PARTICLE REMOVAL AND FEATURE DAMAGE REDUCTION USING CARBONATED AMMONIA SOLUTIONS FOR ENHANCED MEGASONIC CLEANING PROCESSES

by

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CARBONATED AMMONIA SOLUTIONS FOR ENHANCED MEGASONIC
CLEANING PROCESSES

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SIGNED: Zhenxing Han
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ABSTRACT

In integrated circuit (IC) manufacturing, particulate contamination from hundreds of process steps is a major cause of yield loss. The removal of particles is typically achieved through liquid chemical formulations aided by a sound field in the MHz frequency range. When liquid is irradiated with megasonic waves, dissolved gases play an important role in particle removal and feature damage. To take the advantage of the beneficial effect of CO$_2$ (aq.), this thesis describes the development and optimization of a megasonic cleaning process using a chemical system containing NH$_4$OH and NH$_4$HCO$_3$ at an alkaline pH in which a specific amount of aqueous CO$_2$ can be maintained to minimize feature damage. In addition, certain etching effects at a slightly alkaline pH were supported for achieving high particle removal. Sonoluminescence (SL) data were collected from these cleaning solutions and correlated with the cleaning performance. The intensity of SL is believed to be a sensitive indicator of transient cavitation during megasonic irradiation, which is thought to be responsible for fragile feature damage. To further analyze the SL signal with respect to the emission from hydroxyl radicals, single-band filters were used to collect the SL signal in different wavelength ranges.

The study of particle removal and feature damage was performed using a single-wafer cleaning tool, MegPie® (ProSys, Inc.), which provided acoustic irradiation at a frequency of 0.925 MHz. Commercially available SiO$_2$ slurry with 200 ± 20 nm particles was used
for particle contamination. Particle removal was investigated on both blanket SiO$_2$ samples and patterned samples. Feature damage studies were conducted on patterned samples by examining the number of line breakages per unit area. By adjusting the pH in NH$_4$OH/NH$_4$HCO$_3$ solutions from 7.8 to 8.5, the amount of CO$_2$ (aq.) was varied. At a pH of 8.2 with ~ 320 ppm CO$_2$ (aq.) in the cleaning solution, a high particle removal efficiency was achieved (> 90%) at an acoustic power intensity of 1 W/cm$^2$ for an exposure time of 60 s, and the feature damage was reduced by > 50%.

For SL signal analysis, band filters in the wavelength range of (i) 280 – 305.5 nm, (ii) 300 – 340 nm, (iii) 335 – 375 nm, and (iv) 374.5 – 397.5 nm were used to resolve the SL spectrum in these wavelength ranges. The filters were sandwiched, one at a time, between the optical window and the photomultiplier tube (PMT) in the Cavitation Threshold (CT) cell. Air-, Ar-, and CO$_2$-containing DI water (at pH 4.53 with ~ 90 ppm aqueous CO$_2$) was pumped through the cell at a flow rate of 130 ml/min. The acoustic power was ramped from 0.1 to 4 W/cm$^2$ at an acoustic frequency of 0.925 MHz. The SL signal intensity showed the highest value in the ranges of 300 – 340 and 335 – 375 nm in air- and Ar-saturated DI water, which is due to the emission from excited hydroxyl radicals. These results are consistent with an SL spectrum analysis performed using expensive optical set-ups. In CO$_2$-containing DI water, the SL signal intensity was suppressed by a factor of 100. The methodology reported in this work is simple, inexpensive, and capable of capturing SL spectral features due to hydroxyl radicals.
1. **Explanation of the problem and its context**

An integrated circuit is nothing more than a very advanced electric circuit, which is made from different electrical components such as transistors, resistors, capacitors, and diodes connected to each other in different ways. With the continuous effort being made to reduce the size of these individual components, more components can be integrated in a chip, thus significantly enhancing the performance of IC systems while reducing the cost. In the 1960s, the co-founder of Intel, Gordon Moore, first described a trend observed for computer hardware that is now known as Moore’s Law: the number of transistors in integrated circuits doubles approximately every two years (1). Under such vigorous growth, challenges in each manufacturing step have risen. One of the biggest concerns in all of the manufacturing steps is the removal of contamination, which is a major cause of yield loss in integrated circuit (IC) manufacturing (2).

Particles need to be removed from the surface of the wafers many times during the hundreds of manufacturing processes. Particles result from etching processes, chemical-mechanical planarization, chemical and physical vapor deposition, and many other fabrication steps. Such particles may obstruct many processing operations and ultimately
result in open or short circuits. Therefore, in the IC fabrication process, trenches and vias must be cleaned before subsequent processing steps. Particle location and size are the main factors determining whether a killer defect occurs during processing. Particles that exceed one-fourth of the minimum feature size have the potential to cause fatal device defects. With the continuous efforts being made to decrease the feature size, technologies that can remove smaller particles are also required. By 2018, the critical particle size in the front end of line (FEOL) processes is expected to be 9 nm (3).

The objective of today’s cleaning technologies is to remove all the contaminants from the wafer surface without damaging the fine structures on the surface. Several cleaning techniques have been used in the semiconductor industry. They can be divided into two main types: dry and wet cleaning methods. Dry (vapor-phase) cleaning methods include jet scrubbing using dry carbon dioxide, cryogenic argon aerosol jet impingement, supercritical carbon dioxide, gas plasma cleaning, etc. Wet cleaning methods employ liquid-based chemistries such as hydrofluoric acid solutions, sulfuric acid – peroxide mixtures, alkaline and acidic peroxide solutions (SC1 and SC2 solutions), and sulfuric acid-ozone mixtures (4). Figure 1 shows a typical sequence of wet cleaning steps and operation conditions used in the semiconductor industry.
The mixture of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 96% by volume) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 30% by volume), also known as Piranha solution (piranha etch) is used to remove organic residues from substrates at an operation temperature in the range of 120 to 150 \textdegree C. Because the mixture is a strong oxidizing agent, it will remove most of the organic matters and form a thin oxide layer. It will also hydroxylate most surfaces (add OH groups), making them highly hydrophilic (water compatible). A typical mixture is 3:1 concentrated sulfuric acid (98%) to 30% hydrogen peroxide solution.

Dilute HF (DHF) solution is typically used to etch and remove the oxide layer formed by Piranha. The ratio of HF (49%) to water is usually varied from 1:50 to 1:100. The removal process usually takes 1 min at room temperature.
The SC-1 solution (also known as APM), where SC stands for Standard Clean, is prepared with NH$_4$OH (29%), H$_2$O$_2$ (30%) and H$_2$O at a ratio from 1:1:5 to 1:1:200. The cleaning operation is usually done at 75 or 80 °C for 10 minutes. This treatment results in the formation of a thin silicon dioxide layer (normally about 1 nm) on the silicon surface by the oxidization effect from H$_2$O$_2$, followed by the etching effect from NH$_4$OH. The SC1 solution is very effective in removing particulate contaminants from wafer surface.

The SC-2 solution is prepared with HCl (36.5%), H$_2$O$_2$ (30%) and H$_2$O in a ratio between 1:1:5 and 1:1:200. The mixture is also called HPM. The cleaning process using HPM is typically performed at 75 or 80 °C for 10 min. This treatment effectively removes the remaining traces of metallic (ionic) contaminants. Between each cleaning step, de-ionized water (with resistance more than 18 MΩ) is used for rinsing.

The cleaning efficiency of SC1 (APM) can be enhanced with acoustic irradiation. Sound waves are applied through a liquid medium to the wafer surface. Removal of particles is typically achieved through liquid chemical formulations aided by a sound field in the MHz frequency range (5, 6). In the fabrication of state-of-the-art sub-45 nm devices, the challenge for megasonic cleaning processes in both front-end-of-line (FEOL) and back-end-of-line (BEOL) processes is to maintain a high particle removal efficiency (PRE) without damaging small features (7-10).
During acoustic irradiation of liquids, two types of phenomena are known to occur, namely acoustic streaming and cavitation. Acoustic streaming refers to time independent motion of liquid due to viscous attenuation. In the case of acoustic cavitation, bubbles formed during low pressure cycle of the sound wave either continuously oscillate over many cycles (stable bubbles) or grow in size and eventually collapse in less than a few cycles (transient bubbles). The flow generated from oscillating bubbles, known as microstreaming, is considered to be instrumental in particle removal whereas shock waves and micro jets generated from transient bubbles are believed to be responsible for damage. Acoustic cavitation is accompanied by a number of physical and chemical effects. It is known that due to high temperature (>4000 °C) conditions reached inside the bubble during its collapse, excitation of various species as well as formation of radicals occurs. When the excited species go back to the ground state, light is emitted, and this phenomenon is known as sonoluminescence (SL). The intensity of SL is considered to be a sensitive indicator of cavitation events and therefore can be a good predictor of the extent of feature damage on patterned wafers. The intensity of SL depends on solution parameters such as the level of dissolved gases, pH, etc. and megasonic frequency and power density.

Dissolved gases play an important role in megasonic cleaning processes. Gases such as N₂, O₂, air or inert gases usually induce high level of transient cavitation, then generate a
lot of feature damage in the cleaning process. Aqueous CO\textsubscript{2} has been observed much different from other gases, with which in the cleaning solution much less intensity of SL signal was measured. The objective of this work is to take advantage of the beneficial effect of CO\textsubscript{2} in reducing feature damage, developing a chemical system containing a specific level of aqueous CO\textsubscript{2} at alkaline pH to achieve high particle removal and generate less damage to the patterned structures. By optimizing the megasonic cleaning conditions, a formulation containing NH\textsubscript{4}OH and NH\textsubscript{4}HCO\textsubscript{3} was developed as an effective cleaning solution in semiconductor manufacturing. The NH\textsubscript{4}OH provides some etching effect for particle removal at slightly alkaline pH and NH\textsubscript{4}HCO\textsubscript{3} serves to maintain some level of aqueous CO\textsubscript{2} in the cleaning solution for feature damage reduction.

Another objective of this work is to conduct resolved SL signal in specific wavelength ranges. At MHz frequencies, the SL signal is typically very weak and requires very sensitive spectrometers to resolve the SL spectra. Additionally, in most of the published work, SL spectral features were reported in relative intensity values making it difficult to determine if the peaks are real. The emission of SL is believed to be due to excited hydroxyl radicals falling back to their ground state. The emission is typically in the wavelength range of 280 to 400 nm. A simple methodology using a photo-multiplier tube (PMT) in conjunction with single band filters at specific range of wavelengths: 280 – 305.5 nm, 300 – 340 nm, 335 – 375 nm, and 374.5 – 397.5 nm has been developed.
2. A Review of the Literature

2.1 Megasonic Cleaning

Megasonic cleaning was first introduced by the Radio Corporation of America (RCA) to the semiconductor industry in 1985 (11). Megasonic cleaning has become a highly advanced cleaning technology for removing nanoparticles. The acoustic waves with a frequency in the MHz range are generated by exciting a piezoelectric crystal. Piezoelectric crystals vibrate when they are subjected to an alternative electric field. Most of the electrical energy can be converted into acoustic energy when a piezoelectric ceramic is excited at its resonance frequency and under optimized physical parameters. The acoustic wave is propagated through a liquid medium along with the generated pressure fluctuation.

During acoustic irradiation of liquids, two types of phenomena are known to occur: acoustic streaming and cavitation. These two phenomena are considered to be the main mechanisms for particle removal. Acoustic streaming refers to the time-independent motion of a liquid due to viscous attenuation. Three types of streaming phenomena are known to exist in solutions subjected to a sound field: namely, Eckart streaming, Raleigh streaming, and Schlichting streaming. Eckart streaming, which is mainly bulk flow, is
characterized by vortices much larger than the wavelength of sound (12), whereas Schlichting and Raleigh streaming result in liquid flow close to a solid boundary with length scales much smaller and on the order of sound wavelengths, respectively (13). Particle removal in a megasonic field relies on a reduction in the boundary layer thickness at the solid-fluid interface. Eckart streaming mainly reduces the diffusion boundary layer thickness and thus increases the chemical reactivity at the surface. Schlichting streaming (boundary layer streaming) enhances the particle removal within a viscous boundary layer by a rolling mechanism. The acoustic boundary layer thickness ($\delta$) in a fluid with a kinematic viscosity of $\nu$ decreases with an increase in the angular acoustic frequency ($\omega$).

$$\delta = \left( \frac{2\nu}{\omega} \right)^{\frac{1}{2}}$$  \hspace{1cm} (1)

In a sound field at a frequency of 1 MHz in water, the acoustic boundary layer thickness is approximately 0.5 $\mu$m. In comparison, the turbulent hydrodynamic boundary layer on a flat surface is greater than 1600 $\mu$m for a free stream velocity of 10 m/s in water.
The acoustic streaming velocity \( U_a \) is proportional to the product of the square of the acoustic frequency and transducer power density and inversely proportional to the viscosity.

\[
U_a \propto \frac{\omega^2 P}{\eta}
\]  

(2)

where \( P \) is the transducer power density. For example, in an acoustic field with a transducer intensity of 10 W/cm\(^2\), the streaming velocity can be as high as 5.4 m/s at 0.925 MHz in water. Thus, the viscous stresses and large velocity gradients combined with boundary layer thickness reduction expose particles to a much higher fluid velocity than that in a hydrodynamic flow, which enhances particle removal from a substrate.

In the case of acoustic cavitation, bubbles formed during the low-pressure cycle of the sound wave either continuously oscillate over many cycles (stable cavitation) or grow in size and eventually collapse in less than a few cycles (transient cavitation). Stable cavitation acts as a secondary sound source and leads to fluid flow adjacent to the bubble wall, which is called microstreaming. Stable cavitation is referred to bubbles oscillating at an equilibrium size and will usually eventually disappear, and at 1 MHz, the resonant bubble size is roughly 3.7 µm. Transient cavitation is characterized by large bubble size
variations and eventually by bubble collapsing. This process involving bubble collapse can cause extremely high temperature and pressure conditions, from which shock waves and microjets are formed. Both microstreaming and shock waves or microjets are considered to be instrumental in particle removal (14, 15). Figure 2 presents these different particle removal mechanisms that occur during the megasonic cleaning process.

Figure 2: Schematic of different phenomena action in an acoustic field at a frequency of MHz

Acoustic cavitation is accompanied by a number of physical and chemical effects (16-18). It is known that because of the high temperature conditions reached inside the bubble during its collapse, the excitation of solvent molecules and the formation of radicals
occur. When the excited species go back to the ground state, light is emitted, and this phenomenon is known as sonoluminescence (SL), as shown in Fig. 3 (19). The intensity of sonoluminescence is considered to be a sensitive indicator of cavitation events (20, 21) and therefore can be a good predictor of the extent of feature damage on patterned wafers. The intensity of SL depends on solution parameters such as cleaning chemistry and level of dissolved gases and on sound field variables such as megasonic power density and acoustic frequency.

Figure 3: SL emission in the megasonic field (adapted from Ref. 19)
Megasonic cleaning can be practical in single wafer and batch mode processes. Single wafer cleaning/processing has become more important than conventional batch cleaning/processing in recent years because it allows better processing control and better process uniformity across the wafer surface. Single wafer spin cleaning tools are used to meet stricter wafer cleaning requirements. Cleaning chemicals are continuously supplied over a spinning wafer resulting in a thin boundary layer. Particle removal efficiency can be further enhanced upon use of megasonic energy in such single wafer spin cleaning tools. As opposite to single wafer cleaning, batch cleaning process is referred to the procedure in which many wafers are processed simultaneously with cleaning solutions and then rinsed by de-ionized water.

Original equipment manufacturing (OEM) companies such as PCT Systems, Inc., SUSS MicroTec company, ProSys, Inc. et al provide megasonic cleaning tools used in wet cleaning process. A single wafer megasonic cleaning tool, MegPie® (ProSys, Inc.), has been used in the present study for particle removal and feature damage study of blanket and patterned wafers. MegPie® consists of a transducer with area of 32.3 cm², designed to apply uniform acoustic energy to the rotating substrate at a frequency of 0.925 MHz. The transducer power density can vary from 0.1 to 4 W/cm². The distance between the transducer and wafer is designed to be ~1.5 mm.
The whole MegPie® system contains the following parts:

- **Transducer (MegPie V3):** is triangular in shape and designed to apply uniform acoustic energy on a rotating substrate. A temperature sensor is integrated to prevent overheating on the transducer surface.

- **The MicroDuo 200 (RF Generator):** supplies RF energy to the Megasonic Transducer (MegPie V3). The MicroDuo 200 provides both RF Supply and control interface to the Megasonic System. Any operation of the System requires the MicroDuo 200.
- **Impedance Matching Network**: is used to connect the MicroDuo to the Megasonic array assembly.

- **Polos spinner**: consists of a chuck on which the wafer is held (Fig. 8). The rotation speed of the wafer is controlled by adjusting the settings in the control panel as described in the later sections.

Megasonic Immersion Tank (ProSys, Inc.) contains the following components:

- **An immersion tank** (15 L capacity) made of KYNAR® (polyvinylidene fluoride) equipped with four 0.925 MHz transducers covered by the resonator (quartz) on the top

- **MegaPulse unit**: the Megasonic System Controller – contains an oscillator and an embedded microcomputer with two communication interfaces to create the signals which feed to the MegaPower

- **MegaPower unit**: the Megasonic Power Source – amplifies the signal from MegaPulse to a specific power density to the Transducer

- **Impedance Matching Network**: is used to connect the MegaPower to the megasonic array assembly, which matches the impedance of the oscillator circuit tree to that of the transducer.
Figure 5 shows the picture of immersion megasonic cleaner and its dimension with 4 transducers on the bottom of the tank. The total active area of the 4 transducer is 200 cm$^2$. The power density applied to the transducer is from 0.1W/cm$^2$ (corresponds to 20 W power output) to 2.88W/cm$^2$ (corresponds to 576 W power output). Standard Transducer Arrays operate at process temperatures up to 65 degrees C.

Figure 5: Immersion megasonic tank and its schematic
2.2 Megasonic Cleaning Mechanisms

Particles can be removed from the substrate wafer through the following mechanisms: lifting, sliding, and rolling. The removal process may be a combination of two of these mechanisms. In the megasonic noncontact cleaning process, the rolling mechanism is dominant. The removal under megasonic irradiation relies on acoustic streaming and on the reduction of the boundary layer thickness on the substrate surface. In this section, the forces on particles in a megasonic field will first be described, and then different cleaning mechanisms will be summarized.

2.2.1 Forces on particles in a megasonic field

- Adhesion forces

The adhesion of particles was determined in the first instance by the omnipresent van der Waals forces. Van der Waals forces arise due to the polarizability of the molecules. This force arises from the short-period movement of the electrons in the atoms or molecules, which gives rise to momentary areas of charge concentrations called dipoles. No net charge needs to be present; the dipole-induced effect gives rise to attractive forces, which are electrical in nature (22).
For the case of an undeformed sphere and rigid plane, this force is proportional to the radius of the sphere (23). Because the magnitude of the adhesion force between a particle and a substrate depends on the contact area, deformations of the contacting materials can therefore increase the adhesion forces (24). When a sphere and a flat substrate come into contact with each other, according to Bowling (23), the attractive force $F_{vdW}$ deforms the interface, and a circular adhesion area is formed between the adherents. The total adhesion force consists of two additive components, namely, the force acting between the adherents before deformation at the instant of the first contact, $F_{vdW}$, and the force acting on the contact area due to the deformation, $F_{vdW-deform}$,

$$F_a = F_{vdW} + F_{vdW-deform} = F_0 \{1 + \frac{a^2}{Rz_0}\}$$  \hspace{1cm} (3)

where $F_0 = \frac{A_H R}{6z_0}$ is the van der Waals force for the spherical particle, $A_H$ is the Hamaker-van der Waals constant, $R$ is the radius of the spherical particle, $z_0$ is the separation distance between the particle and the substrate (for a smooth surface, it is taken as 4 Å), and $a$ is the contact radius between the deformed particle and the surface. Therefore, in the case of a spherical particle resting on a flat substrate, the particle adhesion force, including the van der Waals force and the adhesion-induced deformation, can be expressed as:

$$F_a = F_{vdW} + F_{vdW-deform} = \frac{A_H R}{6z_0} \{1 + \frac{a^2}{Rz_0}\}$$  \hspace{1cm} (4)
The contact radius, $a$, results from adhesion-induced plastic deformation.

$$a = \sqrt{\frac{2W_aR}{H}}$$

where $W_a$ is the work of adhesion between the particle and the surface. $W_a = 2\sqrt{\gamma_1\gamma_2}$, where $\gamma_1$ and $\gamma_2$ are the surface free energy of the two contact materials. H is the hardness of the deformation part. The relations (25) between the Hamaker constants of two dissimilar materials may be represented by

$$A_{12} = \sqrt{A_{11} \cdot A_{22}}$$

$A_{11}$ and $A_{22}$ are the Hamaker constants for substances “1” and “2”. In the presence of a medium denoted by “3”, the net interaction between substances 1 and 2 is given by

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}}) \cdot (\sqrt{A_{22}} - \sqrt{A_{33}})$$

where $A_{33}$ is the Hamaker constant for medium “3”. Hamaker constants for a typical substrate-medium-particle system are given in Table 1 (26):
Table 1: Hamaker constants $A_{132}$

<table>
<thead>
<tr>
<th>Substrate-medium-particle</th>
<th>$A_{132}$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$-H$_2$O-SiO$_2$</td>
<td>$3.40 \times 10^{-21}$</td>
</tr>
<tr>
<td>SiO$_2$-H$_2$O-Al$_2$O$_3$</td>
<td>$1.07 \times 10^{-20}$</td>
</tr>
<tr>
<td>SiO$_2$-H$_2$O-PSL</td>
<td>$3.90 \times 10^{-21}$</td>
</tr>
<tr>
<td>SiO$_2$-H$_2$O-Si$_3$N$_4$</td>
<td>$1.60 \times 10^{-20}$</td>
</tr>
</tbody>
</table>
• **Electrical double layer forces**

Double layer forces occur between charged objects across liquids, typically water. This force acts over distances that are comparable to the Debye length, which is on the order of one nanometer to a few tenths of a nanometer. Electrical double layer interaction forces can be explained in the following way: when a substrate or a particle is immersed in a solution containing ions, its surface acquires charge through the adsorption of potential-determining ions (PDI). The distribution of ions in the interfacial region is disturbed, resulting in an increased concentration of counter ions close to the surface of either the substrate or particles. Consequently, an electrical double layer is formed around each particle and substrate surface that is immersed in a solution containing ions. Two layers exist in the liquid surrounding the particle: an inner region called the Stern layer, where the ions are strongly bound to the particle, and an outer, diffuse region where the ions are less firmly attached. The electrical double layer contains both the Stern layer and the diffuse layer. An imaginary plane called the shear plane exists inside the double layer. Inside this plane, the ions move along with the particles as the particles move in the solution. The potential that exists at this plane is called the zeta potential.

The electrostatic double layer force between a spherical particle (1) and a flat surface (2) in a liquid medium (3) under conditions of low surface potential is given by

$$F_{EDL} = -\frac{dE_{EDL}}{dh} = 2\pi \varepsilon_r \varepsilon_0 R_p \left( \Psi_0^2 + \Psi_0^2 \right) \left( \frac{ke^{-kh}}{1 - e^{-2kh}} \right) \left( \frac{2\Psi_{01} \Psi_{02}}{\Psi_{01}^2 + \Psi_{02}^2} - e^{-kh} \right)$$

(8)
where $\Psi_{01}$ and $\Psi_{02}$ are the surface potentials of the particle (1) and the surface (2), $E_{EDL}$ is the electrical double layer interaction energy, $R_p$ is the radius of the particle, $\kappa$ is the inverse Debye length, and $h$ is the shortest distance between the particle and the substrate.

The solution ionic strength and pH played an important role in the particle adhesion force and removal force. Such a dependence may be exploited for efficient removal of particles from wafer surfaces. In the previous work done by Kumari et al., silica particles with a diameter of ~185 nm were removed from blanket SiO$_2$ wafers using NH$_4$OH and NH$_4$OH/NH$_4$HCO$_3$ solutions at pH 8.2 (28). The zeta potential or surface potential of the dispersion was -0.030 V. The ionic strength of the NH$_4$OH solution at pH 8.2 was 15 µM, whereas it was 0.5 M for the NH$_4$OH/NH$_4$HCO$_3$ solution at the same pH. The calculated interaction force between the particles and wafer under the particle deposition condition was 24 pN (at 10 Å). The component van der Waals and electrical double layer interaction forces and energies for the particle-substrate pair were calculated using the following parameters:

$$E_{EDL} = \pi \varepsilon_r \varepsilon_0 R_p \left( \frac{\Psi_{01}^2}{\Psi_{02}^2} + \frac{\Psi_{02}^2}{\Psi_{01}^2} \right) \left\{ \frac{2 \Psi_{01} \Psi_{02}}{\Psi_{01}^2 + \Psi_{02}^2} \ln \left( \frac{1+e^{-\kappa h}}{1-e^{-\kappa h}} \right) + \ln \left( 1 - e^{-2\kappa h} \right) \right\}$$

(9)

and $\kappa = \frac{1000 q^2 N_A}{\varepsilon_r \varepsilon_0 k_B T \times 2 \times \text{Molar Ionic Strength}}$

(10)
Table 2: Parameters and constants used in the calculation of interaction forces

<table>
<thead>
<tr>
<th>Parameters and Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Hamaker constant ($A_{132}$)</td>
<td>$1.53948 \times 10^{-21}$ J</td>
</tr>
<tr>
<td>Radius of particle ($R_p$)</td>
<td>$(185 \times 10^{-9})/2$ m</td>
</tr>
<tr>
<td>Relative permittivity of water ($\varepsilon_r$)</td>
<td>80</td>
</tr>
<tr>
<td>Permittivity of vacuum ($\varepsilon_0$)</td>
<td>$8.85 \times 10^{-12}$ F/m or $C^2/(Nm^2)$</td>
</tr>
</tbody>
</table>

$\Psi_{01}$ (Particle) = $\Psi_{02}$ (Wafer) during cleaning

<table>
<thead>
<tr>
<th>$\Psi_{01}$ = $\Psi_{02}$ during particle deposition</th>
<th>-0.030 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic charge ($q$)</td>
<td>$1.6 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>Avogadro number ($N_A$)</td>
<td>$6.023 \times 10^{23}$</td>
</tr>
<tr>
<td>Boltzmann constant ($k_B$)</td>
<td>$1.38 \times 10^{-23}$ J/K</td>
</tr>
<tr>
<td>Temperature ($T$)</td>
<td>298 K</td>
</tr>
</tbody>
</table>

During cleaning process, the solution pH is 8.2 and pzc (both particle and wafer) is 2. The ionic strength of the solution during particle deposition is 0.5 nM; the molar ionic strength during cleaning is 0.5 M for NH$_4$HCO$_3$/NH$_4$OH and 15 µM for NH$_4$OH solution.

Figure 6 shows the calculated wafer-particle interaction forces conducted by Kumari et al. Blue curves represent Van der Waals interaction; red curves represent electrical double layer interaction and green curves show the total interaction between silica wafer and silica particles. At a normal particle-wafer separation distance, 10 Å, the calculated repulsive forces in the NH$_4$OH solution and NH$_4$OH/NH$_4$HCO$_3$ solution were 0.7 nN and
23 nN. This is an approximation of the actual values because the surface potential was calculated as 366 mV. The double layer interaction equation is valid when the surface potential is less than 50 mV. However, the calculated repulsive electrostatic double layer force is beneficial during the cleaning process to prevent particles from re-deposition.

Figure 6: Wafer-particle interaction in (a) \( \text{NH}_4\text{HCO}_3/\text{NH}_4\text{OH} \) and (b) \( \text{NH}_4\text{OH} \) cleaning solutions at pH 8.2 (Ref. 28)
2.2.2 Particle Removal Mechanisms

Particle removal is achieved by optimization of the megasonic cleaning conditions, including the megasonic power density (intensity), frequency (mainly in the MHz range), exposure time, and cleaning chemicals. Several mechanisms exist; microstreaming and acoustic cavitation are the two main mechanisms that are widely accepted. Acoustic streaming is the time-independent fluid motion generated due to the loss of acoustic momentum in a sound field, resulting from the attenuation of a sound field in viscous fluids. Based on the work on nanoparticle removal done by McQueen, the use of acoustic streaming to reduce the boundary layer thickness is thought to contribute to the removal process (29, 30). Busnaina et al. calculated and compared the acoustic boundary layer thickness with the hydrodynamic boundary layer thickness. Compared with the hydrodynamic boundary layer thickness, the acoustic boundary layer thickness is 1000 times smaller (31).

The acoustic boundary layer thickness is given by equation (1), which was introduced previously:

\[ \delta_{ac} = \left( \frac{2 \rho}{\omega} \right)^{1/2} \] (1)
where $\omega = 2\pi f$, $f$ being the acoustic frequency of the sound field, and $\nu$ is the viscosity of the cleaning solution. The hydrodynamic boundary layer is given by equation 11 and 12 for laminar and turbulent flow conditions.

$$\delta_{H,\text{Laminar}} = 5\left(\frac{\theta}{Ux}\right)^{1/2} \cdot x \quad (11)$$

$$\delta_{H,\text{Turbulent}} = 0.16\left(\frac{\theta}{Ux}\right)^{1/7} \cdot x \quad (12)$$

In the above equations, $U$ is the fluid velocity and $x$ is the distance from the leading edge of the wafer. Figure 7 shows the boundary layer thickness vs. velocity of the fluid at different acoustic frequencies. The thickness of the acoustic boundary layer is much smaller than that of the hydrodynamic boundary layer.
In addition to acoustic streaming, acoustic cavitation plays another important role in particle removal. Sound wave propagation in liquids is nothing more than pressure waves passing through the medium. Cavities are usually formed in the low-pressure region. Two kinds of cavities (bubbles) exist, namely, stable cavities and transient cavities. Bubbles that implode within a few acoustic cycles are known as transient cavities, whereas those that remain stable over several acoustic cycles are known as stable cavities. Oscillation of stable cavities generates microstreams, which can facilitate the cleaning process. When a bubble collapses, high temperature and pressure conditions can occur inside the bubble, which generates shock waves and microjets. Shock waves and micro-jets are very effective at removing particles, but they also damage the fragile wafer structures. The
higher the acoustic power used, the more the damage that can occur due to increased transient cavitation. This fact has limited the use of megasonic applications in the cleaning of patterned wafers (32). Therefore, it is important to find conditions in which transient cavitation is considerably suppressed and stable cavitation is preserved for damage-free megasonic cleaning.

The role of acoustic streaming and cavitation in the megasonic cleaning process was explored by Gale et al. (33). They claimed that cavity events can help dislodge particles from the substrate surface and that microstreaming transports the dislodged particles away from the surface. Deymier et al. (34) studied the first-order acoustic field and second-order acoustic streaming. The results showed that the removal forces (streaming forces) resulting from the scattering of an acoustic wave by a particle adhered on the substrate surface are too small to remove submicron-sized particles. However, the parallel component of the streaming forces at the solid-fluid interface was large enough to remove particles through rolling and tugging mechanisms.

When particles are detached from a solid substrate, they may either slide, roll, or be lifted away from their initial deposition site during the removal process (31).

- **Sliding detachment**

  In the wet cleaning process, particles will be removed by sliding if
\[ F_r \geq F_a \]  

(13)

where \( F_r \) is the external removal force (i.e., the fluid drag force) acting on particles parallel to the substrate surface and \( F_a \) is the adhesion force between the particles and the solid surface.

- **Lifting detachment**

When external forces (i.e., the fluid lift force and electrostatic double layer repulsion force) overcome the adhesion force, the particles will be lifted up and detached from the substrate. However, in a megasonic field, the lifting force is very small and can be neglected compared with the adhesion force (35).

- **Rolling moment detachment**

The rolling mechanism plays the dominant role among the three detachment mechanisms. Figure 8 shows the geometric features of a deformed spherical particle attached to a plane substrate surface.
Figure 8: Rolling moment detachment

where $F_d$ is the drag force, $F_{el}$ is the electrostatic double layer repulsive force, and $F_a$ is the adhesion force. The removal of particles by rolling occurs when the ratio of the hydrodynamic rolling moment to the adhesion resisting moment, $RM$, is much larger than 1 (36).

$$RM = \frac{\text{Removal moment}}{\text{Adhesion resisting moment}}$$

For a linear shear flow boundary layer, the distribution of the drag force on a particle is shown in Fig. 5. The arm of the drag moment is 1.399R from the plane surface, which can be found by
Thus, \( \frac{\text{Sum of moment}}{\text{Sum of force}} = \frac{\int_0^{2R} F_d(y) dy}{\int_0^{2R} F_d(x) dx} = 1.399R \) \hspace{1cm} (15)

Thus, \( RM = \frac{F_d(1.399R - \delta')}{F_d a} \) \hspace{1cm} (16)

where \( \delta' = R - \sqrt{R^2 - a^2} \) \hspace{1cm} (17)

\( R \) is the radius of the particle and \( a \) is the contact radius. The force required to remove a particle by rolling is less than that required by sliding or lifting.

2.3 Sonoluminescence (SL)

Dissolved gases play an important role in controlling the intensity of transient cavitation in liquids (37, 38). In general, two types of SL occur when liquid is irradiated with sound waves: multi-bubble SL (MBSL) and single-bubble SL (SBSL). The spectrum of MBSL is dominated by atomic and molecular emission peaks (e.g., excited states of OH radicals in water and of diatomic carbon \( C_2 \) (-C=C-) in hydrocarbons), whereas the SBSL spectrum is essentially featureless. Solution parameters such as type of chemical and level of dissolved gases and sound field variables such as megasonic power density and acoustic frequency are known to influence the intensity of the SL signal, which is generally determined as the measured total photons emitted per second in the megasonic
field. In 1976, Young et al. measured the SL signal from water saturated with different gases using a photomultiplier tube (PMT). The sound frequency used in their study was 20 kHz, and the power density was kept constant at 10 W/cm² (39). The SL intensity followed the following order: Ar > Air = O₂ > N₂ > H₂ = CO₂. Table 3 shows the SL data of Young et al.

Table 3: SL signal measured by Young et al. (Ref. 39).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Luminous intensity at photocathode (Young) (Photons x 10⁻¹⁹)</th>
<th>Sonoluminescence (Prudhomme &amp; Guillart) (Relative results)</th>
<th>Total radiation energy (Muller) (Joules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>1.18</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Neon</td>
<td>3.20</td>
<td>18</td>
<td>0.002</td>
</tr>
<tr>
<td>Argon</td>
<td>30</td>
<td>54</td>
<td>0.014</td>
</tr>
<tr>
<td>Krypton</td>
<td>50</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Xenon</td>
<td>125</td>
<td>540</td>
<td>1.3</td>
</tr>
<tr>
<td>Methane</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>2.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>2.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freon (CCl₂F₂)</td>
<td>3.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
With respect to noble gases, the SL signal in Ar- and Xe-saturated water was collected by Didenko et al. at a sound frequency of 24 kHz and 1 MHz as a function of power density (40). They found that at a given power density, the SL signal in Xe-containing water was much higher than that from Ar-containing water. At higher power densities, a higher SL signal was measured from both Ar- and Xe-containing water. The influence of noble gas (Ar and Xe) doping in single bubble SL was investigated by Hiller et al. at a sound frequency of 24 kHz in water. With 1% noble gases mixed in N₂, the highest intensity SL signal was measured (41). Some SL data have been reported in H₂-containing DI water at the acoustic frequency of MHz; the higher the H₂ concentration, the lower the SL signal that was measured (37).

Kumari et al. made SL measurements in DI water saturated with different dissolved gases at the acoustic frequency of 0.93 MHz in the megasonic power density range from 0.1 to 4 W/cm² (42). Ar-saturated DI water showed the highest SL signal compared with N₂- and O₂-saturated DI water. They reported that CO₂-containing DI water showed a very low level of SL. This effect was attributed to the high solubility of CO₂, which resulted in its diffusion into the cavity and cushioning the collapse, thereby reducing the intensity of transient cavitation. Approximately 130 ppm of CO₂ (aq.) was found to be sufficient to suppress SL generation in DI water under all conditions of transducer power density and duty cycle. The SL signal was collected using a Cavitation Threshold (CT) cell.
Cavitation Threshold (CT) Cell is used to measure sonoluminescence signal (total photon counts per sec) as a function of time in a flowing liquid exposed to an acoustic field at ~1 MHz frequency at a fixed or increasing values of power density.

It is a light tight cell with a liquid holding volume of ~ 163 cm$^3$. As shown in Fig. 9, the cell (body made of a polymer such as chlorinated poly vinyl chloride) is cylindrical in shape (with 104 mm in length and internal diameter of 48 mm) with a piezoelectric crystal transducer located on one side. The transducer operates at a frequency of ~ 1 MHz and a power density in the range of 0.1 to 4 W/cm$^2$. The other side of the cell has a conical PTFE (polytetrafluoroethylene) baffle (height 48 mm) which prevents the sound waves from reflection and the interaction of reflected waves, if any, with the incident waves. This allows for a more uniform distribution of the sound field inside the cell.
Figure 9: Internal construction of the CT cell

The cell has inlet and outlet ports for liquid to flow through it. During irradiation of the flowing liquid with the acoustic energy, the light that is emitted is measured using a photo multiplier tube (PMT, SensTech) located in the middle of the cell body. The interface between the PMT and the liquid is a fused silica window that allows the light to enter into the PMT but prevents its direct contact with the liquid. PMT is a plug-and-play photodetector module configured for photon counting. It comprises a selected type 9111B 25 mm diameter end window photomultiplier tube with blue-green sensitive bialkali photocathode and ultra-low dark counts, a positive high voltage power supply, a high speed amplifier-discriminator, a counter, and a micro-controller. All are encapsulated
within a cylindrical mumetal case, providing a high level of immunity from the effects of external magnetic fields.

The CT cell set up (shown in Fig. 10) consist of a pump, water flow meter (rotameter), oxygen sensor, membrane contactor, gas flow meter and vacuum pump. A direct DI water line is connected to the rotameter with a value to control the water flow rate. If a desired chemical system (liquid) is to be flown through the cell, it may be taken in a container and pumped through the cell using the peristaltic pump.

Figure 10: A Schematic of SL signal measurement and spectra acquisition setup
The liquid is first passed through the membrane contactor to dissolve a gas of interest in the liquid. The membrane contactor contains thousands of Celgard® micro porous polypropylene hollow fibers knitted into an array that is wound around a distribution tube (shown in Fig. 11). The hollow fibers are arranged in a uniform open packing, allowing greater flow capacity and utilization of the total membrane surface area. The liquid flows through the shell side and the gas through the lumenside. An oxygen sensor is connected at the outlet (shell side) of the membrane contactor to measure the amount of dissolved oxygen.

Figure 11: Liqui-Cel® membrane contactor
2.4 Correlation between sonoluminescence, extent of feature damage and particle removal efficiency (PRE)

Some correlation between the SL signal and the extent of feature damage has been established. Kumari et al. (43) measured the feature damage and SL signal in CO$_2$-containing DI water. They used structures consisting of thin (35-56 nm wide) polysilicon or high-k/metal gate lines in their study at a megasonic frequency of 0.93 MHz. Their results revealed that with 1035 ppm CO$_2$ (aq.) in DI water, the number of line breakages dropped from several thousand to ~100 per mm$^2$ at power densities up to 3 W/cm$^2$ for an irradiation time of 2 min (Fig. 12). The damage results were correlated with the SL data collected in CO$_2$-containing DI water.

![Figure 12: Dissolved CO$_2$ in water reduced the number of line breakages (Ref. 43)](image-url)
Kang et al. (46) evaluated both the cleaning performance and the pattern damage events on photoresist (PR) line patterns (300 nm width) at a megasonic frequency of 0.83 MHz using DI water gasified by H₂, N₂, O₂, and Ar. The number of damaged sites on the PR patterns is reduced when DI water and Ar-DIW is used for cleaning. Interestingly, the PR pattern had a lot of damage sites when H₂ gas was used. They claimed that H₂ gas would generate a higher degree of transient cavitation than other dissolved gases due to its high diffusivity in water.

Shende et al. did a study on the effect of dissolved gas properties on megasonic cleaning at 2 and 3 MHz (68). The effect of Ar gas was characterized by measuring the acoustic energy and SL. The phenomenon was further verified with pattern damage studies. Features with aspect ratios ranging from 1:1 to 1.8:1 were tested in the study. Interestingly, the SL measurements conducted at 2 MHz showed non-linear trend with increasing dissolved Ar concentration (as shown in Fig. 13).
Pattern damage study showed that the damage level (normalized data) did not increase with dissolved Ar concentration in DI water (as shown in Fig. 14). They claimed that such phenomena were due to excessive insoluble gas bubbles leading to erratic cavitation behavior. However, the pattern damage study with very low Ar concentrations showed linear trend with Ar concentration DI water.
For the application of megasonic cleaning in semiconductor manufacturing, particle removal efficiency is very critical. Based on different levels of SL signal in the megasonic field, dissolved gases in the cleaning solution have been confirmed to play an important role in the level of cavity intensity. Researchers have also correlated the level of dissolved gases with the PRE. Vereecke et al. investigated the role of gas cavitation in the removal of SiO$_2$ particles of different sizes (126, 78, and 34 nm) (44). In degassed solutions, the PRE was extremely low. From this result, they concluded that gas cavitation is the main mechanism of particle removal in a megasonic field. Figure 8 shows the PRE data collected in this work (as shown in Fig. 15).
In DI water containing CO₂, Ar, O₂, and N₂, Brems et al. (45) conducted particle removal studies on Si wafers at very low megasonic power densities (0.167 to 0.336 W/cm²). They found that it was impossible to remove any particles in DI water saturated with CO₂, even at an applied electric power of 2.5 W/cm². They attributed this to reduced cavitation in CO₂-containing DI water (42).

Kumari et al. measured the efficiency of removal of SiO₂ particles with ~ 185 nm diameter from blanket SiO₂ wafers carbonated ammonium formulation (69). Particle densities were measured counted using SP1. In her study, high particle removal was achieved using a NH₄OH/NH₄HCO₃ formulation at pH 8.2 under ~ 1 MHz acoustic
irradiation for 2 min. However, only two power densities (0.7 W/cm$^2$ and 1.5 W/cm$^2$) and one megasonic exposure time were explored; no feature damage data were reported.
2.5 Sonoluminescence spectrum

Even though many attempts have been made to determine the level of SL signal and correlate it to feature damage and PRE, only limited attempts have been made to characterize the SL spectrum. In general, the SL spectrum covering the wavelengths from 200 nm to 600 nm show reproducible peaks at 310 and 340 nm; these peaks are thought to be due to the emission from the electronically excited hydroxyl radicals (16-17). Numerous investigations of aqueous SL provide evidence of collisions between gas-phase molecules that, during bubble collapse, create high-energy species capable of light emission (47-48). The hydroxyl radicals are formed from the chemical reactions during acoustic cavitation (49). Figure 16 shows different chemical reactions that can occur in the presence of oxygen, ozone, or an inert gas (M) (34).

![Chemical reactions during acoustic cavitation](Ref. 34)

Figure 16: Chemical reactions during acoustic cavitation (Ref. 34)
Among all of the reactions, the hydroxyl radical appears to play the most significant role in emitting photons. In 1979, Sehgal et al. observed SL signals from water saturated with He, Ne, Ar, Kr, O₂, N₂, and air at acoustic frequencies of 333 and 459 kHz (16). In their study, the emission extending from 240 nm to the near-infrared region was measured by using single-photon counting techniques. The results were used to identify hydroxyl radicals and explain the effect of dissolved gases. The sonoluminescence spectra of argon-saturated water were captured by Didenko et al. at sound frequencies of 337 kHz and 1.1 MHz (47). The peaks at 270, 280, 310, and 340 nm and a continuum were clearly seen in the spectra. The effect of the bulk solution temperature on the spectra was also studied (Figs. 17 and 18). The results also showed the effect of temperature in the intensity of SL signal; the lower the solution temperature, the higher the SL signal can be observed.

Figure 17: SL spectra of Ar-saturated water at 337 kHz and various bulk solution temperatures (°C): (A) -13, (B) -22, (C) -30, and (D) -40 (Ref. 47)
Figure 18: SL spectra of Ar-saturated water at 1.1 MHz and various bulk solution temperatures (°C): (A) -11, (B) -30, (C) -39, and (D) -50 (Ref. 47)

At 1.1 MHz, the spectra showed clearer peaks at ~ 270 nm compared with those at 337 kHz. The optical set-up used in this study to capture the SL spectra was a grated monochromator MDR-23 (Russia, LOMO) with a 0.22 cm slit through which the emitted light passed first and an FEU-100 photomultiplier tube (Russia, sensitive in the 200-800 nm range) to detect all the photons.

More and more advanced optical techniques and equipment have been used to capture and study SL spectra in liquid exposed to sound field in the MHz frequency range. In the study of line emissions of sodium and hydroxyl radicals in single-bubble SL conducted by Schneider et al., the spectroscopic measurements were performed in the range of 200-700 nm with an Acton Research SP-300i imaging spectrometer coupled to a charge-
coupled-device detector (PIXIS 100B, Princeton Instrument). They also detected the acoustic pressure using a needle hydrophone (Dapco Industries, model NP-10-1) coupled to an oscilloscope (HAMEG, HM407, SP107) in water and 0.5 M NaCl with 70 mbar of Ar (50). Figure 19 shows the spectra captured in their study at a sound frequency of 27 kHz. With a higher level of Ar maintained in water, the SL spectra showed a more distinct peak at 310 nm.

Figure 19: Single-bubble SL spectra in water with ~ 1 mbar Ar (blue, light blue) and 70 mbar Ar (gray, black) at various acoustic pressures (Pac); (Inset) Enlarged hydroxyl radical peak in water (black) and in 0.5 M NaCl (red) with 70 mbar of Ar (Ref. 50)
Multi-bubble sonoluminescence spectra were measured by Hayashi et al. to study the effect of alcohols in water at the frequencies of 116 kHz and 1.0 MHz (48). The emitted light was detected by a photomultiplier tube (Hamamatsu, R1477-06) through a monochromator (Nikon, P250) with a resolution of 4.5 nm and was photon-counted with a photon counting unit (Hamamatsu, C3866). The spectra were collected at different sonic powers. The OH-radical emission peaks at 310 nm were detected at both frequencies in Ar-saturated water (Fig. 20). At 1.0 MHz, the peaks were not as obvious as those at 116 kHz. This is due to the lack of cavity events at higher frequencies, causing weaker light emission. The spectra intensity did not show a linear relationship with the sonic powers. The highest spectral intensities were observed with the sonic power of 7.3 and 7.4 W at both frequencies. Interestingly, at 1.0 MHz, the peak at 310 nm disappeared from the spectra at 16.1 W (highest power applied in their study).
Figure 20: Multi-bubble SL spectra from Ar-saturated water irradiated at 116 kHz (a), and 1.0 MHz (b) for sonic powers of 1.8 W, 7.3 W, and 15.5 W for 116 kHz and 2.0 W, 7.4 W, and 16.1 W for 1.0 MHz. The insets illustrate typical multi-bubble spectra on a linear scale, demonstrating OH-radical emission (Ref. 48).

Xu et al. characterized the molecular emission due to single-bubble sonoluminescence from a 65% H$_3$PO$_4$ solution re-gassed with 50 torr Ar at different acoustic pressures (51). The strong molecular emission from excited OH radicals at 310 nm was again observed (Fig. 21). The spectral intensity increased with acoustic pressure.
In the study of the effect of the rare gases on SL spectra performed by Pflieger et al., SL spectra generated in a 607 kHz sound field were captured in the range of 200 to 450 nm (52). Figure 22 shows the spectra in water with different rare gases.

In addition to the peak at 310 nm, which has been captured by other researchers, another very strong emission at ~240 nm was observed (as shown in Fig. 22). This peak was hypothesized as the OH-radical emission through water vapor and in water radiolysis. Such an emission was also treated as clear evidence for plasma formation during multi-bubble cavitation in water. The optical set-up for capturing SL spectra consisted of a spectrometer (SP 2356i; Roper Scientific) coupled to a liquid-nitrogen–cooled CCD camera (SPEC10-100BR with a UV coating; Roper Scientific).
Figure 22: Effect of rare gases on SL spectra in water (11 °C, 0.17 W/ml) at 607 kHz.

Insert: zoomed to approximately 310 nm (Ref. 52)

Table 4 summarized the methodology and results of some key investigations on SL spectra.
Table 4: Summary of key investigations on the collection and resolution of SL spectra

<table>
<thead>
<tr>
<th>Authors</th>
<th>Acoustic Frequency</th>
<th>Acoustic Power</th>
<th>Liquid medium</th>
<th>Equipment Used</th>
<th>Peaks (nm) in the emission spectra</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Didenko et al.</td>
<td>22 kHz, 337 kHz,</td>
<td>10, 4, and 22</td>
<td>Deionized water (Ar saturated)</td>
<td>MDR-23 monochromator (Russia, LOMO) and FEU-100 PMT</td>
<td>270, 280, 310, and 340</td>
<td>Peaks due to OH radicals</td>
</tr>
<tr>
<td></td>
<td>and 1.1 MHz</td>
<td>W/cm²</td>
<td></td>
<td>Cornerstone 130 monochromator and PMT (Oriel Instruments)</td>
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<td></td>
<td></td>
<td>SP 2356i spectrometer and SPEC10-100BR liquid-nitrogen–cooled CCD camera (Roper Scientific)</td>
<td></td>
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<tr>
<td>Pflieger et al.</td>
<td>205, 358, 618, and</td>
<td>5.1 W/cm²</td>
<td>Ultra-pure water (Ar saturated)</td>
<td>Ar-, Kr-, or Xe-containing DI water</td>
<td>310</td>
<td>Maximum intensity at 358 kHz</td>
</tr>
<tr>
<td></td>
<td>1071 kHz</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Hayashi et al.</td>
<td>20, 200, and 607</td>
<td>0.17 W/ml</td>
<td>Very weak emission at 1.0 MHz</td>
<td>Monochromator (Nikon, P250) and PMT (Hamamatsu, C3866)</td>
<td>290, 310, and 340 nm</td>
<td>Very weak emission at 1.0 MHz</td>
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<td>kHz</td>
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<td></td>
<td>116 kHz and 1.0</td>
<td>1.8, 7.3, and</td>
<td>Ar-saturated DI water</td>
<td></td>
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<tr>
<td></td>
<td>MHz</td>
<td>15.5 W for 116 kHz; 2.0, 7.4, and 16.1 W for 1 MHz</td>
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2.6 Radicals formation in aqueous solutions under megasonic irradiation

In aqueous solutions, acoustic cavitation is generated by the growth of preexisting nuclei during the alternating expansion and compression cycles of sound waves. In the process of transient cavitation (bubble collapse), temperatures higher than 4000 K and pressures over 1000 atm can exist within gas- and vapor-filled microbubble following an adiabatic collapse (53, 54). Under such conditions, the excitation of water molecules can be promoted, and free radicals will be formed. These high-energy species release photons when they fall back to their ground states.

Many investigations have been conducted to study the role of different species in light emission. In terms of water molecules within bubbles during a collapse, the kinetic energy of water molecules can be converted into internal energy via inelastic collisions with gas-phase molecules. For example, with an inert third molecule (M, such as argon), water molecules will be excited into various rotational, vibrational, or electronic states (55):

\[ H_2O + M \rightarrow H_2O^* + M \] (18)
The excited water molecules will relax and fall back to their ground states via reaction 19, producing a luminescence continuum in the wavelength range of 380 – 600 nm ($\lambda_{\text{max}} \sim 425$ nm) (56).

$$H_2O^* \rightarrow H_2O + h\theta_1$$

(19)

With sufficient energy, excited water molecules may dissociate into hydrogen atoms and hydroxyl radicals. Hydroxyls radicals may stay either in their ground state (reaction 20) or excited state (reaction 21) and will emit light at the wavelength of 280, 310, or 340 nm (53).

$$H_2O \rightarrow H + \cdot OH$$

(20)

$$H_2O \rightarrow H + \cdot HO^* \rightarrow H + \cdot OH + h\theta_2$$

(21)

The study of such emission spectra from hydroxyl radicals has shown a continuum in the wavelength region of 200 – 400 nm (56).

When hydroxyl radicals are formed in the gas phase in the presence of other species, such as inert gases, the radicals may react and recombine to form hydrogen peroxide. Excited species with an emission maximum at 310 nm (18) (56) may be produced when inelastic collisions occur between hydroxyl radicals and inert gases.
Reactions 21 and 22 are considered predominant during acoustic cavitation, and the SL spectra introduced in the SL spectra section showed consistent results, with the maximum emission at ~ 310 and 340 nm from DI water saturated with inert gases.

\[
\cdot OH + M \rightarrow \cdot OH^* + M \rightarrow \cdot OH + M + h\theta_3
\]  

(22)

\[
H \cdot + \cdot OH + M \rightarrow [H \cdots OH \cdots M]^\# \rightarrow H_2O + M + h\theta_4
\]  

(23)

However, because of the broad continuum, it is difficult to differentiate the peaks solely due to excited hydroxyl radicals from the peaks from other species (reaction 23). The \# symbol in reaction 6 denotes an excited quasi-molecule at its vibration state, which can emit at a wavelength of ~ 400 nm (56-58).

Some other excited species, such as (M\cdotOH)^*, M_2^*, or (M\cdotH_2O)^*, can also be formed, possibly because of the immense transient pressures and densities created upon bubble implosion. These species are usually formed by three-body collisions and contribute to the broad continuum in the lower wavelength range (< 300 nm) (59).

\[
H_2O^* + 2M \rightarrow H_2O^* \cdot M + M \rightarrow H_2O \cdot M + M + h\theta_5
\]  

(24)
Such a process has to occur at a short distance between $\text{H}_2\text{O}^*$ and M. The collision potential has to be equal to or greater than the thermal energy of $\text{H}_2\text{O}$ and M. For example, when argon is present in DI water, $\text{Ar}\cdot\text{OH}^*$ (with $\lambda \sim 310, 316,$ and $318$ nm) and $\text{Ar}\cdot\text{HO}^*$ (with $\lambda \sim 340$ nm) can exist (reaction 25) at the same time (60):

$$\text{Ar} + \text{OH}^* \rightarrow \text{Ar} \cdot \text{OH}^* (\text{Ar} \cdot \text{HO}^*) \rightarrow \text{Ar} + \text{OH} + h\nu$$  \hspace{1cm} (25)

Under sonic irradiation, liquids containing oxygen will undergo additional reactions that produce other free radicals within the gaseous bubble phase (61–63). Sonolytic reactions of $\text{O}_2$ generate $\cdot\text{OH}, \cdot\text{OOH},$ and $\cdot\text{O}$ radicals. Because of their highly reactive nature in the gaseous phase (61), the $\cdot\text{O}$ atoms are more likely to play an indirect role by providing radical species (through reactions with oxygen and water vapor) with longer lifetimes that can subsequently move to the interfacial region and react with a target compound (64, 65). All free radicals may react with other molecules encountered within and around the cavitation bubbles.

Dissolved gases play an important role in SL generation. The temperature in the center of a collapsed cavitation bubble can be estimated with the following equation:

$$T_{\text{max}} = T_0 \left( \frac{P_0 (y-1)}{P} \right) = T_0 \left( \frac{R_0}{R_{\text{min}}} \right)^3 (y-1)$$  \hspace{1cm} (26)
where $T_0$ is the temperature of the bulk solution, $\gamma$ is the polytropic index of the saturation gas ($= C_p/C_v$), $P$ is the pressure in the bubble at its maximum size, $P_m$ is the pressure in the bubble upon collapse, $R_0$ is the resonance bubble radius, and $R_{\text{min}}$ is the bubble radius upon collapse (66, 67). During acoustic cavitation, the presence of gases with high polytropic indexes and low thermal conductivities will lead to more intense conditions within a collapsing bubble because less heat is dissipated to the surrounding aqueous environment during the rapid implosion. The polytropic index of Ar is 1.66 and of air is 1.41. In the case of CO$_2$, the polytropic index is 1.31.
3. Explanation of the Dissertation Format

This dissertation has been prepared in accordance with the format prescribed by the University of Arizona Graduate College *Manual for Electronic Theses and Dissertations* and is consistent with the formatting requirements of the Department of Chemical and Environmental Engineering. My work has been presented in three chapters and five appendices. The central problem addressed in this research and its context is introduced in Chapter 1. Chapter 2 summarizes the most important findings of research described in each of the first two appendices and the details of operation procedures of MegPie, MegTank and CT cell. The conclusion and future directions of this study are presented in Chapter 3. My contributions to each manuscript and the operation manuals are summarized here.

**Appendix A. Megasonic Cleaning of Blanket and Patterned Samples in Carbonated Ammonia Solutions for Enhanced Particle Removal and Reduced Feature Damage.**

All the particle removal and feature damage experiments on blanket and patterned samples, including particle characterization, particle dispersion preparation for deposition, particle density counting, blanket and patterned samples preparation, sample surface analysis before and after cleaning and cleaning solution preparation were done by me. Dr. Sangita Kumari and Dr. Manish Keswani trained me on the operation of MegPie and CT cell. I developed the methodology using ImageJ software to simultaneously analyze
particle density and feature damage on the optical images of patterned samples. The results from ImageJ analysis is consistent with that from SEM images taken by me. I wrote the manuscript. Dr. Manish Keswani and Dr. Srini Raghavan edited the manuscript and provided enough guidance in the project. ProSys, Inc. (Campbell, CA) constructed the single wafer megasonic cleaning tool (MegPie) for the cleaning performance study and cavitation threshold (CT) cell for SL measurements.

Appendix B. Use of a Simple Cavitation Cell Set-up with Replaceable Single Band Filters for Analysis of Sonoluminescence Signal from Megasonic Irradiated Gasified Aqueous Solutions. All the SL data were collected by me. The series of filters which were used to locate hydroxyl radicals emission were selected and found by me. I wrote the manuscript. Dr. Manish Keswani and Dr. Srini Raghavan edited the manuscript and provided enough guidance in the process of the methodology development. ProSys, Inc. (Campbell, CA) constructed the CT cell and the assembly part on the cell body for sandwiching the filters between the fused silica window and the PMT.

Appendix C–E. Operation Manuals of MegPie®, MegTank® and CT cell. The three operation manuals were written by me. Dr. Keswani and Dr. Raghavan edited the manuals and provided enough guidance. ProSys, Inc. provided all the technical information of each component of the equipments.
CHAPTER 2. PRESENT STUDY

The experimental methods, results and conclusions of my study are presented in the appendices. The following is a summary of the most significant findings in each of the studies reported in the first two appendices.

1. Appendix A. Megasonic Cleaning of Blanket and Patterned Samples in Carbonated Ammonia Solutions for Enhanced Particle Removal and Reduced Feature Damage. The challenge of megasonic cleaning process is to achieve high particle removal while minimizing feature damage. Aqueous CO\(_2\) has been well known to suppress SL signal in liquid when it is under megasonic irradiation. The intensity of SL signal is believed to be a sensitive indicator of transient cavitation, which has been claimed to cause feature damage. The objective of this study is to take advantage of the beneficial effect of CO\(_2\) (aq.) in reducing feature damage in developing alkaline formulation needed for removing particulate contamination.

Ammonium bicarbonate was used to maintain a specific amount of CO\(_2\) (aq.) in the formulations. By varying the amount of added NH\(_4\)OH, the amount of CO\(_2\) (aq.) was adjusted. The PRE and feature damage experiments were performed using a single wafer megasonic cleaning tool (MegPie) for on blanket SiO\(_2\) and patterned samples. The patterned samples (1 cm × 2 cm) were diced from a 300 mm wafer (provided by IMEC) consisting of long (2 mm) lines of 40 nm in width separated by 500 nm. The lines were
gate stacks consisting of HfO$_2$/AlO (10 nm)/TiN (5 nm)/Si (5 nm)/a-Si (100 nm). Figure 23 shows an SEM image of the structure and its schematic. Silica particles with ~200 nm diameter were used for contamination. The density of deposited particles was ~3500/mm$^2$. The target CO$_2$ (aq.) level was >150 ppm based on the fact that the SL signal was completely suppressed with 150 ppm CO$_2$ (aq.) maintained in DI water. A system containing different levels of CO$_2$ (aq.) generated by adjusting the pH of NH$_4$HCO$_3$ solution by NH$_4$OH was developed and tested. The effect of pH in the range of 7.8 to 8.5 was first tested at megasonic power density of 1 W/cm$^2$ for 1 min. The results revealed that when pH was higher than 8.2 with ~320 ppm CO$_2$ (aq.) maintained in the cleaning solution, high particle removal (>90%) could be achieved. The effect of megasonic exposure time was then studied using the same formulation at pH 8.2. Exposure time from 0 to 120 sec was studied. The results revealed that when the exposure time was more than 60 sec, high PRE can be achieved.

Figure 23: The patterned structure (a) under SEM and (b) its schematic
Based on the particle removal results on blanket silica samples, PRE and feature damage was investigated simultaneously on patterned samples using \( \text{NH}_4\text{OH}/\text{NH}_4\text{HCO}_3 \) cleaning system at pH 8.2 and 8.5 under an acoustic power density of 1 W/cm\(^2\). High PRE was achieved at both pH values for megasonic exposure time of 1 min. However, the feature damage was much higher (double amount of line breakages) at pH 8.5 (with \(~150\) ppm \( \text{CO}_2 \text{(aq.)} \)) than that at pH 8.2. Compared to the feature damage data using \( \text{NH}_4\text{OH} \) alone at the same pH 8.2, using \( \text{NH}_4\text{OH}/\text{NH}_4\text{HCO}_3 \) solution reduced more than 50% of the number of line breakages. Feature damage data on non-contaminated patterned samples using the carbonated ammonium solution at pH 8.2 showed that there is no effect on the number of line breakages from particle deposition.

The beneficial effect of \( \text{CO}_2 \text{(aq.)} \) is most likely due to suppression of transient cavitation. To test this hypothesis, SL measurements were done in both solutions (\( \text{NH}_4\text{OH} \) alone and \( \text{NH}_4\text{OH}/\text{NH}_4\text{HCO}_3 \)) at pH 8.2 as a function of power density in the range of 0.1 to 4.0 W/cm\(^2\). In \( \text{NH}_4\text{OH} \) solution, SL signal was very weak until a power density of 0.6 W/cm\(^2\) was reached. Above this power density, the SL signal was found to increase continuously. In the case of \( \text{NH}_4\text{OH}/\text{NH}_4\text{HCO}_3 \) solution, SL signal was weak in the entire power density range of 0.1 to 4.0 W/cm\(^2\). These results indeed suggest that transient cavitation is significantly suppressed in \( \text{NH}_4\text{OH}/\text{NH}_4\text{HCO}_3 \) solutions of pH 8.2.

This study has shown that addition of ammonium bicarbonate to ammonium hydroxide solutions allows significant reduction of feature damage while providing high particle
removal efficiency during megasonic cleaning of patterned wafers. Sonoluminescence studies indicate that transient cavitation is suppressed in carbonated ammonium hydroxide solutions. Based on these results, ammonium bicarbonate/ammonium hydroxide solutions have the potential to serve as effective megasonic cleaning formulations.

2. Appendix B. Use of a Simple Cavitation Cell Set-up with Replaceable Single Band Filters for Analysis of Sonoluminescence Signal from Megasonic Irradiated Gasified Aqueous Solutions. The measurement of SL in liquid under megasonic irradiation has been reported by many researchers. However, at MHz frequencies, the SL signal is typically very weak (with pico level watts of incident light power) and requires very sensitive spectrometers to resolve the SL spectra. Additionally, in most of the published work, SL spectral features were reported in relative intensity of values making it difficult to determine if the peaks are real. This manuscript describes a simple methodology to study the characterization of SL spectra.

The SL signal generated in aqueous solutions containing dissolved gases was collected using a modified version of cavitation threshold (CT) cell. Specifically, a single band filter was sandwiched between the UV grade fused silica window in the cell and the photomultiplier tube (PMT) to characterize photon emission in a very narrow range of wavelengths. Four different single band filters were used; these are 280 – 305.5 nm, 300 – 340 nm, 335 – 375 nm and 374.5 – 397.5 nm. These filters were chosen based on the
fact that excited hydroxyl radicals predominantly emit light in these specific wavelength ranges. Air, Ar or ammonium hydroxide containing DI water was pumped through the cell at 130 ml/min and irradiated with a ~ 0.935 MHz transducer. The power density was ramped from 0.1 to 4.0 W/cm$^2$ in 90 sec at 100% and 10% duty cycles. In some experiments, no filters were used and the spectral signal in the range of 280 – 630 nm was recorded using the PMT.

The results of measurements made using band-pass filters indicate that the SL signal is higher in the absence of filters at all power densities for both air and Ar saturated DI water. In air saturated water, at power densities greater than 1 W/cm$^2$ in the continuous mode (100% duty cycle), the SL signal is reduced by 90% when any of the filters is used. In the case of Ar saturated solutions, a roughly similar trend is seen. Further, there appears to be a threshold in power density below which the SL signal remains at the background level. This threshold power density was measured to be about 0.9 W/cm$^2$ for both air and argon saturated DI water. In Ar saturated water, the measured PMT output with 300-340 nm and 335-370 nm filters is slightly higher than that measured with the other two filters. In the case of air saturated water, the SL signal intensity is roughly the same with any of the four filters in place. In the wavelength range of 280 to 400 nm, the total SL intensity is ~ 930,000 counts/sec in air saturated DI water at 4 W/cm$^2$, which is ~ 43% of the intensity in the entire wavelength range of 280 to 630 nm covered by PMT. In Ar saturated DI water, this value is ~ 63%.
In the case of the SL measurement at 10% duty cycle, the trends in SL signal are somewhat similar to those observed under 100% duty cycle. The signal was highest without any filter; when different filters were used, the SL signal was highest in the wavelength range of 335-375 nm for air saturated water (at power densities higher than ~0.5 W/cm\(^2\)) and in the 300-375 nm range for Ar saturated DI water (entire power density range). Compared to 100% duty cycle, the SL signal intensity in each wavelength range is lower at 4 W/cm\(^2\), but a similar trend is seen.

Keswani et al. reported the generation rate of hydroxyl radicals (~0 to 0.2 µM/min) in ammonium hydroxide solutions irradiated with megasonic waves using a fluorescence technique that works on the capture of hydroxyl radicals (OH\(^{•}\)) by terephthalic acid. The generation rate of OH\(^{•}\) decreased from ~0.16 µM/min to ~0.005 µM/min as ammonia concentration increased from 0.001% to 1% (in volume). They attributed this to scavenging of OH\(^{•}\) by ammonia. To check if these results bear any relationship to SL signals, dilute ammonia solutions of different concentrations were pumped through the CT cell and data were collected in the absence of different filters. However, the intensity of SL signal from ammonium hydroxide solutions at different concentrations did not show any difference from each other.

The results for air and Ar saturated DI water are consistent with those reported in the literature and obtained using expensive spectrometers. The SL signal collected in ammonium hydroxide solutions indicated that at higher power densities the signal
intensity may not be relatable to the generation rate of hydroxyl radicals in their ground state.
3. Conclusions and Future Directions

This thesis presents a systematic study aimed at the development of carbonated ammonium solutions for particle removal and feature damage reduction in megasonic cleaning process. By adding NH₄OH to NH₄HCO₃ solution, specific amount of CO₂ (aq.) can be generated at slightly alkaline pH. The results have shown that using the carbonated ammonium solution at pH 8.2 (with ~ 320 ppm CO₂ (aq.)), high particle removal efficiency (> 90%) can be achieved on both blanket and patterned samples under acoustic irradiation of ~ 1 MHz using power density of 1 W/cm² for an exposure time of 60 sec. Feature damage study has shown that the number of line breakages can be reduced by ~ 50% using the carbonated ammonium solution compared to that using plain NH₄OH solution at the same pH. Sonoluminescence studies indicate that transient cavitation is suppressed in carbonated ammonium hydroxide solutions. Based on these results, ammonium bicarbonate/ammonium hydroxide solutions have the potential to serve as effective megasonic cleaning formulations.

A simple and inexpensive method for capturing the features of sonoluminescence spectrum from aqueous solutions due to hydroxyl radicals has been developed. The method consists of using single band filters in the wavelength range 280-400 nm to filter the SL signal prior to its capture by a photomultiplier tube in air saturated DI water. At power densities in the range of 1 to 4 W/cm², the intensity of the signal in the 280-400 nm range is roughly 40% of the intensity in the detection wavelength range of PMT,
which is 280-630 nm. In Ar saturated DI water, this value is roughly 60%. Work with ammonium hydroxide solutions has shown that the intensity of signal may not be directly related to concentration of hydroxyl radicals in their ground state.

Use of sound field with frequencies much higher than 1 MHz would increase the cavitation threshold values. Hence a study on the developed carbonated ammonia formulations under higher frequency sound fields for the purpose of damage reduction is worth exploring. The particles used as contamination source in the present study were silica particles with ~ 200 nm diameter. However, the ITRS has shown that larger than 20 nm diameter contaminations are able to kill the circuits in the state-of-art manufacturing process. Removal of particles with sub-50 nm diameter using megasonic will be a valuable extension of the current study.

With the methodology developed in the present study using single-band filters in the CT cell, it is possible to identify radicals other than hydroxyl radicals such as hydroperoxyl radicals. This would be a very fruitful area of research.
4. Reference


APPENDIX A

MEGASONIC CLEANING OF BLANKET AND PATTERNED SAMPLES IN CARBONATED AMMONIA SOLUTIONS FOR ENHANCED PARTICLE REMOVAL AND REDUCED FEATURE DAMAGE

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Megasonic Cleaning of Blanket and Patterned Samples in Carbonated Ammonia Solutions for Enhanced Particle Removal and Reduced Feature Damage

Zhenxing Han, Manish Keswani, and Srinivasa Raghavan

Abstract—An investigation of particle removal efficiency and feature damage has been conducted in NH$_3$/NH$_4$/HCO$_3$ cleaning solutions irradiated with megasonic energy. By adjusting the pH of the solution in the range of 8.2 - 8.5, high particle removal efficiency (PRE) was achieved while feature damage was reduced significantly. The solubility data collected from NH$_3$/NH$_4$/HCO$_3$ solutions indicate significant suppression of transient cavitation in alkaline solutions containing aqueous CO$_2$.

Index Terms—Megasonic cleaning, particle removal efficiency (PRE), feature damage, CO$_2$ (aq), solubilization (SL)

I. INTRODUCTION

Printable contamination is a major cause of yield loss in integrated circuit (IC) manufacturing [1]. Removal of particles is typically achieved through liquid chemical formulations aided by sound fields in the MHz frequency range [2], [3]. In the fabrication of the state-of-the-art sub-45 nm devices, the challenge of megasonic cleaning process at both front-end-of-line (FEOL) and back-end-of-line (BEOL) is to provide high particle removal efficiency (PRE) without inducing damage to small features [4]-[7].

During acoustic irradiation of liquids, two types of phenomena are known to occur, namely acoustic streaming and cavitation. Acoustic streaming refers to time independent motion of liquid due to viscous attenuation. Three types of streaming phenomena are known to exist in solutions subjected to sound field, namely Eckart streaming, Raleigh streaming, and Schlichting streaming. Eckart streaming, which is mainly bulk flow, is characterized by vortices much larger than the wavelength of sound whereas Schlichting and Raleigh streaming result in liquid flow close to a solid boundary with length scales much smaller and on the order of sound wavelength, respectively. In the case of acoustic cavitation, bubbles formed during low pressure cycle of the sound wave either continuously oscillate over many cycles (stable bubbles) or grow in size and eventually collapse in less than a few cycles (transient bubbles). The flow generated from oscillating bubbles, known as microstreaming, is considered to be instrumental in particle removal whereas shock waves and micro jets generated from transient bubbles are believed to be responsible for damage [8]-[10].

Acoustic cavitation is accompanied by a number of physical and chemical effects. It is known that due to high temperature (>4000°C) conditions reached inside the bubble during its collapse, excitation of various species as well as formation of radicals occurs [11]-[13]. When the excited species go back to the ground state, light is emitted, and this phenomenon is known as solubilization (SL). The intensity of solubilization is considered to be a sensitive indicator of cavitation events [14], [15] and therefore can be a good predictor of the extent of feature damage on patterned wafers. The intensity of SL depends on solution parameters such as cleaning chemistry and level of dissolved gases as well as on sound field variables such as transducer power density and acoustic frequency.

It has been reported in literature that dissolved gases play an important role in controlling the intensity of transient cavitation in liquids [16], [17]. Young et al. measured the SL signal from water saturated with different gases in a 20 kHz sound field at a power density of 10 W/cm$^2$ [18]. The SL intensity followed the order of Ar > Air > O$_2$ > N$_2$ > H$_2$ > CO$_2$. With respect to noble gases, the SL signal in Ar and Xe saturated water was studied by Didenko et al. at a sound frequency of 24 kHz and 1 MHz as a function of power density [19]. They found that at a given power density, SL signal in Xe containing water was much higher than that from Ar containing water. At higher power densities, higher SL signal was measured from both Ar and Xe containing water. The influence of noble gas (Ar and Xe) doping in single bubble SL was investigated by Hiller et al. at a sound frequency of 24 kHz in water. With 1% of noble gases mixed in N$_2$, highest intensity of SL signal was measured [20]. Some SL data have been reported in H$_2$ containing deionized water (DIW) subjected to MHz acoustic frequency, higher the H$_2$ concentration, the lower was the SL signal [16].
Kumari et al. made SL measurements in DI water saturated with different dissolved gases at an acoustic frequency of 0.93 MHz in the megasonic power density range of 0.1 to 4 W/cm² at 10 and 100% duty cycles [21]. Air saturated DI water showed the highest SL signal compared to N₂ and O₂ saturated DI water. They reported that CO₂ containing DI water exhibited a much lower level of SL signal. This effect was attributed to the high solubility of CO₂ in water resulting in its diffusion into the cavity and cushioning the collapse, thereby reducing the intensity of transient cavitation. About 130 ppm of CO₂ (aq) was found to be sufficient to suppress SL generation in DI water under all conditions of transducer power density and duty cycles.

Some correlation between SL signal and the extent of feature damage has been established. Kumari et al. [22] measured the feature damage as well as SL signal in CO₂ containing DI water. They used structures consisting of thin (35-56 nm wide) polysilicon or high-k/metal gate stack lines (67 and 114nm) in their study at a megasonic frequency of 0.93 MHz. Their results revealed that with 10ppm of CO₂ (aq) in DI water, the number of line breaks dropped from several thousands to ~100 per mm² at power density up to 2.94 W/cm² for an irradiation time of 2 min. The damage results were correlated to the SL data collected in CO₂ containing DI water.

The role of gas cavitation in the removal of Si₃N₄ particles of different sizes (126, 75 and 34 nm) from SiN₄ substrate was investigated by Veronee et al. [23]. In deoxygenated solutions, the particle removal efficiency (PRE) was extremely low. From this result, they concluded that gas cavitation is the main mechanism of particle removal in megasonic field. In DIW containing CO₂, Ar, O₂, and N₂, Beemts et al. [24] conducted particle removal studies on Si wafer at very low megasonic power densities (0.167 to 0.336 W/cm²). They found that it was nearly impossible to remove any particles in DIW saturated with CO₂ even at an applied power density of 2.5 W/cm². This was attributed to reduced cavitation in CO₂ containing DIW as well as acidic pH of the solution [21]. There is only one study that reports using carbonated ammonia solutions for particle removal [25]. However, this study was conducted at only one pH value and high power density. Cleaning performance and pattern damage events on photoresist (PR) line patterns (300 nm width) were investigated by Kang et al. [26] in DI water gassed by H₂, N₂, O₂ and Ar. H₂O containing DI water yielded the highest particle removal efficiency but also generated most damage sites.

The objective of the current study is to take advantage of the beneficial effect of CO₂ (aq) in reducing feature damage in developing alkaline formulation needed for removing particulate contamination. A system containing different levels of CO₂ (aq) generated by adjusting the pH of NH₄HCO₃ solution by NH₄OH was developed and tested. Additionally, sonoluminescence data have been collected in these solutions and correlated to the cleaning performance and feature damage.

II. MATERIALS AND METHODS

The experiments reported in this work were divided in two parts: (1) PRE study on blanket SiO₂ samples and (2) PRE and defects study on patterned samples.

The blanket samples (2 cm x 2 cm) used in the experiments were diced from 8” oxide wafers (thermally grown 5000 Å SiO₂ film on boron doped Si). The patterned samples (1 cm x 2 cm) were diced from a 300 mm wafer (provided by IMEC) consisting of long (2 mm) lines of 40 nm in width separated by 500 nm. The lines were gate stacks consisting of HfO₂/Al₂O₃ (10 nm)/TiN (5 nm)/Si (5 nm)/a-Si (100 nm). Commercially available SiO₂ slurry with 200 ± 15 nm particles was used to prepare 0.001% (by weight) dispersion to contaminate the samples. The pH of the dispersion during contamination was 5.8.

All the experiments were conducted in a Class 100 MicroNano fabrication center at The University of Arizona. The blanket and patterned samples were subjected to megasonic irradiation in a single wafer spin cleaning tool, MegPix® (picture and schematic sketch shown in Fig. 1) manufactured by ProSys (Campbell, CA). It consists of a radial transducer (area 32.3 cm²) [1 (a)] to apply uniform acoustic energy to a rotating substrate (0.6-0.9 mm) at a frequency of 0.925 MHz [22]. Acoustic power density can be varied in the range of 0.15-2.94 W/cm².

Blanket SiO₂ samples were first pre-cleaned using dilute HF (1:100) for 1 min followed by DI water rinsing for 5 min. Patterned samples were cleaned by APM (1:1:50 NH₄OH: H₂O: H₂O₂) for 1 min followed by 5 min DI water rinsing and then dried by IPA. The samples were quickly examined under an optical microscope (Leica DM4000B) at 20X magnification to make sure the samples were clean and damage-free before contamination. Then the samples, one at a time, were placed on the chuck of a spin cleaner and 1 ml of the 0.001% dispersion was dispensed onto the samples at a rotation rate of 500 rpm for 1 min. After contamination, the samples were aged for 24 hr in a polystyrene wafer holder. The particle density after contamination was approximately 3500/mm².

The contaminated samples were attached to a blanket SiO₂ wafer at a radial distance of 5 cm from the center and placed in the MegPix unit. Freshly prepared solution containing either NH₄OH or NH₄HCO₃, and NH₄OH was dispensed on the surface of the substrate at a rate of 300 ml/min while the substrate was rotated at 30 rpm. The transducer was then switched on to generate acoustic energy for different times (0 – 120 s) at the power density of 1 W/cm². The samples
were then rinsed by DI water for 1 min and dried by IPA. On each blanket and patterned sample that was cleaned, 10 regions (each of 0.3 mm × 0.4 mm area) were imaged at a magnification of 200X using a Leica DM400M microscope. The images were processed using the ImageJ software. By adjusting threshold value of the image contrast, the Imaged software was used to count particles and distinguish between particles and defects on the same samples. SLD data were collected from NH₃OH and NH₄HCO₃/ NH₄OH solutions using a cavitation threshold cell (CT cell). The details of CT cell setup and the experiment procedures are available in the literature [27]. Briefly, the power density was ramped from 0.1 to 4 W/cm² and the intensity of the SLD signal was measured by a photomultiplier tube (PMT) sensitive in the wavelength range of 280 to 650 nm.

III. RESULTS AND DISCUSSION

In order to maintain a specific level of CO₂ (aq) in the solution at alkaline pH values, NH₃HCO₃ and NH₄OH were used. To keep the level of NH₃HCO₃ significantly below its solubility limit in water (~ 2.7 M at 20°C), a 0.5 M NH₃HCO₃ solution was first prepared. Different amounts of NH₄OH were then added to adjust the pH of the solution. Charge and mass balance calculations developed for the NH₄OH/NH₃HCO₃ system were used to estimate the equilibrium concentrations of the CO₂ (aq) and pH values. Pertinent equations used in the calculations are provided in Appendix.

Fig. 2 is a plot that shows the amount of CO₂ (aq) and pH as a function of NH₄OH concentration (based on the amount added) in NH₃OH/NH₃HCO₃ solutions. The original pH of the solution with no added NH₄OH is 7.8; this solution contains 800 ppm CO₂ (aq). By increasing the concentration of added NH₄OH, the solution pH increases while the amount of CO₂ (aq) decreases. Specifically, at pH 8.2 and 8.5, the CO₂ (aq) level is 320 and 150 ppm respectively. In some of the tests, NH₃OH alone was used to adjust the pH of DI water in the range of 7.8-8.5.

Fig. 3 displays the results of particle removal tests conducted on blanket SiO₂ samples for a cleaning time of 60 s in NH₃OH and NH₄OH/NH₃HCO₃ solutions of different pH values (7.8 to 8.3) at a power density of 1 W/cm². The PRE from samples cleaned in NH₃OH solutions is close to 100%. In NH₃HCO₃/NH₃OH solution, the PRE is not as high as that in NH₃OH solution until the pH reaches 8.2. PRE > 90% at pH 8.2 and 8.5. It may be recalled that NH₄OH/NH₃HCO₃ (0.5 M) solution of pH 8.2 contains ~ 320 ppm of CO₂ (aq).

The effect of megasonic exposure time in the two cleaning solutions at pH 8.2 was then investigated. The megasonic exposure time was chosen to be 0, 20, 40, 60 or 120 s. In the NH₃OH solution, the PRE on blanket SiO₂ samples is close to 100% when the exposure time is longer than 40 s; in contrast, in the NH₄OH/NH₃HCO₃ solution, high PRE can be only achieved when exposure time is ≥ 60 s. This slight difference may be attributed to reduced etching of oxides due to the presence of dissolved carbonates.

Simultaneous PRE and damage studies were conducted on patterned samples. Fig. 5 shows the PRE from patterned samples using the two cleaning solutions. The particle contamination level on patterned samples was the same as that on blanket SiO₂ samples, which was ~ 3500/mm². The results
and these are shown in Fig. 6. Under optical microscope, line breakages are observed as dark spots in the image. The SEM images of selected areas show the nature of line breakages. To further analyze the line breakages, 50 SEM images (10 x 15 mm area) for each sample were taken. The size of the broken regions was observed to be in the range of ~200 nm to 1.5 μm in the NH₄OH solution while a maximum size of ~10 μm was seen in the NH₂OH/NH₄HCO₃ solution. Interestingly, as may be seen from Fig. 6 (b), some fractured lines in the NH₂OH/NH₄HCO₃ solution were lifted but not totally removed. This suggests that CO₂ (aq) in the amount of 320 ppm lowers intensity of transient cavitation.

Fig. 7 shows the defect density on patterned samples after cleaning in NH₂OH and NH₂OH/NH₄HCO₃ solutions. As exposure time increases from 30 s to 120 s, defect density increases in both solutions at pH 8.2. At megasonic exposure times between 60 and 120 s, feature damage is much lower in the NH₂OH/NH₄HCO₃ solution compared to that in NH₂OH solution. For the exposure time of 60 s, the feature damage is reduced by ~50% at pH 8.2 when compared to pH 8.5. Since the level of CO₂ (aq) increases with decreasing pH, the beneficial effect of CO₂ (aq) should be evident.

The damage study was also done on patterned samples without any particle contamination. Table I lists the defect results on both contaminated and non-contaminated samples cleaned in NH₂OH and NH₂OH/NH₄HCO₃ solutions at pH 8.2. From the data, it appears that particles on the patterned samples do not influence the defect density.
The beneficial effect of CO$_3$ (aq) is most likely due to suppression of transient cavitation. To test this hypothesis, SL measurements were done in both solutions at pH 8.2 as a function of power density in the range of 0.1 to 4.0 W/cm$^2$ and the results are displayed in Fig. 8. In NH$_3$OH solution, SL signal was very weak until a power density of 0.6 W/cm$^2$ was reached. Above this power density, the SL signal was found to increase continuously. In the case of NH$_3$OH/NH$_3$HCO$_3$ solution, SL signal was weak in the entire power density range of 0.1 to 4.0 W/cm$^2$. These results indeed suggest that transient cavitation is significantly suppressed in NH$_3$OH/NH$_3$HCO$_3$ solutions of pH 8.2.

The effect of CO$_3$ (aq) in quenching the SL signal is still being debated. Three possible reasons are: (i) scavenging effect due to CO$_3$ entering the bubble and preventing its collapse, (ii) reduction of the temperature during bubble implosion and (iii) scavenging of hydroxyl radicals generated in the megasonic field [23]. Lower SL signal measured in NH$_3$OH/NH$_3$HCO$_3$ solutions indicates lower transient cavitation activity in the solution compared to the NH$_3$OH solution. This is an important result as it illustrates that lowering of damaging transient cavitation can be achieved for the protection of fragile features without the loss of cleaning efficiency by using alkaline carbonate solutions.

IV. CONCLUSION

Addition of ammonium bicarbonate to ammonium hydroxide solutions allows significant reduction of feature damage while providing high particle removal efficiency during megasonic cleaning of patterned wafers. Sonoluminescence studies indicate that transient cavitation is suppressed in carbonated ammonium hydroxide solutions. Based on these results, ammonium bicarbonate/ammonium hydroxide solutions have the potential to serve as effective megasonic cleaning formulations.

APPENDIX

The amount of CO$_3$ (aq) was calculated as a function of NH$_3$OH added into 0.5 M NH$_3$HCO$_3$ solution from known values of equilibrium constants and using the laws of mass and charge conservation [21]. The relevant equations are as follows:

$$\frac{[HCO_3^-]}{[CO_3^{2-}]} = K_a = 1.7 \times 10^{-7} \quad (1)$$

$$\frac{[H]^+}{[H_2CO_3]} = K_a = 2.5 \times 10^{-4} \quad (2)$$

$$\frac{[CO_3^{2-}][H^+]}{[H_2CO_3]} = K_{a_2} = 5.61 \times 10^{-11} \quad (3)$$

$$\frac{[OH^-][H^+]}{[H_2O]} = K_w = 10^{-14} \quad (4)$$

$$\frac{[NH_4^+][H^+]}{[NH_3]} = [OH^-] = [HCO_3^-] + 2[CO_3^{2-}] \quad (5)$$

$$\frac{[NH_4^+]}{[NH_3]} = B = C_0 \quad (6)$$

$$\frac{[NH_3][OH^-]}{[NH_3]} = K_b = 1.8 \times 10^{-5} \quad (7)$$

$$[CO_3^{2-}(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = C_1 + C_2 \quad (8)$$

Here $C_0 = 0.5 M$, $B = \text{added}$ NH$_3$OH and $C_1$ = total carbonate in solution in the absence of NH$_3$OH and $C_2$ = total carbonate in solution. In the above equations, $[H^+]$, $[OH^-]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[NH_4^+]$ and $[NH_3]$ are unknowns, which were solved for different values of $B$.

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REFERENCES

APPENDIX B

USE OF A SIMPLE CAVITATION CELL SET-UP WITH REPLACEABLE SINGLE BAND FILTERS FOR ANALYSIS OF SONOLUMINESCENCE SIGNAL FROM MEGASONIC IRRADIATED GASIFIED AQUEOUS SOLUTIONS

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Use of a Simple Cavitation Cell Set-up with Replaceable Single Band Filters for Analysis of Sonoluminescence Signal from Megasonic Irradiated Gasified Aqueous Solutions

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A simple method to resolve the features that are characteristic of hydroxyl radicals in sonoluminescence (SL) spectra from aqueous solutions has been developed. Using a modified version of cavitation threshold (CT) cell in which single band filters were sandwiched between the UV grade fused silica window and the photomultiplier tube (PMT) in the cell, photon emission in the wavelength range of 280 to 400 nm was measured. Four different single band filters, 280 – 305.5 nm, 300 – 340 nm, 335 – 375 nm and 374.5 – 397.5 nm were used. The results for air and Ar saturated DI water are consistent with those reported in the literature and obtained using expensive spectrometers. The SL signal collected in ammonium hydroxide solutions indicated that at higher power densities the signal intensity may not be relatable to the generation rate of hydroxyl radicals in their ground state.

Introduction

In the semiconductor industry, there are a number of wet processing steps that are intended for particle removal. Today, removal of particles is typically achieved through liquid chemicals assisted by sound field in the MHz frequency range (1, 2). There are two types of phenomena that occur during acoustic irradiation of liquids; these are acoustic streaming and cavitation. Acoustic streaming refers to liquid motion due to viscous attenuation of the sound wave. Acoustic cavitation is the formation of bubbles in the low pressure cycles during the propagation of a sound wave. The formed bubbles either continuously oscillate over many cycles (stable bubbles) or grow in size and eventually collapse in less than a few cycles (transient bubbles). When bubbles oscillate, microstreaming forces can be generated that aid in particle removal. Micro jet and shock waves generated from bubble collapse are believed to be responsible for feature damage (3).

A number of physical and chemical effects are observed during acoustic cavitation in aqueous solutions containing dissolved gases (4-6). Just prior to bubbles collapse, very high temperature (> 3000 degree C) conditions can be reached inside the bubbles. Such high temperatures result in the formation of radicals such as hydroxyl radicals. These radicals and solvent molecules are excited to high energy vibration states under local high temperature and when they return to their ground states, light is emitted. This phenomenon is known as sonoluminescence (SL) (7). In general, two types, multi-bubble
sonoluminescence (MBSL) and single-bubble sonoluminescence (SBSL) are possible. The spectrum of Multibubble SL is dominated by atomic and molecular emission peaks (e.g. excited states of OH radicals in water and of diatomic carbon C_2 (-C=C- in hydrocarbons), while SBSL spectrum is essentially featureless (8, 9). Solution parameters such as type of chemicals and level of dissolved gases and sound field variables such as megasonic power density and acoustic frequency are known to influence the intensity of SL signal. Additionally, the SL signal intensity has been correlated to extent of damage to patterned structures (10, 11).

The role of dissolved gases in modulating the SL signal has been investigated by a number of researchers. In 1976, Young et al. measured the SL signal from water saturated with different gases using a photomultiplier tube (PMT). The sound frequency used in their study was 20 kHz and the power density was kept constant at 10 W/cm^2 (12). The SL signal intensity followed the order of Ar > Air = O_2 > N_2 > H_2 = CO_2. The influence of noble gas (Ar and Xe) doping on SBSL intensity was investigated by Hiller et al. at a sound frequency of 24 kHz in water (13). The highest intensity of SL signal was measured when 1% of noble gases were mixed with N_2. Kumari et al. made SL measurements in DI water saturated with different dissolved gases at an acoustic frequency of 0.93 MHz and power density range of 0.1 to 4.0 W/cm^2 (14). In the power density range investigated, argon saturated DI water showed the highest SL signal compared to N_2 and O_2 saturated DI water. Carbon dioxide containing DI water showed a very low level of SL. This effect was attributed to the high solubility of CO_2 resulting in its diffusion into cavities and cushioning the collapse, thereby reducing the intensity of transient cavitation.

Several investigators have tried to resolve and analyze the SL spectra collected under different ultrasonic and megasonic conditions. Results of some key investigations are summarized in Table I. As may be evident from the information in this table, spectrometers were used to capture the SL spectrum. Peaks at 280-290, 310 and 340 nm were commonly seen and these are due to emission from electronically excited hydroxyl radicals (5, 15-18). At MHz frequencies, the SL signal is typically very weak and requires very sensitive spectrometers to resolve the SL spectra. Additionally, in most of the published work, SL spectral features were reported in relative intensity of values making it difficult to determine if the peaks are real.

In this paper, a simple methodology is introduced to analyze SL signals. Single band filters were used to allow photons at specific wavelengths to pass through, which are then counted by a photo-multiplier tube. Using this method, SL spectra from air, Ar and ammonium hydroxide containing DI water irradiated with megasonic waves have been characterized.
TABLE I. Summary of Key Investigations on the Collection and Resolution of SL Spectra

<table>
<thead>
<tr>
<th>Authors</th>
<th>Acoustic Frequency</th>
<th>Acoustic Power</th>
<th>Liquid medium</th>
<th>Equipment Used</th>
<th>Peaks (nm) in the emission spectra</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Didenko et al. (16)</td>
<td>22 kHz, 337 kHz and 1.1 MHz</td>
<td>10, 4 and 22 W/cm²</td>
<td>De-ionized water (Ar saturated)</td>
<td>MDR-23 monochromator (Russia, LOMO) and FEU-100 PMT</td>
<td>270, 280, 310 and 340</td>
<td>Peaks due to OH radicals</td>
</tr>
<tr>
<td>Beckett et al. (17)</td>
<td>205, 358, 618 and 1071 kHz</td>
<td>5.1 W/cm²</td>
<td>Ultra-pure water (Ar saturated)</td>
<td>Cornerstone 130 monochromator and PMT (Oriel Instruments)</td>
<td>310</td>
<td>Maximum intensity at 358 kHz</td>
</tr>
<tr>
<td>Pfieger et al. (18)</td>
<td>20, 200 and 607 kHz</td>
<td>0.17 W/ml</td>
<td>Ar, Kr or Xe containing DI Water</td>
<td>SP 2356i spectrometer and SPEC10-100BR liquid-nitrogen cooled CCD camera (Roper Scientific)</td>
<td>~240 and 310</td>
<td>Due to OH radical formation</td>
</tr>
<tr>
<td>Hayashi et al. (19)</td>
<td>116 kHz and 1.0 MHz</td>
<td>1.8, 7.3 and 15.5 W for 116 kHz; 2.0, 7.4 and 16.1 W for 1.0 MHz</td>
<td>Ar saturated DI water</td>
<td>Monochromator (Nikon, P250) and PMT (Hamamatsu, C3866)</td>
<td>290, 310 and 340</td>
<td>Very weak emission at 1.0 MHz</td>
</tr>
</tbody>
</table>

Materials and Methods

All SL signals were collected using a cavitation threshold cell (CT cell) made by ProSys, Inc., which is schematically shown in Figure 1. The cell, 163 cm³ in volume, is light tight and equipped with a transducer (~0.73 cm²) on one end for acoustic wave generation at a frequency of ~0.925 MHz. A photo-multiplier tube (PMT, Sens-Tech P25232, sensitive in wavelength range of 280 – 630 nm) located just outside the optical window in the cell was used to collect photons emitted during acoustic irradiation. Since excited hydroxyl radicals emit light in the wavelength range of 280 to 400 nm, four single band filters (Semrock) covering this wavelength were chosen for use in the experiments. The band pass wavelengths of the four filters are: (i) 280 – 305.5 nm, (ii) 300 – 340 nm, (iii) 335 – 375 nm and (iv) 374.5 – 397.5 nm. These filters were sandwiched, one at a time, between the optical window in the CT cell and the PMT to collect the SL signal in a narrow wavelength range.

Aqueous solutions with dissolved gases were pumped through the bottom of the cell at a flow rate of 130 ml/min and discharged from the top of the cell. Experiments were carried out in both continuous (100% duty cycle) and pulse mode (10% duty cycle with 5 ms pulse time) over the power density range of 0.1 to 4.0 W/cm².
Results and Discussion

Figure 2 (a) and (b) show the SL signal (in counts/s) as a function of increasing power density for air and Ar saturated DI water subjected to megasonic waves at 100% duty cycle in the absence of any filter. The SL signal from Ar saturated DI water is higher than that from air saturated DI water in the wavelength range of 280-630 nm at different power densities. The higher levels of SL intensity from Ar saturated DI water has been explained due to higher polytropic index value of Ar compared to air (20). The results of measurements made using band-pass filters indicate that the SL signal is higher in the absence of filters at all power densities for both air and Ar saturated DI water. In air saturated water, at power densities greater than 1 W/cm², the SL signal is reduced by 90% when any of the filters is used. In the case of Ar saturated solutions, a roughly similar trend is seen. Further, there appears to be a threshold in power density below which the SL signal remains at the background level. This threshold power density was measured to be about 0.9 W/cm² for both air and argon saturated DI water.
Figure 2. SL signal from air (a), Ar (b) containing DI water at 100% duty cycle and comparison of signals at 4 W/cm\(^2\) in the wavelength range 280-400 nm (c).

The bar-graph (based on 4 measurements) shown in Fig. 2 (c) compares the SL signal intensity in the narrow wavelength range of each of the filters for both air and Ar saturated DI water conducted at 4 W/cm\(^2\). In Ar saturated water, the measured PMT output with 300-340 nm and 335-370 nm filters is slightly higher than that measured with the other two filters. As mentioned in the background section, the strongest emission signal from excited hydroxyl radicals occurs in the vicinity of 310 nm and 340 nm, but the intensity of the signals at MHz frequencies is typically not as strong as at ultrasonic frequencies. In the case of air saturated water, the SL signal intensity is roughly the same with any of the four filters in place.

It is worth noting that in the wavelength range of 280 to 400 nm, the total SL intensity is ~ 930,000 counts/sec in air saturated DI water at 4 W/cm\(^2\), which is ~ 43% of the intensity in the entire wavelength range of 280 to 630 nm covered by PMT. In Ar saturated DI water, this value is ~ 63%.
The results for SL measurements carried out at transducer duty cycle of 10% are shown in Fig. 3. The trends in SL signal are somewhat similar to those observed under 100% duty cycle. The signal was highest without any filter; when different filters were used, the SL signal was highest in the wavelength range of 335-375 nm for air saturated water (at power densities higher than ~0.5 W/cm²) and in the 300-375 nm range for Ar saturated DI water (entire power density range). The bar-graph in Fig. 3 (c) displays SL signal intensity at 4 W/cm² in each wavelength range. Compared to 100% duty cycle, the SL signal intensity in each wavelength range is lower at 4 W/cm², but a similar trend is seen.

An area of interest to researchers involved in sonic cleaning techniques is correlation between SL signal and hydroxyl radical concentration in ammonia solutions that are used for cleaning. Very recently, using a fluorescence technique that works on the capture of hydroxyl radicals (OH•) by terephthalic acid, Keswani et al. (21) reported the generation

Figure 3. SL signal from air (a), Ar (b) containing DI water at 10% duty cycle and the comparison at 4 W/cm² (c).
rate of these radicals (≈ 0 to 0.2 µM/min) in ammonium hydroxide solutions irradiated with megasonic waves. The generation rate of OH• decreased from ≈ 0.16 µM/min to ≈ 0.005 µM/min as ammonia concentration increased from 0.001% to 1% (in volume). They attributed this to scavenging of OH• by ammonia. To check if these results bear any relationship to SL signals, dilute ammonia solutions of different concentration were pumped through the CT cell and data were collected in the absence of different filters. The results of these tests displayed in Figure 4 show that NH3 concentration does not affect the intensity of SL signal. This result, though may seem surprising at first, may be explained as follows. It is known that the transition of excited hydroxyl radicals to their ground state is a very rapid process and the PMT in the CT cell, due to its very high time resolution and sensitivity, is able to capture this transition and provide a strong SL signal. The process of scavenging of hydroxyl radicals by ammonia may not be as fast as the transition process and perhaps occurs after the radicals have fallen to their ground state and consequently does not influence the SL signal. These results stress the fact that SL signal, at higher power densities, is indicative of transient cavitation but may not be relatable to concentration of radicals in their ground state.

Figure 4. SL signal from NH₄OH solutions at 100% duty cycle.

Conclusions

A simple and inexpensive method for capturing the features of sonoluminescence spectrum from aqueous solutions due to hydroxyl radicals has been developed. The method consists of using single band filters in the wavelength range 280-400 nm to filter the SL signal prior to its capture by a photomultiplier tube in air saturated DI water. At power densities in the range of 1 to 4 W/cm², the intensity of the signal in the 280-400 nm range is roughly 40% of the intensity in the detection wavelength range of PMT, which is 280-630 nm. In Ar saturated DI water, this value is roughly 60%. Work with ammonium hydroxide solutions has shown that the intensity of signal may not be directly related to concentration of hydroxyl radicals in their ground state.
Acknowledgments

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References

APPENDIX C

OPERATING MANUAL FOR MEGPIE® CLEANING SYSTEM

The manual introduced a detailed procedure for operating MegPie and the function of each electronic component in the whole cleaning system. The particle deposition procedure was also documented and attached at the end of the manual.
Operating Manual for MegPie® Cleaning System

**MegPie® Configuration:** MegPie® consists of a radial transducer array (area 32.3 cm²), designed to apply uniform acoustic energy to a rotating substrate (0-60 rpm) at a frequency of 0.925 MHz, as shown in figure 1. Acoustic power density can be generated in the range 0.15 - 2.94 W/cm². MegPie® is configured for a distance of ~1.5 mm between the transducer and the wafer surface.

![Figure 1: Schematic sketch of the single wafer spin-cleaning tool MegPie®. (a) Cross-sectional view and (b) top view.](image)

**Parts of the MegPie® System**

The complete MegPie® assembly consists of the following parts:

1. **Transducer (MegPie V3 as shown in figure 2):** is triangular in shape and designed to apply uniform acoustic energy on a rotating substrate.

![Figure 2: MegPie V3 system.](image)
1. **The MicroDuo 200 (RF Generator):** supplies RF energy to the Megasonic Transducer (MegPie V3). The MicroDuo 200 provides both RF Supply and control interface to the Megasonic System. Any operation of the System requires the MicroDuo 200 (Fig. 3).

![Figure 3: MicroDuo 200.](image)

2. **Impedance Matching Network:** is used to connect the MicroDuo to the Megasonic array assembly (Fig. 4). Each serial numbered MegPie has a specific corresponding serial numbered Matching Network. **THESE COMPONENTS CANNOT BE INTERCHANGED WITH OTHERS!**

![Figure 4: Impedance Matching Network](image)

3. **Polos spinner:** consists of a chuck on which the wafer is held (Fig. 5). The rotation speed of the wafer is controlled by adjusting the settings in the control panel as described in the later sections. Figure 6 shows a picture of the wafer placed on the chuck.

![Figure 5: Polos spinner system](image)
Figure 6: Wafer placed on the chuck properly.

**Caution:** After using MegPie® system, check the spinner to make sure it is tightly screwed to the chuck, especially when 1000 rpm applied for drying in PRE study. Otherwise, if the spinner is loose, it will throw away the wafer, which can cause damage to the transducer.

**Connection of the MegPie® System**

Figure 7 illustrates the MicroDuo system interconnect diagram.

Figure 7: MicroDuo 200 system interconnect diagram.
Before work on the power input connections, ensure that power is disconnected at the source (e.g. circuit breaker locked off), and a notification sign is posted to advise other personnel not to apply power.

The ProSys MicroDuo 200 requires one AC power source with 208 volts, at 50/60 Hz, and 2 Wire + Ground. Ensure that the Power Switch on the MicroDuo 200 is in the OFF position. Connect the MicroDuo 200 unit to 208 volt 50/60 Hz grounded power source with a minimum 10-amp rating. Connect the BNC RF Cable from the MicroPower RF OUT connector to the Matching Network RF IN connector. Connect the Cable from the MegaSonic Transducer to the Matching Network RF OUT connector. If connecting directly to a PC, connect the crossover network cable to the RJ45 network port. If connecting the system to an internal network a straight RJ45 cable is required.

TCP/IP Setup and Software Operation Procedure

The Single Wafer User Interface Program will operate using only the Ethernet communication. In order to use the MegPie system, we must change the IP address of the PC/Laptop to allow MegPie to connect.

Connect the (Red) crossover cable (provided) from the PC’s Ethernet port to the MicroPulse Ethernet port located on the back of the MicroDuo. Setup the PC for TCP/IP networking per manufacturers specifications. Under ‘Settings’ → ‘Control Panel’ → ‘Network’ Set TCP/IP protocol properties to ‘Specify an I.P. Address:
- I.P. Address: 192.168.10.YYY (Where YYY is any number between 1 to 256 except the address of the MicroPulse.)
- Subnet Mask: 255.255.255.0
- Default Gateway: Not applicable

No other settings or properties need to be Set/Changed from the defaults.

The steps below will describe MegPie software operation procedure:

1. Please ensure the complete system is properly installed and all connections are secure.
2. Connect the red crossover cable (provided with MicroDuo) from the Ethernet port of the PC that has ProSys Single Wafer GUI software installed to the Ethernet port on the ProSys MicroDuo.
3. Switch power on at MicroDuo.
4. Start GUI software.
5. Establish connection to MicroPulse. Choose desired IP and select “CONNECT” (shown in figure 8).
1. The GUI software interface will show up. Select the Recipes button; the interface will come up as shown in figure 9. The Product Systems, Inc. MicroPulse uses four (4) Wave recipes and (4) Process recipes.

- **Wave recipes** contains the detail of the Megasonic operation (example pulse time, power, duty cycles, and Megasonic exposure time as shown in figure 10).
- Process recipes are sequences of wave recipes which include more than one wave recipes.
- Load from Pulse Button retrieves current recipes from the MicroPulse.
- Save to Pulse Button saves current recipe data to the MicroPulse.
- New Button creates a new recipe set.
- Load from file Button loads recipe data from PC file.
- Save to file Button saves recipe data to PC.
- Save as file Button saves current recipe data to PC prompting for a new name.

![Recipe Interface with Wave Details](Figure 10: Recipes interface with wave details)

1. Set the substrate rotating speed between 15 and 50 rpm. A RPM of greater than 60 is not recommended, as higher RPMs may not completely wet the transducer and the substrate. On Polos control panel as shown in figure 11, click “MODE” button to enter set up interface. Up and down arrows (“↑” and “↓” button) can be used to toggle between different items. Input the step number to create new step (always start with step 1), then input the rotation time and speed (rpm) of the step, click the “enter” button on the right bottom corner of the panel to save the step. If more than one step needs to be created, change the step number to “2” to enter the step 2 interface, then edit rotating time and speed for step 2, press the same “enter” button to save it. Up to 99 steps can be saved in one program and 999 sec for each step can be run. Put the wafer or sample to the chuck and close the lid. On the back of the spinner, check the compressed air input (labeled as “CDA”) before running the spinner. Make sure the input compressed air is always on (at ~5psi) during the whole process.
1. Select the Operate Button on the GUI software, the software interface as shown in figure 12 will come up.

- **Mode** (Pull Down Menu):
  I. Wave – Allows selection of wave recipe.
  II. Process – Allows selection of process recipe.

- **Current Recipe** (Pull Down Menu) displays current recipe name after selection.

- **Time Remaining** displays time remaining on current recipe hours, minutes and seconds depending on total time.

- **Cycle** indicates cycle data for process recipes with multiple cycles.

- **Percent Bar** shows percent time remaining.

- **Forward Power** displays the current forward power in watts. If the reflected power goes too high, the RF generators internal protectors may reduce the forward power.

- **Reflected Power** displays the current reflected power in watts.

- **Run/Stop Button** when selected will run or stop the current recipe.

- **Clear Attention Button** clears warning indicator.

- **Clear Alarm Button** clears alarm indicator.
1. Select the recipe on the Operate screen of the GUI.
2. Start flow of process fluid (recommended 300 ml/min) onto the surface of the substrate, wetting the entire surface. Ensure that the fluid has completely wetted the active surface of the MegPie, forming a meniscus between the face of the MegPie and substrate. Then click the "I/O" button on the POLOS control panel to initiate the spinner rotating.

**Caution:** Ensure that the meniscus is maintained at all times.

3. Click Run Button from the GUI operate interface or press the "RUN" button on the front of MicroDuo200 as shown in figure 3. The transducer will power on for the specified time according to the set up in GUI software.
4. Observe the forward and reflected power readings, if the reading appears abnormal (very high, especially for reflected power), stop transducer immediately.
5. Select Stop Button, or wait until the run has finished.
6. Stop the fluid flow in the end. If the wafer needs to be spin-dried, then stop the fluid after the transducer switched off and continue spinning the wafer till the wafer gets completely dried.

**MegPie Cleaning**

Extreme care must be used to maintain and extend the use of the MegPie. Perform periodic inspections for contamination and damage. Clean with appropriate means based on the type of contamination and the MegPie materials of construction.
Procedure for dispersion preparation and particle deposition

For the dispersion preparation and particle deposition on patterned sample which will be used in megasonic cleaning experiments, please refer the following procedure:

1. Commercially available Mirrosol 30180D slurry (30 % by weight) is contained in a 5-gal jar. Shake the slurry vigorously and take ~100 ml of it into a 150 ml polypropylene container.
2. Stir the slurry (using magnetic stirrer) for 10 min and transfer 0.1 ml of it to a 1.5 ml centrifuge tube using a pipette where 0.9 ml of already prepared 5 mM KCl solution was added.
3. Centrifuge the slurry at 17000g for 2 min. Remove the supernatant liquid using a pipette and re-disperse the precipitate in a fresh 1.0 ml of 5 mM KCl solution. These steps need to be repeated 5 times.
4. At the end of step 3, mix the dispersion (1 ml) from the centrifuge tube with 2 ml of fresh 0.5 mM KCl solution. The dispersion at the end of this step will be ~1% in concentration (30 times more dilute than the original slurry).
5. Further dilute the dispersion using DI water for 1000 times. Thus the final stock solution obtained is 0.001 % in concentration. The concentration can be adjusted according to different requirements of the particle density for deposition by changing the DI water amount in the dilution process.
6. 300 mm pattern wafer provided by IMEC is diced into 1 cm × 2 cm samples. Pre-clean the samples using SC1 (1:1:50) for 1 min and use IPA to dry them.
7. Sonicate the stock solution (0.001% by weight) for 2 min using a glass beaker.
8. Place the sample on the spin coater chuck and dispense 1 ml of the stock solution right after sonication on the sample. Spin the sample at 250 rpm for 2 min.
9. Keep the samples after deposition in a clean sample holder for 24 hr.
10. Tape the four corners of the sample to the substrate wafer in MegPie at the center of the substrate wafer radius before running the experiments.
APPENDIX D

COOK BOOK MANUAL FOR THE IMMERION MEGASONIC® CLEANER

The manual introduced a detailed procedure for operating the immersion megasonic tank

and the function of each electronic component in the whole cleaning system.
The ProSys Immersion MegaSonic cleaner contains the following components:

- **An immersion tank** (15 L capacity) made of KYNAR® (polyvinylidene fluoride) equipped with four 0.925 MHz transducers covered by the resonator (quartz) on the top.

- **MegaPulse unit**: the Megasonic System Controller – contains an oscillator and an embedded microcomputer with two communication interfaces to create the signals which feed to the MegaPower.

- **MegaPower unit**: the Megasonic Power Source – amplifies the signal from MegaPulse to a specific power density to the Transducer.

- **Impedance Matching Network**: is used to connect the MegaPower to the megasonic array assembly, which matches the impedance of the oscillator circuit tree to that of the transducer. Each serial numbered MegTank has a corresponding serial numbered Matching Network. **THESE COMPONENTS CANNOT BE INTERCHANGED WITH OTHERS!**

Figure 1 shows the picture of immersion megasonic cleaner and its dimension with 4 transducers on the bottom of the tank. The total active area of the 4 transducer is 200 cm².

The power density applied to the transducer is from 0.1W/cm² (corresponds to 20 W power output) to 2.88W/cm² (corresponds to **576 W** power output). Standard Transducer Arrays operate at process temperatures up to **65** degrees C. The temperature of the liquid in the tank should not exceed 65 deg C.
Equipment Check:

**IMPORTANT NOTE BEFORE RUNNING ANY EXPERIMENT IN THE MEGASONIC TANK:**

**ALWAYS KEEP WATER IN THE TANK!** This will keep the transducers from burning out if accidently turned on.

1. Make sure the **MegaPower** is connected to a **220V** source. Connect each part of the system according to the ProSys wiring diagram for details, Fig. 2.
TCP/IP Setup and Software Operation Procedure: (This is a one time procedure and the system has already been configured with these settings when it was installed for the first time) The Immersion Tank User Interface Program (MUPI_v101) will operate using only the Ethernet communication. In order to use the MegaTank system, we must change the IP address of the PC/Laptop to allow MegaTank to connect. Connect the (Red) crossover cable (provided) from the PC’s Ethernet port to the MegaPulse ethernet port. Setup the PC for TCP/IP networking per manufacturers specifications. Under
1. ‘Settings’ → ‘Control Panel’ → ‘Network’ Set TCP/IP protocol properties to ‘Specify an I.P. Address:

- I.P. Address: 192.168.10.YYY (Where YYY is any number between 1 to 256 except the address of the MegaPulse.)
- Subnet Mask: 255.255.255.0
- Default Gateway: Not applicable

No other settings or properties need to be Set/Changed from the defaults.

**Operation Steps:**

1. **Make sure the tank is always filled.** The DI water valve is located as shown in Fig. 3.

3. If the liquid overflows from the main inner tank into the outer overflow region, the liquid will automatically drain (through an opening at the bottom of the outer region).

![DI water valve](image-url)  
*Figure 3: DI water valve.*
1. Turn on the MegaPower and MegaPulse as shown in Fig. 4.

![Figure 4: MegaPower and MegaPulse.](image)

2. Start up the MPUI_v101 program on the desktop. Make sure the equipments are all turned on and click the “Refresh List” button on the program interface. Select the IP address shown in the list and click connect, Fig. 5.

![Figure 5: MegaPulse is registered by the MPUI_v101 program.](image)

3. The software interface changes to the operation interface as shown in Fig. 6.
Figure 6: The operation interface of MegaTank.

1. Click “Recipes” on the bottom of the interface to make changes of the tank set-up (Fig. 7).

Figure 7: Interface of Recipes.

2. Then the software window (as below) shows up. Click on ‘load’ button to load recipes from the MegaPulse on the Recipes interface. Click Load, the recipe list will show up (Fig. 8).
1. Choose the recipe number which needs to be edited (ex. Wave 1) and click “Display Recipe Details”. The details of Wave 1 will show up (Fig. 9). Change the parameters as desired according to the experiments. Dwell time is not functioning since the 4 transducers are set to run simultaneously by the hardware update from ProSys. Leave the dwell settings as 1000 milliseconds.
1. Click “Save” button on the right side of the interface and go back to the Operation interface by clicking the “Operate” button on the bottom. Then click “Select Rcp” button as shown in Fig. 6, the wave list will show up (Fig. 10). Choose the recipe and click OK, the recipe will be loaded then.

![Wave list on the Operate interface.](image)

**Figure 10: Wave list on the Operate interface.**

2. Click “Run” button on the interface or press the (green) RUN/STOP button on MegaPulse as shown in Fig. 4 to initiate the transducer. When transducers are turned on, the acoustic wave pass through the liquid field. Observe the “Refl Avg” indication as shown in Fig. 6. The reflected power should be less than 10 watts while running 100 watts of power (10% of the power as set up). If not, stop running the system operation immediately, remove power, and contact Zhenxing Han/Manish Keswani.
1. After finishing the experiment, turn off all the electronics and close the software. Drain the liquid left in the tank by unscrewing the tubing which is located at the right top corner from the bottom of the tank (Fig. 11).

![Figure 11: Unscrew the tubing from the bottom of the tank.](image)

2. Screw the tubing back and refill the tank by ~ 10 L DI water. Always keep water in the tank.

3. After using the tank several times, use dilute SC1 (1:1:50) to clean it. Keep the SC1 solution in the tank for 30 min then drain it and use DI water to rinse the inside wall of the tank for a few times.

For any other technical questions, please contact Zhenxing Han/Manish Keswani.
APPENDIX E

OPERATING MANUAL FOR CAVITATION THRESHOLD (CT) CELL

The manual introduced a detailed procedure for operating the CT cell and the function of each electronic component in the whole cleaning system.
Operating Manual for Cavitation Threshold (CT) Cell

**Application:** Cavitation Threshold (CT) Cell is used to measure sonoluminescence signal (total photon counts per sec) as a function of time in a flowing liquid exposed to an acoustic field at ~ 1 MHz frequency at a fixed or increasing values of power density.

**Cell Design:** The CT cell is a light tight cell with a liquid holding volume of ~ 163 cm$^3$. As shown in figure 1, the cell (body made of chlorinated poly vinyl chloride) is cylindrical in shape (with 104 mm in length and internal diameter of 48 mm) with a piezoelectric crystal transducer located on one side. The transducer operates at a frequency of ~ 1 MHz and a power density range from 0.1 to 4 W/cm$^2$. The other side of the cell has a conical PTFE (polytetrafluoroethylene) baffle (height 48 mm) which prevents the sound waves from reflection and interacting with the incident waves. This allows for a more uniform distribution of the sound field inside the cell.

![Figure 1: Internal construction of the CT cell](image_url)
The cell has inlet and outlet ports for liquid to flow through it. During irradiation of the flowing liquid with the acoustic energy, the light that is emitted is measured using a photo multiplier tube (PMT) located in the middle of the cell body. The interface between the PMT and the liquid is a fused silica window that allows the light to enter into the PMT but prevents its direct contact with the liquid. PMT is a plug-and-play photodetector module configured for photon counting. It comprises a selected type 9111B 25 mm diameter end window photomultiplier tube with blue-green sensitive bialkali photocathode and ultra-low dark counts, a positive high voltage power supply, a high speed amplifier-discriminator, a counter, and a micro-controller. All are encapsulated within a cylindrical mumetal case (as shown in figure 2), providing a high level of immunity from the effects of external magnetic fields.

![Figure 2: Photodetector module P25232](image)

The CT cell set up (shown in figure 3) consist of a pump, water flow meter (rotameter), oxygen sensor, membrane contactor, gas flow meter and vacuum pump. A direct DI water line is connected to the rotameter with a value to control the water flow rate. If a desired chemical system (liquid) is to be flown through the cell, it may be taken in a container and pumped through the cell using the peristaltic pump.
The liquid is first passed through the membrane contactor to dissolve a gas of interest in the liquid. The membrane contactor contains thousands of Celgard® micro porous polypropylene hollow fibers knitted into an array that is wound around a distribution tube (shown in figure 4). The hollow fibers are arranged in a uniform open packing, allowing greater flow capacity and utilization of the total membrane surface area. The liquid flows through the shell side and the gas through the lumenside. An oxygen sensor is connected at the outlet (shell side) of the membrane contactor to measure the amount of dissolved oxygen.
Operation steps:

**Caution**: DO NOT run CT cell without flowing liquid through it, which can cause severe damage to the transducer!!

1. Check all the connections first according to fig. 5 (the ProSys_CT-Cell_control system diagram).

![ProSys_CT-Cell_control system diagram](image)

Figure 5. ProSys_CT-Cell_control system diagram

2. Log into the laptop as user name: CAVCELL; Password: ProSys. Open the excel file: *CT-Cell_Template-07-2011.xlsm* which is saved on the desktop. The excel interface will show up as below (fig. 6), which presents the “Summary” worksheet as default. The left side shows the general settings including:

<table>
<thead>
<tr>
<th>PMT SN</th>
<th>Sample Period (secs.)</th>
<th>Array size (cm. sq.)</th>
<th>Resonator/Coating Material</th>
<th>Array SN</th>
<th>(M/u)Pulse IP Address</th>
<th>Pwr Low Limit (Watts/cm²)</th>
<th>Pwr Upper Limit (Watts/cm²)</th>
<th>Duty cycle (%)</th>
<th>Pulse period (ms.)</th>
</tr>
</thead>
<tbody>
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<td></td>
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</tr>
</tbody>
</table>
While the right side shows the cavitation power profile which plots the photons/sec vs. Watts/cm².

Figure 6: Summary worksheet for total cavitation power profile

Figure 6 also shows that we have one “Monitor” worksheet and ten “Profiles” worksheets. The difference between “Monitor” mode and “Profiles” mode is that in “Monitor” mode, the power density is set up before the experiment as well as the duty cycle, plot is showing photons/sec vs. time; while in “Profiles” mode, only duty cycle can be changed, photons/sec is plotted vs. power density range from 0.1 Watts/cm² to 4 Watts/cm² for 90 sec.

Flow the liquid of interest first through the cell, the liquid flow rate is adjusted to be 130 ml/min. The liquid flows through the membrane contactor followed by the dissolved oxygen sensor connected to it. The liquid flow rate is normally less than 2 L/min through the membrane contactor according to the sweeping efficiency. Apply sweeping gas of interest to the membrane contactor through the “sweeping gas in” port; the pressure of the gas is set to be < 0.7 kg/cm² (10 psig, 0.69 bar). Make sure that the DO sensor is mounted vertically within the 45 degree angle, which is required for accurate measurements. Then put the DO sensor
3. Power on. The DO sensor will show the dissolved oxygen level and the liquid temperature accordingly. When the readings from DO sensor become stable, put the CT cell and micro pulse power on. When there is liquid flowing out of the cell from the top, start gently shaking the cell to release bubbles trapped in the cell.

4. Set up the Duty cycle (%) and Pulse period (ms.) in Profiles# worksheet. Duty cycle (%) can be set up as 10, 50, 100, etc. If the duty cycle is not 100% (continuous mode), then Pulse period (ms.) is usually set to 5. Set ATTENUATOR (dB) to “-6”. Then click the “Start Profile” button to start recording data. Figure 7 shows an example result when Duty cycle (%) was set to 100, Pulse period (ms.) was set to 5 and Attenuator (dB) was set to -6; the liquid flowing through the cell was Argon (Ar) saturated DI water with dissolved oxygen level 0.09 ppm at 24 degree C. In the plot, the blue curve is showing the dark count (background count) from the PMT when there is no power applied to the transducer. Dark count is the unwanted signal produced by the photomultiplier tube in the absence of light stimulation. Dark counts are a function of photocathode type and temperature. The photocathode type of the PMT in our set up is bialkali, dark counts of less than 2000/s is acceptable in our experiments. The power density ramps up at 0.016 watt cm\(^{-2}\)s\(^{-1}\) from 0.1 watt/cm\(^2\) to 1.0 watt/cm\(^2\). While from 1.0 watt/cm\(^2\) to 4.0 watt/cm\(^2\), the power density ramps up at 0.083 watt cm\(^2\)s\(^{-1}\).
3. While in Monitor worksheet the Duty cycle (%), Pulse period (ms.), Attenuator (dB) as well as power density need to be set up before running the experiments. First click the “PMT On” button, which can initiate PMT to start recording, usually the data can only show background counting at this moment because there is no power applied. After about 10 seconds of recording, click “Pwr On” button to start transducer to vibrate, the signal will then increase in most of the cases if there is photons releasing in the cell under that power density. When finish recording, stop power first then stop PMT.

4. Summary worksheet only shows the summary of all the Profiles data (as shown in figure 8).
Cell Cleaning:

Cleaning is required after CT cell is being used several times, especially when chemicals are added into the liquid that flow through it. Diluted HCl (1:100) is good to remove metal ions left on the cell wall by flushing it at 300 ml/min through the cell for ~20 min. Then flushing DI water for 20 ~ 30 min after it and drain the cell completely.

General Considerations and Precautions:

The sweeping gas should be oil free prior to the membrane contactor; the gas and water temperature should not exceed 30 degree C in the sweep gas mode. Remove free chlorine, ozone and any other oxidizing elements prior to the membrane contactor to avoid the effect of membrane oxidation.

The liquid flowing through the CT cell should be maintained at a flow rate of >10 ml/min to avoid acoustic heating effect. The liquid temperature is recommended to not exceed 70 degree C through the cell.
Memo:

The typical SL signal in air saturated DI water can be reached up to $10^6$ counts/sec at power density of 4 W/cm$^2$ in both continuous (100% duty cycle) and pulse (10% duty cycle) modes under the “profile” sheet in the excel. When first start running the CT cell, make several dummy measurements in air saturated DI water until the signal goes up to $10^6$ to be sure the cell is running properly.

**Important note when running the cell under the “monitor” sheet:**

The “monitor” sheet was built to run the cell at constant power density, however the excel sheet seems not functioning when changing the power density from the excel sheet. So please refer to the following procedure to run the cell at constant power density.

1. Open the “GUI” software on the desktop from the laptop, the following pic will show up and click “connect” button.

![Figure 9: GUI software connection interface](image)

2. Then the MicroPulse will be connected to the laptop, click the “Recipes” button to enter the recipe interface:
1. Create recipes and processes at this interface including megasonic power, time, pulse period and duty cycle. Then click the "Save to Pulse" button to finish. Since the CT cell system is designed with an attenuator connected in the circuit, which is attenuating the forward power by 0.25. The input power from GUI software should be multiplied by 4 to correspond the correct value as desired for the transducer.

2. Go to the Operate interface and select the wave or process as desired.

Figure 10: the Recipes interface

Figure 11: the Operate interface
1. Then open the EM6 software on the desktop, select the PMT type to be P25232 and turn on the “high voltage”. The PMT reading will be recorded when click the “start” button.