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Effect of ozone concentration on silicon surface passivation by atomic layer deposited Al₂O₃

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We study the impact of ozone-based Al₂O₃ Atomic Layer Deposition (ALD) on the surface passivation quality of crystalline silicon. We show that the passivation quality strongly depends on the ozone concentration: the higher ozone concentration results in lower interface defect density and thereby improved passivation. In contrast to previous studies, our results reveal that too high interface hydrogen content can be detrimental to the passivation. The interface hydrogen concentration can be optimized by the ozone-based process; however, the use of pure ozone increases the harmful carbon concentration in the film. Here we demonstrate that low carbon and optimal hydrogen concentration can be achieved by a single process combining the water- and ozone-based reactions. This process results in an interface defect density of $2 \cdot 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$, and maximum surface recombination velocities of 7.1 cm/s and 10 cm/s, after annealing and after an additional firing at 800 °C, respectively. In addition, our results suggest that the effective oxide charge density can be optimized in a simple way by varying the ozone concentration and by injecting water to the ozone process.

1. INTRODUCTION

Efficient surface passivation is crucial in electronic devices and especially in solar cells, where the generated charge carriers need to diffuse to the contacts before recombining at

the surface. Atomic layer deposited (ALD) Al_2O_3 has been intensively studied in the past decade owing to its excellent passivation ability on crystalline silicon (c-Si) surfaces [1-3]. The high passivation quality obtained by Al_2O_3 is associated with low interface defect density values combined with a high negative charge. The interface defect density D_{it} describes recombination activity through midgap defect levels (ideally suppressed by chemical passivation), while the total charge density Q_{tot} is responsible for creating an electric field that prevents minority carriers from reaching the silicon surface (field-effect passivation).

Trimethylaluminum (TMA) and water serve as typical ALD precursors for Al_2O_3 surface passivation studies. However, recent studies have suggested that ozone as an oxidant in the Al_2O_3 process could result in even lower interface defect density and higher total negative charge [4-6] than the conventional water-based process. Nevertheless, the past studies of ozone-based ALD processes often omit the ozone concentration, although this parameter may be of paramount importance for the quality of ALD films. A more systematic study on the effect of ozone concentration on the passivation and its effects on the chemical composition of the Si/ Al_2O_3 is thus needed. In particular, the effect of ozone-based Al_2O_3 processes on carbon contamination remains controversial. Carbon atoms are common impurities affecting the passivation quality of Al_2O_3 layers [5,7,8], and are considered harmful for surface passivation. Although ozone possesses a stronger oxidation potential than water, and has potentially beneficial effect on the reduction of impurity concentrations, as shown in previous studies [5,8-10], other studies have also reported relatively high carbon concentration in ozone-based ALD films [11,12]. Despite this possible drawback, ozone-based ALD Al_2O_3 shows promising surface passivation quality [6,13].

In addition to carbon, hydrogen impurities play an important role in the passivation quality. For instance, no passivation is usually provided by as-deposited films, which require a post-anneal treatment to sufficiently reduce the D_{it} values [3,14,15]. This has been explained by hydrogen atoms diffusion from the bulk of the aluminum oxide to the film interface during the anneal, thus providing defect passivation therein [2,15-17]. Similarly, a combined process that consists of the reaction between TMA and a mixture of ozone and water has shown a significant lifetime improvement compared to the pure

ozone process [13]. The additional hydrogen content provided by the extra water pulse could thus account for the improved surface passivation, but no experimental evidence has been given so far.

Thus, we investigate here the effect of the ozone concentration on the Si/Al₂O₃ interface quality, and aim at a more thorough understanding of the mechanisms responsible for successful surface passivation. In the last part of the paper, we discuss the improvements obtained with the combined process relative to the pure ozone process.

2. EXPERIMENTAL DETAILS

The wafers used in this study were 4'' double-side polished Magnetic Czochralski p-type silicon of resistivity $\sim 2.5 \Omega \cdot \text{cm}$, (100)-oriented and $(400 \pm 10) \mu\text{m}$ -thick. Double-sided 20 nm -thick Al₂O₃ layers were deposited in a Beneq TFS 500 tool at a temperature of 200 °C after dipping the wafers in a 1 % HF solution for 60 s. Al₂O₃ was deposited using Trimethylaluminum (TMA) from Sigma-Aldrich with a purity of at least 98 %, which is a typical solar-grade precursor for ALD Al₂O₃. Two types of ALD processes were used in this study: the first one from pure ozone as oxygen source, and the second one from a combination of ozone and water during the same half-cycle, water being injected before the ozone pulse (referred to as the “combined process”). The ozone pulse time was optimized and a value of 7 s was chosen in order to reach ALD growth at each ozone concentration used in this study. The TMA pulse and purge times were 250 ms and 3 s, respectively, and the ozone purge time was 9 s in both ozone processes. Ozone was produced from O₂ (99.999%) with a Wedeco Ozomatic 4 (TFS 500) generator with a flow of 15 L/h. The ozone concentration was varied in both processes according to Table I. The ozone concentration can be described by the ozone molar ratio, which corresponds to the ratio between the ozone flow and the total gas flow in the travelling-wave deposition chamber. The gas flow during the oxidative precursor pulse consisted of nitrogen carrier gas, oxygen and ozone with nitrogen and oxygen flow rates of 0.4 L/min and 0.25 L/min in standard conditions, respectively.

An anneal in N₂ at 400 °C for 30 min followed the Al₂O₃ deposition, after which the samples were fired in N₂ at 800 °C for 3 s in a rapid thermal annealing (RTA) furnace.

The purpose of the firing anneal is to reproduce the firing step used in industrial production for the screen printed metal contacts, in order to study the stability of passivation quality under high temperature.

The film thickness was measured by a Plasmos SD2300 Ellipsometer at a wavelength of 632.8 nm. The interface charge and defect densities were measured by Semilab SDI PV2000 using the COCOS (Corona oxide characterization of semiconductors) contactless measurement method [18]. In addition, MOS capacitors were fabricated by evaporating aluminum contacts of 100 μm diameter on top of the oxide. They were used in contact-CV measurements to obtain the interface characteristics of the as-deposited samples, i.e. of the samples before heat treatments. The minority carrier lifetimes were measured by QSSPC (Quasi-Steady State Photoconductance) with Sinton WCT-120 equipment and the values were taken at an injection level of $5 \cdot 10^{15} \text{ cm}^{-3}$. The elemental concentrations were quantified by the time-of-flight elastic recoil detection analysis (ToF-ERDA) tool in the University of Jyväskylä [19] using a 13.6 MeV $^{63}\text{Cu}^{7+}$ ion beam. The Al_2O_3 films measured by ToF-ERDA were 100 nm-thick in order to study more accurately the elemental composition at the interface between silicon and aluminium oxide, and were annealed and fired at the temperatures mentioned above before the measurements.

	Ozone concentrations	
Concentration range	low	high
Output O_3 concentration (g/Norm.m ³)	48	162
O_3 dose (g/h)	0.72	2.4
O_3 mole ratio in the reactor* (%)	0.85	2.8

* $\text{O}_3 \text{ mole}/(\text{O}_3+\text{O}_2+\text{N}_2)\text{mole} \times 100$

Table 1. Description of the two ozone concentrations in terms of dose and of proportion in the ALD reactor. The concentration of the ozone flow issued by the generator is given in gram per normal cubic meter (g/Norm.m³), meaning that the concentration is given at a temperature of 0 °C and at a pressure of 1013 hPa.

3. RESULTS

3.1. Passivation quality

In agreement with previous results [6,13], the ozone ALD Al_2O_3 process results in better passivation than the pure water process (Figure 1). The passivation quality was further

improved by increasing the ozone concentration both in the case of pure ozone and the combined process. In the latter in particular, increasing the concentration by a factor of 4 improved the post-anneal lifetimes by 33 %, which corresponds to a maximum surface recombination velocity of 7.1 cm/s. In comparison, maximum surface recombination velocities of approximately 2000 cm/s were measured in the as-deposited samples. In comparison, maximum surface recombination velocities over 10 cm/s are usually measured in low resistivity p-type CZ silicon passivated by annealed or fired Al_2O_3 , while somewhat lower values are reported with Float-Zone substrates [1,2,4,15,17]. In addition, all ozone-based samples exhibit an improved thermal stability compared to the reference water-based sample. The impact of the firing step was the smallest in the samples deposited using the combined process, where no significant increase of the surface recombination velocity was observed after high temperature treatment.

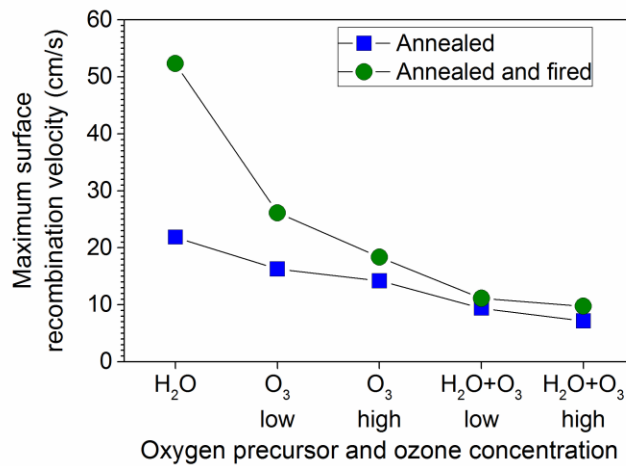


Figure 1: Maximum surface recombination velocities at an injection level of $5 \cdot 10^{15} \text{ cm}^{-3}$ as a function of ALD ozone concentration with two different processes: i) ozone ii) water + ozone. The substrates were passivated by 20 nm of Al_2O_3 . The terms “low” and “high” refer to ozone concentrations of 48 g/m^3 and 162 g/m^3 , respectively (see Table 1). The term “annealed” refers to a post-anneal at $400 \text{ }^\circ\text{C}$ for 30 min and the term “fired” to a firing anneal at $800 \text{ }^\circ\text{C}$ for 3 s. The lines are guides to the eye.

3.2. Electrical properties of the $\text{Si}/\text{Al}_2\text{O}_3$ interface

The as-deposited state in Al_2O_3 grown from TMA and water is typically characterized by a low interface charge density and a rather low interface defect density, which are not

adequate for efficient passivation. As-deposited films grown by the ozone process do not provide surface passivation either, but on the contrary, they have been reported to provide a high effective charge and a high defect density [6,20]. In our samples, similar results were obtained as a high negative charge over $6 \cdot 10^{12} \text{ cm}^{-2}$ was measured in all ozone-based as-deposited samples, regardless of the ozone concentration and of the addition of a water pulse. The poor passivation quality of these samples is explained by high D_{it} of $(7 \pm 2) \cdot 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$.

The interface defect density was greatly improved after annealing and firing, as observed in the Figure 2, which presents the D_{it} variation as a function of the surface band bending for each sample. This improvement after heat treatments explains the low surface recombination velocities obtained in Figure 1. Note that only the midgap defect densities will be considered here, since they are the most decisive for recombination processes. An uncertainty of 25 % is typically found for the midgap D_{it} values [21].

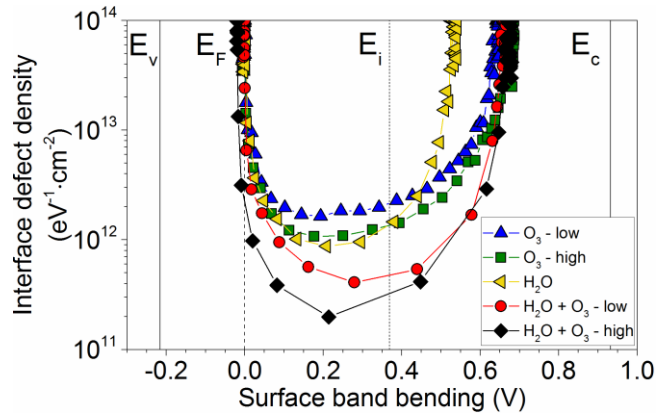


Figure 2: Repartition of the interface defect density over the bandgap for different ozone concentrations after annealing at 400 °C and firing at 800 °C of the 20 nm-thick Al_2O_3 films. The term “low” refers to an ozone concentration of 48 g/m^3 and “high” refers to an ozone concentration of 162 g/m^3 .

Moreover, the ozone concentration increase correlates with a D_{it} reduction. The lowest D_{it} value of $(2.0 \pm 0.5) \cdot 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ is obtained for the highest ozone molar ratio of 2.8, and corresponds to a surface recombination velocity of 10 cm/s after firing. Remarkably, the lowest D_{it} values were systematically obtained with the combined process, which is in agreement with the low recombination velocities measured.

Additionally, the fixed oxide charge remains high in all samples regardless of the O_3 concentration, so that Al_2O_3 still provides adequate field-effect passivation. However, an increase of ozone concentration seems to cause a reduction of the oxide fixed charge, as shown in Figure 3, and the charge can be further reduced by the injection of water during the ozone process. This effect may be related to a thickness variation of the interfacial oxide (SiO_x) between silicon and aluminum oxide that grows during the first cycles of ALD [3,17,22-24]. Recent studies have indeed shown that an increase of the SiO_x interlayer thickness causes a reduction of the negative charge in $Si/SiO_x/Al_2O_3$ stacks, due to the positive bulk charge density in SiO_x and to the low probability of charge tunneling from silicon to Al_2O_3 through thick silicon oxide [25,26]. We thus suspect that higher ozone concentrations and water injection increase the thickness of the SiO_x interlayer.

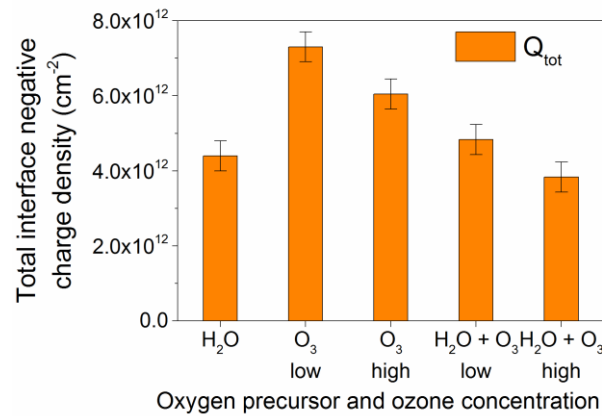


Figure 3: Total negative interface charge density Q_{tot} measured on 20 nm-thick Al_2O_3 films by COCOS after annealing at 400 °C and firing at 800 °C. The term “low” refers to an ozone concentration of 48 g/m^3 and “high” refers to an ozone concentration of 162 g/m^3 .

Additionally, it appears that the D_{it} of the pure ozone samples exceeds that of the water reference sample. This drawback is compensated by the significantly larger charge present in the ozone-based Al_2O_3 layers, which explains the lower surface recombination velocities shown in Figure 1.

3.3. Elemental analysis

Elemental characterization of the Al_2O_3 films can reveal further information regarding the origin of the defects at the interface between the film and silicon. As stated in the

introduction, carbon impurities constitute typical Al_2O_3 defects that are detrimental for silicon surface passivation, while hydrogen passivates silicon dangling bonds. Those elements are thus investigated in the following section. Note that the absolute values of the measured elemental concentrations may vary depending on the quality of the TMA used.

A reliable characterization of the $\text{Si}/\text{Al}_2\text{O}_3$ interface by ToF-ERDA requires thicker films; hence 100 nm-thick films were prepared for the study. Despite the difference of Al_2O_3 thickness, those samples exhibit the same trends as the 20 nm-thick Al_2O_3 samples in terms of lifetimes and electrical interface characteristics. The ERDA profiles are presented in Figure 4. The carbon profiles present a surface peak due to contamination from the ambient, which however does not affect the bulk nor the interface concentrations.

As mentioned in the introduction, the effect of hydrogen is the most decisive at the $\text{Si}/\text{Al}_2\text{O}_3$ interface, where it passivates the silicon surface defects. For this reason, this part focuses specifically on the hydrogen densities at the $\text{Si}/\text{Al}_2\text{O}_3$ interface and not in the bulk.

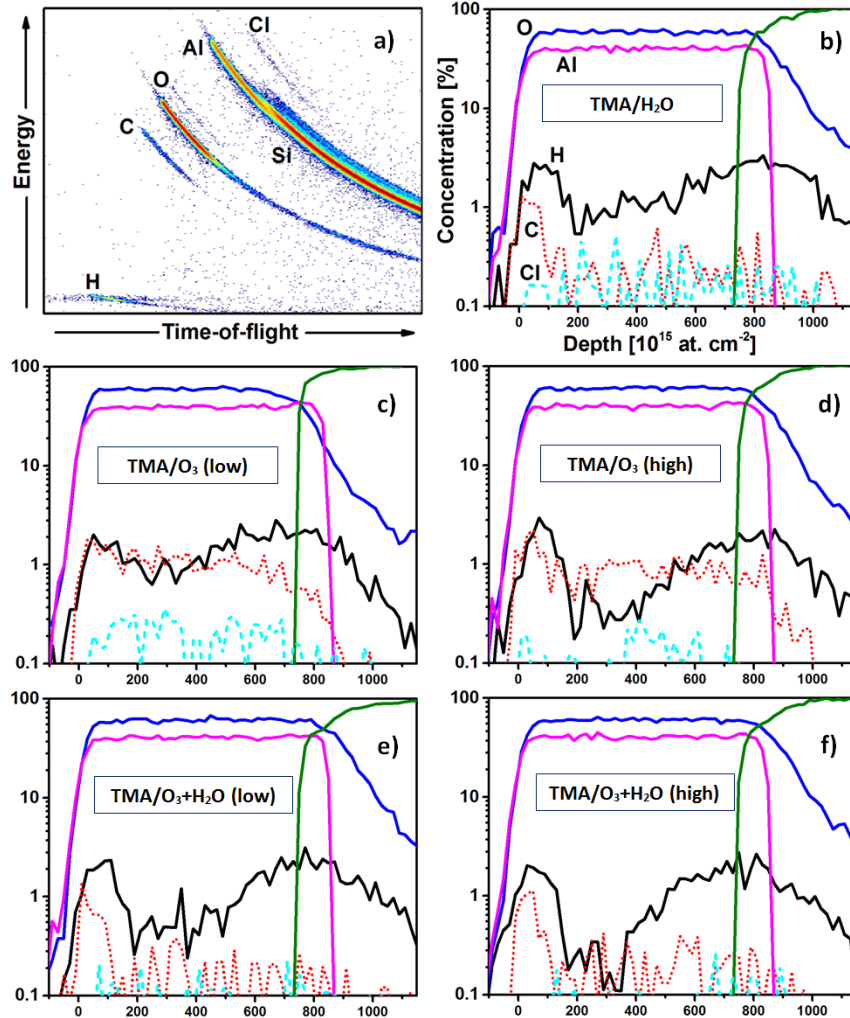


Figure 4: Typical raw TOF-energy histogram of an Al_2O_3 film (a) and concentration depth profiles of the five films grown with different oxygen sources (b, c, d, e, f). The Al_2O_3 layers had a thickness of 100 nm and were annealed at 400 °C for 30 min and fired at 800 °C for 3 s.

Figure 5 presents the average carbon concentrations in the 100 nm aluminum oxide layers as well as the interface hydrogen concentrations. The values of carbon concentration in Figure 5a are consistent with the values usually reported in the literature for TMA-based Al_2O_3 deposited at 200 °C with either water or ozone, in the order of magnitude of 1 at.% [23,27,28]. According to our results, the values measured in the pure ozone samples exceed notably the carbon concentration measured in the water-based reference sample – (0.20 ± 0.05) at. %. The carbon atomic percentage in the pure ozone samples was not clearly affected by the ozone concentration, with values of 1.1 at.% and 0.9 at.% at low and high ozone concentration, respectively. It should however be noted that the

difference in the ozone concentrations studied here might be insufficient to significantly affect the carbon content in the layers. Moreover, extremely low carbon concentrations of approximately 0.2 at % were achieved with the combined process, most probably due to the addition of water. The same densities were indeed already obtained with the pure water process, and as a result, the ozone concentration showed no effect on the carbon densities due to their low initial level. In summary, the relatively low carbon concentrations measured in all samples correlate well with the low D_{it} values obtained. The lower carbon content in the combined process can partly explain the lower D_{it} [29], and thus the lifetime improvement compared to the samples deposited using ozone as sole oxygen source.

The hydrogen interface concentrations in the five samples are shown in Figure 5b. Ozone appears to reduce the hydrogen concentration at the interface of both pure ozone and combined samples in comparison to the reference water sample. In addition, it seems that the interfacial hydrogen density is slightly higher in the combined process. The hydrogen reduction in the ozone-based samples could consequently be related to the ozone reaction mechanism, while the combined process may provide extra hydrogen from water molecules. Interestingly, the addition of water to the ozone process does not allow hydrogen recovery to the level observed in the pure water process. The higher reactivity of ozone could lead to a more efficient removal of the adsorbed hydroxyl groups, thus preventing excessive hydrogen inclusion.

Surprisingly, it appears that better lifetimes correlate with lower interfacial hydrogen levels, although high hydrogen levels are traditionally associated with effective surface passivation. In fact, Tsetseris et al. have shown by first principles calculations that hydrogen may be detrimental for passivation after high temperature treatments, because it can dissociate Si-Si bonds, thus creating more defects in the form of Si-H bonds [30]. Consequently, high hydrogen levels combined with high temperature treatments, such as firing at 800 °C, could impair the passivation quality – the inserted hydrogen atoms contributing to the final hydrogen content without participating to the passivation. By lowering the hydrogen content in the aluminum oxide, ozone could thus prevent the formation of such defects after high temperature treatments. The high hydrogen concentration measured in the water sample also sustains this hypothesis, since the

corresponding D_{it} is higher than in the combined samples despite similar carbon concentrations.

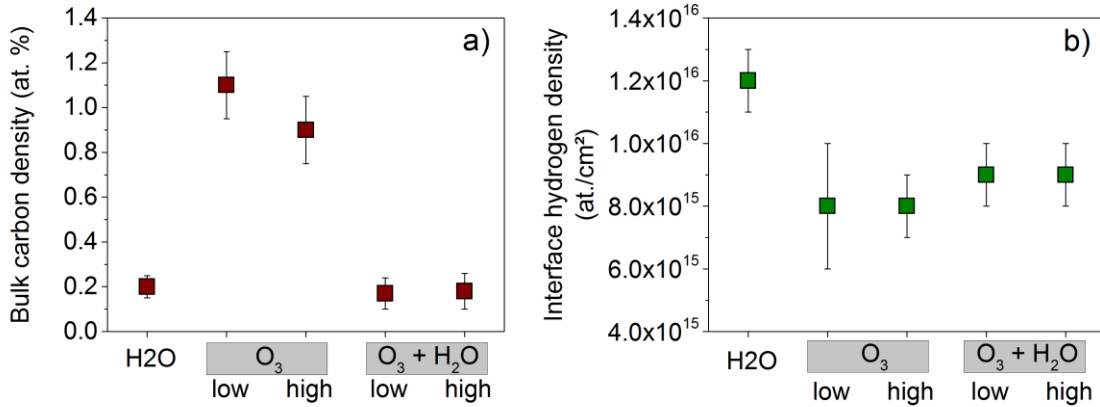


Figure 5: a) Carbon concentrations in the bulk of a 100 nm-thick aluminum oxide layer and b) hydrogen concentrations at the Si/Al₂O₃ interface in the five types of studied. The terms “low” and “high” refer to ozone concentrations of 48 g/m³ and 162 g/m³, respectively.

4. CONCLUSIONS

We have studied the effect of the ozone concentration on the ALD Al₂O₃ passivation quality. An increase of ozone concentration causes a clear reduction of defect density at the interface between Al₂O₃ and silicon, which correlates well with the minority carrier lifetime improvement. The negative charge present in Al₂O₃ also seems to be affected by an increasing ozone concentration. We have shown that ozone is beneficial to the passivation, but a too low ozone concentration might be detrimental for the quality of the interface, and could lead in particular to a higher carbon density in comparison to the pure water process. We suggest that the D_{it} can be improved using higher ozone concentration and adding water to the ozone process, which seems to be related to a reduction of both carbon and hydrogen in the ALD film. Our results imply that too high hydrogen concentrations can be detrimental after high temperature treatment. Using a process combining water and ozone, a maximum surface recombination velocity of 10 cm/s was obtained after high-temperature firing, owing to excellent interface characteristics.

To conclude, we have suggested a simple way to modify the interface properties of Si/SiO_x/Al₂O₃ stacks, such as interface charge density and interface defect density, by varying the ozone concentration and by injecting water during the ozone process.

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