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Megasonic Metrology for Enhanced Process Development

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Acoustic cavitation is known to be a primary source of both cleaning and damage of wafers during their megasonic processing. Understanding the response of process fluids to variables like acoustic power recipe and dissolved gases is an important first step in achieving damage-free megasonic cleaning of wafers. This paper reports the development of a portable, UV light tight, cavitation threshold (CT) cell to measure sonoluminescence (SL) signal arising from cavitation. The closed cell, integrated with a gas sensor and contactor, allows SL measurements under very controlled conditions. Using the CT cell the effect of the concentration of dissolved O_2, CO_2 and air on SL signal has been investigated. Results show that SL varies linearly with dissolved O_2 concentration while CO_2 is found to be incapable of supporting SL. This study also demonstrates a novel method for precise control of SL through addition of an O_2 scavenger with fast O_2 removal kinetics.

Introduction

Megasonic cleaning has been the method of choice for cleaning of wafers at technology nodes larger than 90 nm where the wafer features were relatively robust. With the advent of the sub-45 nm technology nodes, megasonic cleaning of wafers at both front-end-of-line (FEOL) and back-end-of-line (BEOL) processes is faced with an increasing challenge to maintain cleaning efficiency without inducing damage (1, 2). With decreasing feature size and increasing aspect ratios, the forces required to dislodge a contaminating particle have increased and come closer to the forces that can damage wafer features (3). It is widely believed that acoustic cavitation is responsible for both cleaning and damage. Development of improved megasonic cleaning technologies to enhance cleaning without causing damage requires a fundamental understanding of cavitation response of cleaning fluids to variables like power recipe and nature and concentration of dissolved gases.

Sonoluminescence (SL), the phenomenon of release of light by liquids when agitated by sound waves of sufficient intensity, is a sensitive indicator of cavitation events (4). Traditionally SL is measured by a dip-type probe. It is influenced by several factors such as hydrostatic pressure, surface tension, temperature, nature and concentration of dissolved gases and ions (5), intensity and frequency of sound waves (4, 6) and secondary effects arising from interaction of sound waves with wafer interfaces and container walls (7, 8) and hence careful control of experimental conditions is critical to the interpretation of results. A real-time SL monitor capable of following cavitation events has been described in the literature (9).

Recently, a new type of instrument known as cavitation threshold (CT) cell has been designed to measure SL of stationary or continuously flowing liquid under tightly regulated conditions. Continuous-flow mode measurements provide a significant advance over previous designs as it overcomes the history dependence of cavitation events. In addition, sound waves in the present device can be generated in either pulse or continuous modes and can be varied in intensity and duration. This instrument allows integration with O_2 and temperature sensors as well as a membrane contactor for exchange of dissolved gases, thus enabling study of a number of important factors influencing SL / cavitation in a manner that is reliable and reproducible.

This paper reports the results of a systematic study conducted with the CT cell on the roles of dissolved O_2, CO_2 and air in the SL of deionised water (DIW). CO_2 is commonly injected into DI water to increase conductivity and reduce static charging during drying. The extent of dissolved oxygen was controlled either mechanically by vacuum degassing or chemically through the use of an oxygen scavenger with fast O_2 removal kinetics.

Materials and Methods

The CT (Cavitation Threshold) Cell is a small (163 cm^3), UV light tight cell, with an integral acoustic transducer. The process fluid flows through the cell, is exposed to the acoustic energy and emits UV light as a result of stable or transient cavitation. Sensors collect the UV light emitted from the cavitations and provide an output of photons per second.

Figure 1A is a schematic sketch of the set up used to make CT cell measurements. The set up consists of a membrane contactor (Liqui-cel extra-flow 2.5 x 8 inch) for contacting liquids with gases, a vacuum pump, (Welch Vacuum model 2545B-01) to degas the liquids, and an O_2 and temperature sensor (Rosemount Analytical model 499A DO) to measure O_2 concentration and temperature of the liquids entering the CT cell. Figure 1B is a schematic sketch of the internal construction of the CT cell. The cell is cylindrical in shape (length 104 mm and internal diameter 48 mm) with a piezoelectric crystal and resonator at one end for sound wave generation and a conical acoustic baffle (height 48 mm) at the other end for minimizing reflection of sound waves. Measurements reported in this paper were done in a Class-10 Micro/Nano Fabrication Center at the University of Arizona using either a DIW supply line or chemicals in a dedicated container. Experiments were carried out in continuous as well as pulse modes (10% duty cycle) over the range of 0.1 to 4.0 Watts/cm^2 of power density. Sound generation at each of the measured power densities was switched on for either 50 ms (continuous mode) or for 0.5 ms at 10% duty cycle (pulse mode) and the resulting SL was measured.

Air saturated DIW samples were prepared by exposing DI water contained in a one liter container to ambient clean room air for roughly twenty four hours without stirring. Saturation at a given temperature was confirmed by measuring the O_2 concentration and comparing it to theoretical values expected for 100% saturation at that temperature. Liquids were passed through the CT cell at a nominal rate of 130 ml/min. SL measurements were initiated after the O_2 and temperature sensor readings became stable to indicate equilibrium conditions. Measurements made under each of the two modes (continuous and pulse) were repeated 2 to 4 times and average values were calculated.

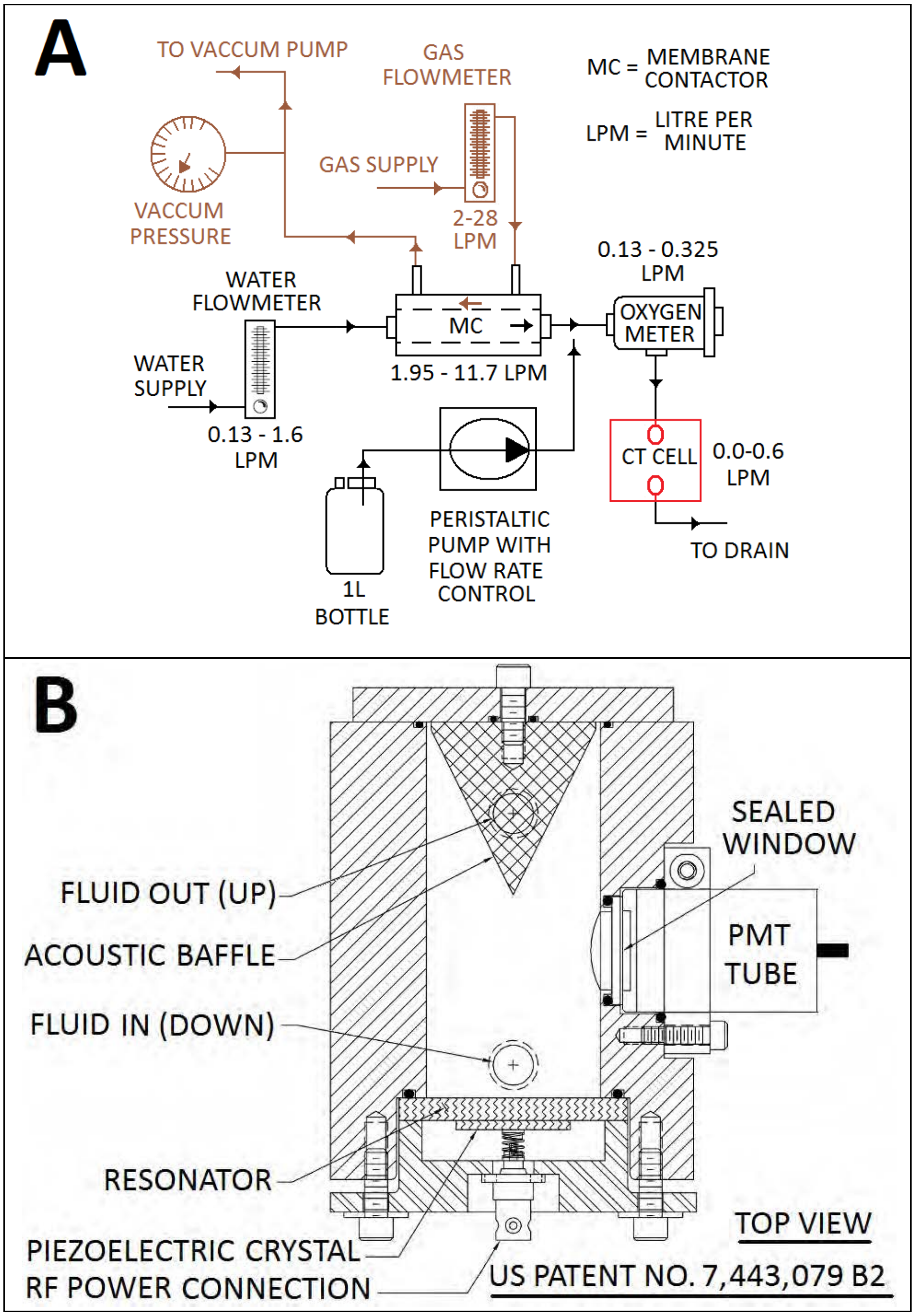

Figure 1. Schematics of SL signal measurement setup (A) and the internal construction of the CT cell (B).

To generate four different concentrations of dissolved O_2 in DIW, four liters of air saturated DIW was divided into four equal parts and required amounts of freshly prepared 1 M stock solution of the O_2 scavenger was added to each of them just before the start of the experiment. The samples were then sealed to prevent atmospheric O_2 from re-dissolving. The stoichiometry of the reaction of the scavenger with oxygen is such that one mole of scavenger is capable of removing half a mole of oxygen. The kinetics of oxygen removal by the scavenger was extremely rapid, of the order of seconds, which is several orders faster than the rate at which O_2 from atmosphere could re-dissolve into the solutions. Under these conditions, the dissolved O_2 concentrations were found to be stable at the time scale (~ 5 minutes) of our experiments.

To generate different concentration of dissolved CO_2 in DI water, CO_2 was passed through the membrane contactor at different positive gauge pressures and DIW was passed through the contactor counter to the gas flow at a fixed flow rate of 130 ml/min. The pH of the water leaving the contactor was monitored and converted to dissolved CO_2 concentrations using equation 1. This equation is derived from the equilibrium constant of hydration (K_h) of CO_2 to form H_2CO_3, the first acid dissociation constant (K_{a1}) of H_2CO_3, electrical neutrality condition and the fact that in the pH range 4 to 7, $[CO_3^{2-}]$ is negligible in comparison to $[HCO_3^-]$.

$$[CO_2] \approx \frac{10^{14-2\times pH} - 1}{Ka1 \times Kh \times 10^{14}} \qquad [1]$$

$$where\ Ka1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 2.5 \times 10^{-4}\ \mathrm{M}\ and\ Kh = \frac{[H_2CO_3]}{[CO_2]} = 1.7 \times 10^{-3} \qquad [2]$$

To obtain an explicit dependence of SL intensity on dissolved O_2 concentration, the average SL intensity in the power range 0.1 – 4.0 Watts/cm^2 was computed from figure 2, pulse mode curves, using the formula:

$$Average\ SL = \frac{\int_{0.1}^{4.0} f(x)dx}{\int_{0.1}^{4.0} dx} \qquad [3]$$

$$Where\ x\ is\ power\ density\ and\ f(x)\ is\ SL\ intensity$$

Results and Discussion

The effect of dissolved O_2, controlled by the addition of an oxygen scavenger, on SL intensity is shown in Figure 2 as a function of power density. It should be noted that unlike vacuum degassing, oxygen scavenger addition does not remove nitrogen and argon. There is a clear dependence of SL intensity on O_2 concentration in the power range of 0.1 to 4 Watts/cm^2. Removal of O_2 down to a level of 0.17 ppm resulted in a weak SL signal, with no evidence of onset of cavitation up to 4 W/cm^2. While decrease in SL intensity with decreasing O_2 levels is clearer in the pulse mode, the increase in cavitation threshold is more evident in the continuous mode, as seen from the insert in figure 2.

In light of the facts described in the paragraph above, we view our results showing decrease in SL intensity upon removal of O_2 as the indirect effect of reduction of total dissolved gas concentration rather than an effect of O_2 *per se*. A certain threshold concentration of total dissolved gases, irrespective of the individual gas identities, must also be present for SL to occur. We therefore expect that compensating lost O_2 by equivalent amounts of other gases should increase the SL intensity by an amount that would depend on the SL capability of the replacing gas. In other words, adding N_2, which is mostly recognized to be capable of supporting SL in DIW (11), is likely to restore SL that is lost upon removal of O_2 while CO_2, found to be incapable of supporting SL by us, is unlikely to do so. These predictions are based on the assumption that role of individual gases in the SL of DIW are independent of each other, which may or may not be true. We are in the process of testing these hypotheses and further clarify the roles played by individual gases in the SL of DIW.

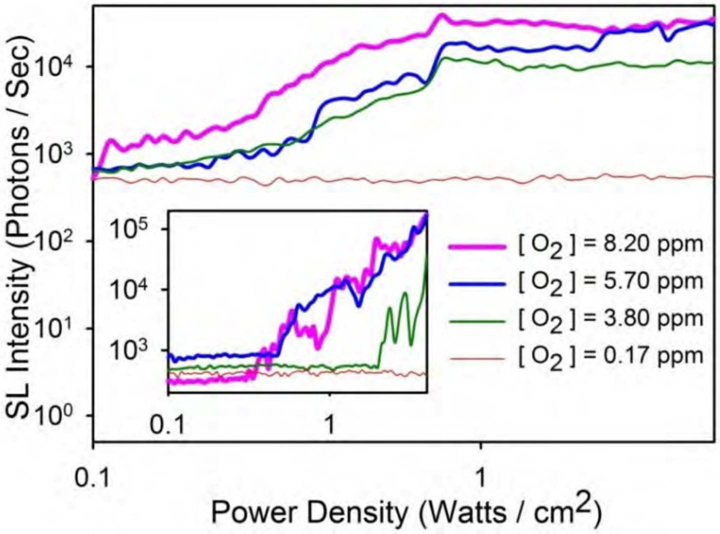

Figure 2. Pulse and continuous mode (inset) SL intensity as a function of power density for DI water with different levels of dissolved O_2.

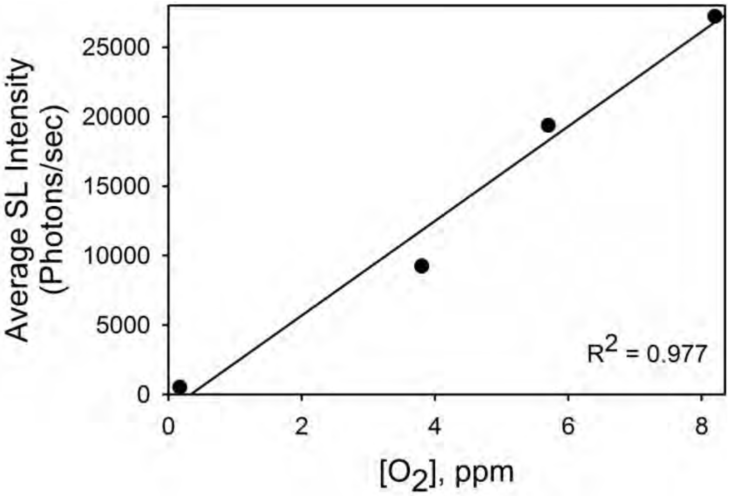

Figure 3. Average SL intensity in the power range 0.1 to 4.0 Watts/cm^2 as a function of oxygen concentration

To compare chemical method with mechanical method of O_2 removal, air-saturated DIW was degassed using a vacuum pump, until O_2 concentration decreased from 8.2 to 3.8 ppm (~50%) and SL intensity was measured. The results, plotted in figure 4, show that a 50% reduction of dissolved O_2 by the traditional vacuum degassing technique resulted in a near zero SL response whereas reduction of oxygen level by about the same amount using O_2 specific scavenger resulted in only 50% decrease in SL intensity. This is likely due to removal of other dissolved gases (N_2 and Ar) along with O_2 in the mechanical degassing method.

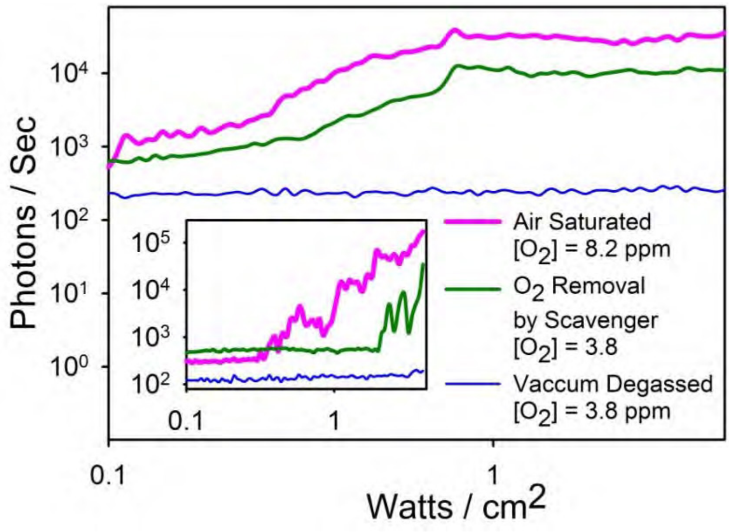

Figure 4. Comparison of chemical and mechanical methods of gas removal. Pulse and continuous mode (inset) SL intensity as a function of power density for DI water with partial removal of dissolved oxygen.

Reduction in O_2 concentration is unlikely to be the sole effect of the added O_2 scavenger. Effects arising from changes in pH, ionic strength, etc., upon addition of the scavenger, may also contribute to the observed reduction in SL. To address these possibilities, the following experiment was conducted. Stock solution of the O_2 scavenger was pre-exposed to O_2 until the scavenger became incapable of consuming further O_2, as confirmed in a separate experiment using an O_2 electrode. Small aliquot of this inactive O_2 scavenger was then added to air saturated DIW to the same final concentration as active scavenger was added previously for O_2 removal and SL intensity was measured. The results, shown in figure 5, showed no essential difference between the SL intensity measured for air saturated DIW with and without the addition of inactive O_2 scavenger. This confirms that the decrease in SL observed in figure 2 is indeed due to decrease in dissolved O_2 levels and not due to any other side effect of the added scavenger.

Using the CT cell, the effect of CO_2 gas on SL signal was also investigated. In these tests, the concentration of dissolved CO_2 was varied using the membrane contactor in the range of 0.5 to 1600 ppm (pH range = 5.7 to 3.9). Introduction of CO_2 displaced existing dissolved gases and this was confirmed from the reduction in the dissolved O_2 concentration from 8.2 to 0.2 ppm. Figure 6 shows that at CO_2 concentration of 110 ppm or higher ($[O_2] = 0.2$ ppm), the SL signal obtained was very low throughout the power density range of 0.1 to 4 Watts/cm^2, in both pulse and continuous modes. In order to determine whether high levels of carbon dioxide alone can induce SL, experiments were conducted with water saturated with CO_2 to a maximum possible level of ~1600 ppm at 23°C. Lack of any SL from this CO_2 saturated DIW confirmed that CO_2 alone is incapable of supporting SL in the absence of other gases. This is in sharp contrast to published results suggesting that SL intensity of CO_2 saturated water is nearly one-third that of air-saturated water (4, 11).

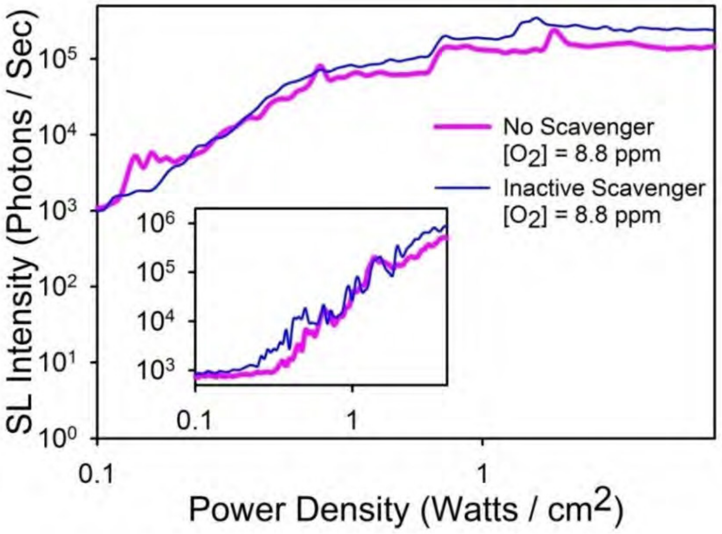

Figure 5. Pulse and continuous mode (inset) SL intensity as a function of power density for DI water with or without inactive oxygen scavenger.

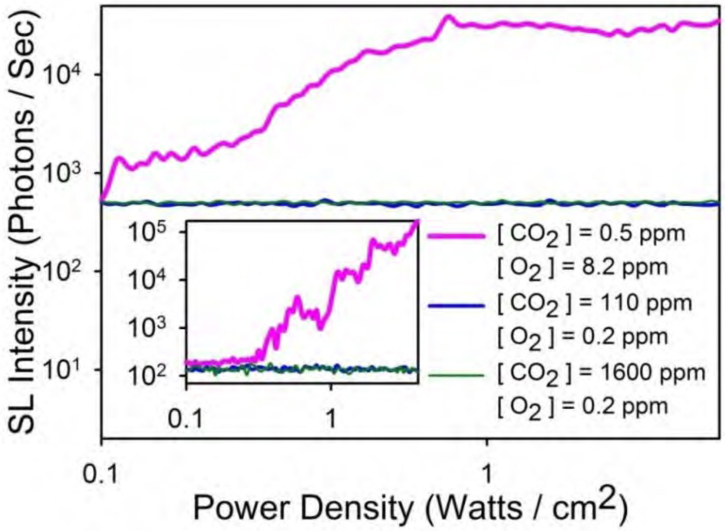

Figure 6. Pulse and continuous mode (inset) SL intensity as a function of power density for DI water with different levels of dissolved carbon dioxide.

Conclusions

Successful development and use of a robust, modular and portable cavitation threshold cell for SL measurements has been established. Using this cell, a novel chemical method for selective removal of dissolved O_2 and its use as a means for precise reduction of SL in DIW has been demonstrated. In contrast to the role of O_2, we have found dissolved CO_2 to be completely incapable of supporting SL, offering another potential means of controlling SL. Since SL directly correlates with damage, control of SL through O_2 removal may offer a potential, cost-effective means for damage-free megasonic cleaning.

Chemical removal of O_2 as demonstrated in this study offers the advantages of selectivity and precise control over mechanical methods of degassing that can also be used to reduce SL. In addition, removal of O_2 which is capable of producing harmful reactive oxygen species during cavitation, may be specially suitable for controlling unwanted chemical reactions. Further studies on the effect of O_2 removal on cleaning efficiency and damage to wafers will be needed to establish optimal O_2 levels for best cleaning performance.

Acknowledgements

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