the ozone concentration at $t = 0$. $k_L a$ was determined from the slope of a plot of the left side vs. the bubbling time, t : Fig. 3. Similar experiments were repeated for several temperatures, pH values, and various additives (HNO_3 , HCl). The values of the mass transfer coefficient are summarized in Table I.

Table I. Mass transfer coefficient of ozone $k_{L}a$ (h^{-1}) as function of temperature, pH, and additive.

Temperature ($\pm 0.2^\circ\text{C}$)	pH (± 0.05)	Ionic strength (μ)	Additive	$[\text{O}_3]_{\text{gas}}$ (g/m^3)	$[\text{O}_3]_{\text{liq}}^*$ (mg/L)	$k_{L}a$ (h^{-1})
15.6	2.32	0.005	HCl	44.6	14.6	7.1 ± 0.2
19.9	5.40	4×10^{-6}	None	58.0	11.9	9.9 ± 0.6
25.8	1.38	0.04	HNO_3	31.1	7.5	10.8 ± 0.2
26.0	2.24	0.006	HNO_3	50.5	12.1	10.3 ± 1.4
35.3	3.39	4×10^{-4}	HCl	52.5	10.0	9.7 ± 0.4
44.4	1.52	0.03	HNO_3	49.7	7.9	9.5 ± 0.2
Average						9.6 ± 1.3

Note that $k_{L}a$ is neither a function of the pH nor temperature. The average value of the mass transfer coefficient in this particular reactor setup is $(9.6 \pm 1.3) \text{ h}^{-1}$. The value determined in this work is at the lower side of some literature values which were found to be in the range between 10 and 240 h^{-1} .^{18,21-23} This is due to the design characteristics of the ozone diffuser (E) which determines the size of the gas bubbles and thus the surface to volume ratio of the gas bubble. Another factor is the ionic strength, μ , which influences the surface tension of the solution, and thus, has an effect on the bubble size.¹⁸ Literature data indicate that, at ionic strength μ between 0.1 and 1.0 in Na_2SO_4 solution, $k_{L}a$ slightly increases with μ from 72 to 105 h^{-1} .¹⁸ In our experiments, μ varied between 10^{-5} and 0.03 (Table I), and at this low ionic strength, $k_{L}a$ is not affected. No attempt was made to maximize the magnitude of $k_{L}a$ because this experimental setup will not be used for cleaning or oxidizing semiconductor surfaces under practical circumstances. However, $k_{L}a$ can be an important parameter for some practical applications where a short time for reaching the maximum ozone concentration is required, for example, in the treatment of process rinse water in view of its possible reuse.

The solubility of ozone in aqueous solutions.—As can be seen from Eq. 2, the amount of a gas X dissolved in any kind of solution is not a fundamental physical constant since it depends on the partial pressure of X in the gas phase in equilibrium with the solution. Therefore, the solubility of ozone is treated in this paper by means of the value of the Henry's law coefficient. Once this value is determined, the solubility of ozone can easily be calculated when the gas phase partial pressure of ozone is known.

According to the simple Henry's law, the dissolved gas behaves as an inert compound in the solution and one has a pure gas/liquid equilibrium (Eq. 1-2) as is the case for nitrogen or oxygen in water. Under this condition of ideal behavior, the Henry's law coefficient is mainly temperature dependent. But in reality, the ideal behavior is not applicable for many gases which are reactive in solution, e.g., CO_2 (reaction to H_2CO_3 , HCO_3^- , and CO_3^{2-})²⁴ and NO_2 (reaction to HNO_2).²⁵ This nonideality is also the case for ozone where Henry's law coefficient is not only temperature dependent, but is also pH dependent especially at a $\text{pH} > 4$. Indeed, a large body of literature exists on the decomposition processes of ozone at higher pH and it is well documented that the reaction rate r_{O_3} (Eq. 4) strongly increases when the pH becomes larger than 5. Also, a nonequilibrium condition exists when the temperature of the O_2/O_3 gas stream is at room temperature but different from the temperature in the liquid phase.

As a result of both nonideal conditions, a pseudo-Henry's law coefficient $*H_{\text{O}_3}^T$ for ozone needs to be defined for a continuous flowing gas at room temperature ($\approx 20^\circ\text{C}$), bubbling into a liquid at a temperature T

$$*H_{\text{O}_3}^T = \frac{[\text{O}_3]_{\text{liq,ss}} (\text{mol}/\text{L})}{[\text{O}_3]_{\text{gas}} (\text{atm})} \quad [7]$$

After a sufficient time, $[\text{O}_3]_{\text{liq,t}}$ reaches a plateau or steady state value $[\text{O}_3]_{\text{liq,ss}}$ and $*H_{\text{O}_3}^T$ can be calculated from $[\text{O}_3]_{\text{liq,ss}}$ and $[\text{O}_3]_{\text{gas}}$ for that set of reaction conditions as shown in the next sections.

At steady state, $d[\text{O}_3]_{\text{liq}}/dt$ can be set equal to zero and Eq. 4 can be reduced to Eq. 8

$$k_{L}a([\text{O}_3]_{\text{liq}}^* - [\text{O}_3]_{\text{liq,ss}}) = (r_{\text{O}_3})_{\text{ss}} \quad [8]$$

or the steady state concentration becomes equal to

$$[\text{O}_3]_{\text{liq,ss}} = [\text{O}_3]_{\text{liq}}^* - \frac{r_{\text{O}_3}}{k_{L}a} \quad [9]$$

Combining Eq. 9 and 7 leads to Eq. 10

$$*H_{\text{O}_3}^T = \frac{[\text{O}_3]_{\text{liq,ss}}}{[\text{O}_3]_{\text{gas}}} = \frac{[\text{O}_3]_{\text{liq}}^* - \frac{r_{\text{O}_3}}{k_{L}a}}{[\text{O}_3]_{\text{gas}}} = H_{\text{O}_3}^T - \frac{r_{\text{O}_3}}{[\text{O}_3]_{\text{gas}}k_{L}a} \quad [10]$$

In the case that r_{O_3} is negligibly small (thus at low pH), the steady state concentration of ozone equals the saturation concentration $[\text{O}_3]_{\text{liq}}^*$ for that temperature and $*H_{\text{O}_3}^T$ becomes equal to $H_{\text{O}_3}^T$.

$*H_{\text{O}_3}^T$ was determined in this work as a function of pH, temperature, and the nature of the additive, hydrochloric, nitric, or acetic acid. In each experiment the ozone concentration in the gas phase was measured (ranging from 20 to $80 \text{ g}/\text{m}^3$) and the ozone concentration in the liquid phase as a function of time was followed using the UV absorbance of ozone at 260 nm.

$*H_{\text{O}_3}^T$ as a function of pH and temperature.—In Fig. 4, a compilation is shown of $*H_{\text{O}_3}^T$ as a function of pH and temperature. The

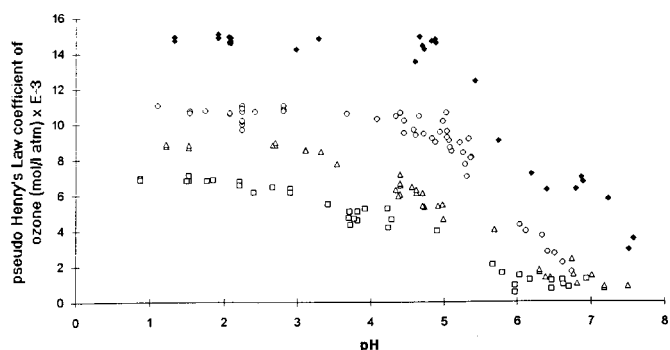


Figure 4. $*H_{\text{O}_3}^T$ as a function of pH and temperature (\blacklozenge ; 16, \circ ; 26, \triangle ; 35, and \square ; 45°C) whereby nitric acid or NaOH were used to cover the whole pH range.

Table II. $H_{O_3}^T$ as a function of temperature in nitric and hydrochloric acid. Data marked with an asterisk (*) are measured only at one pH value and not for a broad pH range.

Temperature ($\pm 0.5^\circ\text{C}$)	pH (± 0.05)	$H_{O_3}^T$ (mol/L atm) $\times 10^{-3}$
Nitric acid		
7.8*	1.03	22.50 \pm 1.30
16.8	2.08	14.91 \pm 0.11
26.0	2.24	10.48 \pm 0.50
26.0	1.40	10.70 \pm 0.10
26.6	1.08	11.37 \pm 0.10
30.2*	2.49	9.79 \pm 0.60
35.2	2.68	8.86 \pm 0.10
44.6	0.87	6.92 \pm 0.04
53.8*	0.93	5.67 \pm 0.06
68.0*	0.94	3.53 \pm 0.06
Hydrochloric acid		
15.6	2.32	15.04 \pm 0.40
16.0	1.81	14.87 \pm 0.10
21.2*	2.35	13.04 \pm 0.10
26.1	3.12	11.2 \pm 0.10
35.2	2.58	8.85 \pm 0.10
44.3	2.22	6.67 \pm 0.14

solution was acidified with HNO_3 . For pH values above 5.5, NaOH was used. Note that at the lowest temperature of 16°C , $*H_{O_3}^T$ remains quasi-independent of pH at low pH between 1 and 4, and reaches a plateau value of (0.01491 ± 0.00011) mol/L atm. Increasing the pH above 4 leads to a sharp decrease of $*H_{O_3}^T$ to the value of 0.00292 mol/L atm at a pH of 7.5. At higher temperatures of 26.2 , 35.1 , and 44.7 ($\pm 0.5^\circ\text{C}$), a similar profile of the pH dependence as at 16°C is seen and as expected the plateau value at low pH decreases with temperature.

At higher pH, the ozone decomposition rate r_{O_3} will increase and this will result in a steady state concentration of ozone which is lower than $[\text{O}_3]_{\text{liq}}^*$. This will of course lead to a decrease of $*H_{O_3}^T$ (Eq. 10) as is seen in the profile of $*H_{O_3}^T$ as a function of pH in Fig. 4.

The effect of the temperature on $H_{O_3}^T$ is summarized in Table II and this for the two additives HNO_3 and HCl . For some temperatures, indicated with an asterisk, $*H_{O_3}^T$ was measured only at one constant (low) pH and not in a broad pH range.

The observed temperature dependence of $H_{O_3}^T$ is in qualitative good agreement with literature data although there appears to be some divergence especially at low and high temperatures (Fig. 5).²⁶⁻²⁹ This is most probably caused by the fact that pH, purity of

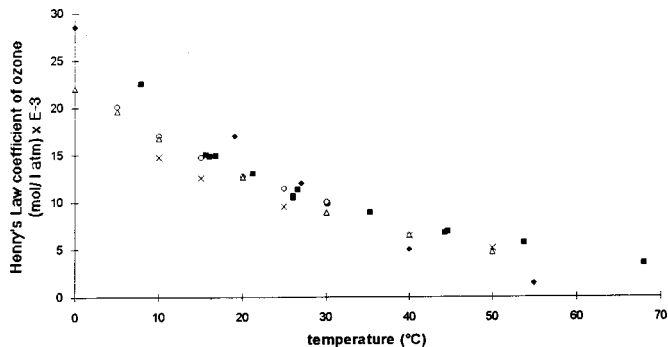


Figure 5. $H_{O_3}^T$ as a function of temperature; (■) this work and literature data: (●) Ref. 26, (○) Ref. 27, (×) Ref. 28, (△) Ref. 29.

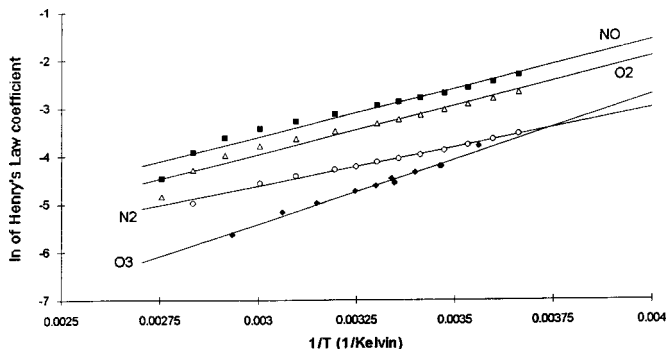


Figure 6. Natural logarithm of $H_{O_3}^T$ vs. $1/T$ for various inert molecules O_2 , N_2 , NO (literature data²⁶), and O_3 (this work).

the water, and the reagents used in the other studies were not so well controlled as in our work. It should be noticed that the values of $H_{O_3}^T$ are independent of the anion NO_3^- or Cl^- , but as discussed further in the text an anion effect will be noticed with chloride and acetate in some pH ranges.

For analysis of the temperature dependence of the Henry's law coefficient, the Van 't Hoff relation can be applied (Eq. 11)

$$\ln H_{O_3}^T = \text{const} + \frac{\Delta H_{\text{sol}}^0}{RT} \quad [11]$$

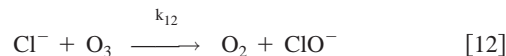
where ΔH_{sol}^0 is the solubility enthalpy (kJ/mol) in water, T the temperature (kelvin), and R the universal gas constant (8.31 J/K mol). By plotting the natural logarithm of $H_{O_3}^T$ vs. $1/T$, a straight line should be obtained with as slope $\Delta H_{\text{sol}}^0/R$.

This is illustrated in Fig. 6 for a number of inert gasses such as oxygen, nitrogen, nitric oxide,²⁶ and also for ozone: one sees that in the temperature region from 273 to 373 K a fairly good linear relationship is obtained. From the slope $\Delta H_{\text{sol}}^0/R$ of these lines, one can calculate a solubility enthalpy ΔH_{sol}^0 of -22.38 ± 0.74 for ozone which is of the same magnitude as for oxygen (-16.69 ± 1.16), nitric oxide (-16.73 ± 1.15), and nitrogen (-13.45 ± 0.39), each expressed in kJ/mol.

For the unreactive compounds O_2 , N_2 , and NO , the solubility enthalpy is determined by pure physical interactions between the gas and the solution, in this case water. For the solubility enthalpy of ozone, one finds a value in the same range indicating that ozone at low pH behaves as a quasi-inert gas in diluted nitric and hydrochloric acid. Our experimentally determined value, ΔH_{sol}^0 , for ozone is also in fairly good agreement with the scarce literature data which are in the 16.4 to 22.3 kJ/mol range.³⁰⁻³²

Anion effects on $*H_{O_3}^T$.—It was shown in the previous section that a low pH and in the presence of nitric acid ozone almost behaves as a typically inert gas in solution. However, at low pH, $*H_{O_3}^T$ behaves differently in hydrochloric acid than in nitric acid. This is illustrated in Fig. 7 where $*H_{O_3}^T$ was determined in the pH range from 1 to 4 at temperatures between 16 and 44°C . Where $*H_{O_3}^T$ is independent of pH between 2 and 4, and roughly equal to the value in nitric acid (Fig. 4 and Table II), below pH 2, $*H_{O_3}^T$ starts to decrease, and this profile is seen at all temperatures.

The fact that $*H_{O_3}^T$ decreases again below pH 2.0 in the presence of HCl can be ascribed to the destruction reaction r_{O_3} of ozone with chloride ions^{33,34}



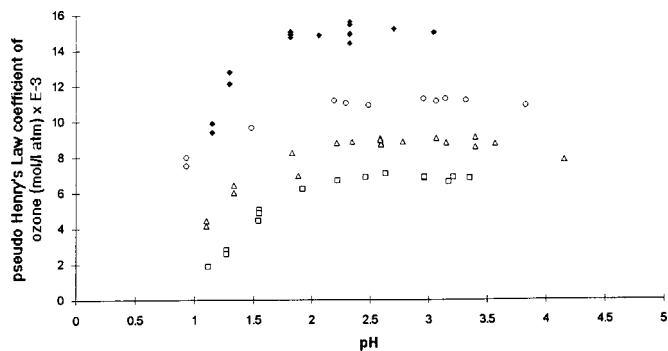


Figure 7. $*H_{O_3}^T$ as a function of pH and temperature with hydrochloric acid as additive (\blacklozenge : 16, \circ ; 26 \triangle ; 35, and \square 45°C).

or at constant chloride concentration $k_{12}[\text{Cl}^-] = k'_{12}$

$$r_{O_3} = \frac{d[\text{O}_3]_{\text{liq}}}{dt} = -k_{12}[\text{O}_3]_{\text{liq}}[\text{Cl}^-] = -k'_{12}[\text{O}_3]_{\text{liq}} \quad [13]$$

which after integration yields Eq. 14

$$\ln[\text{O}_3]_{\text{liq},t} = -(k'_{12}) \cdot t + \ln[\text{O}_3]_{\text{liq},t=0} \quad [14]$$

The ozone decay rate was experimentally determined in a static system at temperature of $21.0 \pm 0.1^\circ\text{C}$ as a function of the chloride concentration. The ozone concentrations were followed as a function of time using the UV absorbance at 260 nm at various excess chloride concentrations. Subsequently, the left side of Eq. 14 was plotted vs. time (Fig. 8). It was found that the ozone decay is first order in the ozone concentration with the slope of the line equal to k'_{12} .

The second order rate constant, k_{12} , was determined by plotting k'_{12} as a function of the $[\text{Cl}^-]$ (Fig. 9). This results in a value of $k_{12} = (0.0042 \pm 0.0020) \text{ M}^{-1} \text{ s}^{-1}$ which falls within its error margins within the literature value of $0.003 \text{ M}^{-1} \text{ s}^{-1}$.³³

The uncertainty on k_{12} is of the order of 50% as can be expected from the slight curvature exhibited by the points shown in Fig. 9 as this experimental setup was not designed to derive the rate constant k_{12} accurately. It was rather our intention to explain the unusual decrease of $*H_{O_3}^T$ with lowering the pH. The observed curvature is most probably due to the contribution of the additional ozone decomposition reactions which become more and more important at the low chloride concentrations. The measurement at the lowest chloride concentration of $1.6 \times 10^{-3} \text{ mol/L}$ corresponds to a pH of

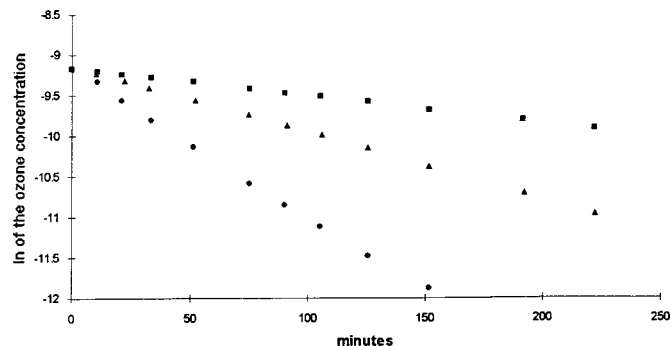


Figure 8. Natural logarithm of $[\text{O}_3]_{\text{liq}}$ vs. time (Eq. 14). Temperature: 20.5°C ; chloride concentrations are \blacksquare : 3×10^{-3} , \blacktriangle : 2.1×10^{-2} , and \bullet : $6.3 \times 10^{-2} \text{ M}$.

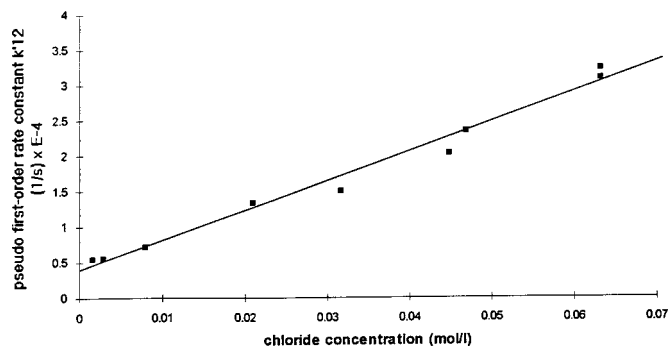


Figure 9. Plot of the pseudo-first-order rate constants k'_{12} vs. the chloride concentration ($T = 20.5^\circ\text{C}$).

2.8 at which ozone decay rates in nitric acid are of the order of $0.5 \times 10^{-4} \text{ s}^{-1}$.

It is obvious that the observed decrease of $*H_{O_3}^T$ below pH 2 is caused by an increased ozone destruction rate due to the reaction with chloride. Based on the experimentally determined pseudo-first-order rate constant k'_{12} , the $*H_{O_3}^T$ profile as a function of pH can be calculated by rearranging Eq. 10 to

$$*H_{O_3}^T = \frac{H_{O_3}^T}{1 + \frac{k'_{12}}{k_{1a}}} = \frac{H_{O_3}^T}{1 + \frac{k_{12}[\text{Cl}^-]}{k_{1a}}} \quad [15]$$

Based on Eq. 15, the value of $*H_{O_3}^T$ can be calculated as a function of pH for $k_{1a} = 9.6 \text{ h}^{-1}$ and the value of $H_{O_3}^T = 0.013 \text{ M/atm}$ (pH 2.35, $T = 21^\circ\text{C}$). An example of a simulated profile at 26°C is shown in Fig. 10 which is in fairly good agreement with the experimentally determined $*H_{O_3}^T$ pH profiles.

Anion effect: acetic acid/acetate.—As already mentioned $*H_{O_3}^T$ decreases again at higher pH values (see Fig. 4) due to an enhanced ozone decomposition process.³⁵ It is known from literature data that the addition of acetic acid/acetate inhibits the ozone decomposition.^{36,37}

To test the effect of these additives on the value of $*H_{O_3}^T$, experiments at a temperature of 35°C have been performed using acetic acid (HAc) and sodium acetate (NaAc). The results are shown in Fig. 11.

As can be seen in Fig. 11, the presence of the acetate ion (Ac), which is the dominant species above pH 4.8, has a pronounced

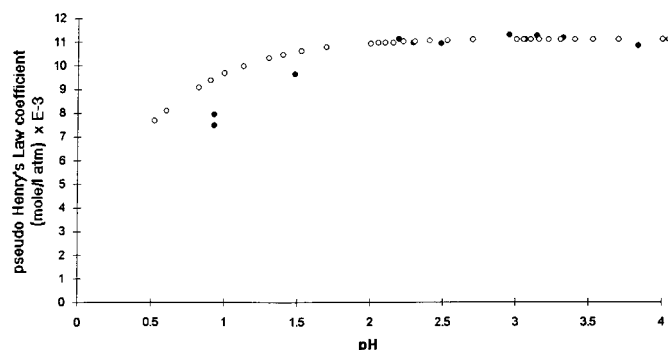


Figure 10. Comparison between the pseudo-Henry's law coefficient of ozone as a function of pH in HCl at 26°C (\bullet) with a simulated profile (\circ) according to Eq. 15 at 21°C .

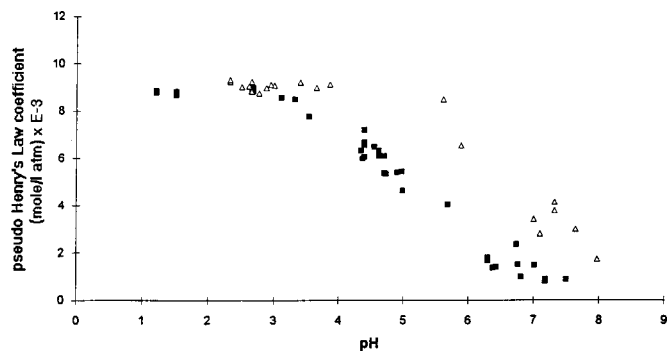
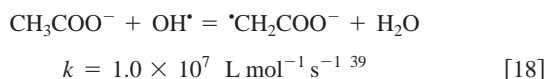
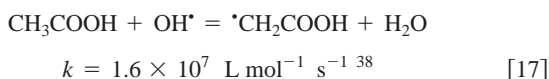


Figure 11. $*H_{O_3}^T$ at 35°C as a function of pH with (■) nitric acid and NaOH as additives, and (△) acetate as anion.

effect on $*H_{O_3}^T$, which is higher when acetate is present. This is most certainly caused by the inhibiting effect of HAc/Ac^- on the ozone decomposition rate, r_{O_3} which can be explained by the following reaction sequence



The hydroxyl radical is one of the main radicals in the overall radical catalyzed ozone destruction mechanism besides the HO_2^\bullet and $\cdot O_2^-$ radicals.³⁶ The addition of HAc/Ac^- inhibits this reaction because of the reaction of both acetic acid and acetate with the OH radical (Eq. 17, 18).^{38,39} The positive effect of HAc/Ac^- on $*H_{O_3}^T$ is clearly seen above pH 3, where the ozone destruction becomes important. At low pH, the ozone destruction is negligible, and the value of $*H_{O_3}^T$ is the same in nitric or acetic acid.

Applications in Semiconductor Cleaning

Using ozone in semiconductor cleaning applications such as for oxide growth or resist stripping is an important research topic because of its much smaller environmental impact than the other cleaning procedures involving sulfuric acid. To remove metals from silicon surfaces, oxides can be grown in which the metal contamination gets incorporated. When the oxide layer is etched away in hydrofluoric acid, the metal contamination can be removed in this way from the silicon surface. For the growth of such thin silicon dioxide layers by means of ozonated solutions, neither the ozone concentration nor the temperature are critical parameters.¹³ Indeed, the electric field across the oxide layer and the resulting field-imposed drift of O anions through the oxide toward the silicon bulk is the rate limiting step in the oxidation process.

For the process of resist stripping, a reaction between ozone and the organic contamination must occur, and thus, both the ozone concentration and the temperature are the important parameters. But at high temperature implying high reaction rate constants, the ozone solubility becomes lower and thus, the concentration decreases. A compromise between these two parameters needs thus to be found in order to optimize the stripping rate. Furthermore, the nature of the additive has an effect on the solubility under acidic conditions: when nitric acid is used, one can work at any pH below 4 in order to achieve the maximum ozone solubility, in hydrochloric acid, one needs the process to operate in the pH window between 2 and 4. At higher values of the pH, the ozone solubility decreases as is illustrated for various temperatures in Table III.

Table III. Ozone concentration in the solution $[O_3]_{liq}$ as a function of temperature, T , (°C), pH (low pH in nitric acid and near-neutral in NaOH), and ozone concentration in the gas phase $[O_3]_g$.

Temperature (°C)	pH	50 g/m ³ ozone	200 g/m ³ ozone
16	2.1	16.7 mg/L	66.8 mg/L
	6.9	7.7 mg/L	31.1 mg/L
26	1.4	12.0 mg/L	47.9 mg/L
	6.7	1.9 mg/L	7.6 mg/L
35	2.7	9.9 mg/L	39.7 mg/L
	6.8	1.7 mg/L	6.7 mg/L
45	1.0	7.8 mg/L	31.0 mg/L
	6.6	1.4 mg/L	5.5 mg/L
68	1.0	3.9 mg/L	15.8 mg/L

Besides the effect of temperature and pH, the ozone concentration which can be achieved in the gas phase is another important parameter. It depends on the performance of the ozone generator, the oxygen flow, and the applied current. The higher the ozone concentration in the gas phase the higher the concentration in the solution as is established by the equilibrium Eq. 1. As an example, the achievable ozone concentrations in the solution $[O_3]_{liq}$ are shown for two gas phase concentrations of, respectively, 50 and 200 g/m³ (see Table III). Note that ozone concentrations of tens of milligrams per liter can easily be realized at low pH. However, it should be stressed that the limiting factor is safety.

Safety note: ozone concentrations in a gas stream of more than 15% can be explosive.

Another application is the treatment of contaminated process water with ozone where a factor which can be of importance is $k_L a$. Its magnitude determines the time needed to achieve the maximum ozone concentration in the solution. When organic contamination must be removed from the rinse water, it will be advantageous to work with an ozone concentration in the solution as high as possible within the shortest time delay. For the laboratory setup used in this study with $k_L a = 9.6 \text{ h}^{-1}$, about 20 min are needed to obtain the maximum ozone concentration in the solution. If with a modified design of the ozone diffuser a value of $k_L a = 100 \text{ h}^{-1}$ can be achieved, this delay time will be reduced to approximately 2 min.

Conclusions

The behavior of ozone in aqueous solutions was investigated, especially its solubility under various experimental conditions. This solubility was expressed as $*H_{O_3}^T$ which was measured over a broad pH and temperature range in the presence of several additives (HCl, HNO_3 , HAc , $NaAc$, $NaOH$). Besides $*H_{O_3}^T$, the $k_L a$ was also determined as a function of pH, temperature, and additive.

The mass transfer coefficient, $k_L a$, for this particular setup was found to be equal to $(9.6 \pm 1.3) \text{ h}^{-1}$ and independent of pH and temperature from 15 to 45°C. This value is low compared with other systems, but no effort was put to optimize the gas inlet system (ozone diffuser).

The solubility of ozone in aqueous solutions determined by $*H_{O_3}^T$ was investigated over a temperature range of 7-70°C and pH 1-8. At pH below 4 in nitric acid, the value of $*H_{O_3}^T$ is independent of pH; at higher pH, $*H_{O_3}^T$ is decreasing due to destruction processes of ozone.

Anion effects on the ozone solubility are also playing an important role. Cl^- enhances the ozone decay while acetate has an inhibiting effect on the ozone decomposition rate in the pH range from 3 to 8. Below pH 2, the magnitude of $*H_{O_3}^T$ decreases in hydrochloric acid due to the chloride/ozone reaction, while at $pH > 4$, the pres-

ence of acetic acid/acetate causes $*H_{O_3}^T$ to decrease less with pH than seen in near neutral solutions.

As the temperature of the solution rises, the maximal solubility of ozone $H_{O_3}^T$ decreases as expected. This is mainly due to the physical phenomenon of decreased solubility at higher temperature as is also the case with other (inert) gasses. The solubility enthalpy, ΔH_{sol}^0 , for ozone was found to be (-22.38 ± 0.79) kJ/mol which is in line with the literature values.

The implications of this study for the use of ozone in semiconductor cleaning processes were briefly discussed. For the growth of thin oxides to encapsulate metal contamination, neither the ozone concentration nor the temperature are important parameters. The situation is quite different when ozone solutions will be used for resist stripping compromise has to be sought between the highest temperature of the process and the solubility of ozone the ozone diffuser system should be optimized.

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References

- W. Kern and D. Puotinen, *RCA Rev.*, **31**, 197 (1970).
- M. Meuris, P. W. Mertens, A. Opdebeeck, H. F. Schmidt, M. Depas, G. Vereecke, M. M. Heyns, and A. Philipossian, *Solid State Technol.*, **1995**, 109 (July).
- M. Niwano, J. Kageyama, K. Kinashi, and N. Miyamoto, *J. Vac. Sci. Technol. A*, **12**, 465 (1994).
- I. W. Boyd, R. Gwilliam, and A. Kazor, *Appl. Phys. Lett.*, **65**, 412 (1994).
- J. R. Vig, in *Semiconductor Cleaning Technology 1989*, J. Ruzyllo and R. E. Novak, Editors, PV 90-9, p. 105, The Electrochemical Society Proceedings Series, Pennington, NJ (1990).
- A. Licciardello, O. Puglisi, and S. Pignataro, *Appl. Phys. Lett.*, **48**, 41 (1986).
- H. Ellis, *Book of Data*, 14th ed., Published for the Nuffield-Chelsea Curriculum Trust by Longman Group Limited, Edinburgh Gate, U.K. (1996).
- S. De Gendt, P. Snee, I. Cornelissen, M. Lux, R. Vos, P. W. Mertens, D. M. Knotter, and M. M. Heyns, in *Digest of Technical Papers of the Symposium on VLSI Technology*, p. 168 (1998).
- S. Yasui, N. Yonekawa, and T. Ohmi, *Semicond. Pure Water Conf.*, **13**, 64 (1994).
- T. Isagawa, M. Kogure, T. Futatsuki, and T. Ohmi, *Semicond. Pure Water Chem. Conf. Annual*, **12**, 117 (1993).
- T. Ohmi, T. Isagawa, M. Kogure, and T. Imaoka, *J. Electrochem. Soc.*, **140**, 804 (1993).
- J. K. Tong and D. C. Grant, in *Cleaning Technology in Semiconductor Device Manufacturing*, J. Ruzyllo and R. E. Novak, Editors, PV 92-12, p. 18, The Electrochemical Society Proceedings Series, Pennington, NJ (1992).
- F. De Smedt, C. Vinckier, I. Cornelissen, S. De Gendt, and M. M. Heyns, *J. Electrochem. Soc.*, **147**, 1124 (2000).
- M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and M. Ohwada, *J. Appl. Phys.*, **63**, 1272 (1990).
- M. Kogure, T. Isagawa, T. Futatsuki, N. Yonekawa, and T. Ohmi, in *Proceedings of the Conference International Environmental Science*, Vol. 39, p. 380 (1993).
- CRC Handbook of Chemistry and Physics*, 62nd ed., CRC Press, Boca Raton, FL (1981-82).
- E. J. Hart, K. Sehested, and K. Holcman, *Anal. Chem.*, **55**, 46 (1983).
- M. D. Gurol and P. C. Singer, *Environ. Sci. Technol.*, **16**, 377 (1982).
- J. L. Sotelo, F. J. Beltran, F. J. Benitez, and J. Beltran-Heredia, *Ind. Eng. Chem. Res.*, **26**, 39 (1987).
- A. Virdis, A. Viola, and G. Cao, *Ann. Chim. (Rome)*, **85**, 633 (1995).
- G. Anselmi, P. G. Lignola, C. Raitaino, and G. Volpicelli, *Ozone. Sci. Eng.*, **6**, 17 (1984).
- M. D. Gurol and S. Nekouinaini, *J. Water Pollut. Control Fed.*, **57**, 235 (1985).
- F. J. Beltran, J. F. Garcia-Araya, and J. M. Enchinar, *Ozone. Sci. Eng.*, **19**, 281 (1997).
- D. A. Skoog, D. M. West, and F. J. Holler, *Fundamentals of Analytical Chemistry*, 6th ed., p. 266, Saunders College Publishing, Fort Worth, TX (1992).
- J. Y. Pack and Y. N. Lee, *J. Phys. Chem.*, **92**, 6294 (1988).
- A. Seidell, *Solubilities of Inorganic Compounds*, 3rd ed., Vol. 1, Van Nostrand Reinhold, New York (1940).
- L. F. Kosak-Channing and G. R. Helz, *Environ. Sci. Technol.*, **17**, 145 (1983).
- R. Roth and D. E. Sullivan, *Ind. Eng. Chem. Fundam.*, **20**, 137 (1981).
- Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 14, p. 142, Wiley, New York (1978).
- E. Wilhelm, R. Battino, and R. J. Wilcock, *Chem. Rev.*, **17**, 219 (1977).
- A. C. Chew, R. Atkinson, and S. W. Aschmann, *J. Chem. Soc., Faraday Trans.*, **94**, 1083 (1998).
- R. Sander and P. J. Crutzen, *J. Geophys. Res., [Atmos.]*, **101**, 9121 (1996).
- J. Hoigné, H. Bader, W. R. Haag, and J. Staehelin, *Water Res.*, **19**, 993 (1985).
- L-R. B. Yeatts, Jr. and H. Taube, *J. Am. Chem. Soc.*, **71**, 4100 (1949).
- F. De Smedt, Ph.D. Dissertation, Department of Chemistry, University of Leuven, Belgium (2000).
- K. Sehested, H. Corfitzen, J. Holcman, and E. J. Hart, *J. Phys. Chem.*, **96**, 1005 (1992).
- K. Sehested, J. Holcman, E. Bjergbakke, and E. J. Hart, *J. Phys. Chem.*, **91**, 2359 (1987).
- J. Staehelin and J. Hoigné, *Environ. Sci. Technol.*, **19**, 1206 (1985).
- M. M. Fisher and W. H. Hamil, *J. Phys. Chem.*, **77**, 171 (1973).