Control of Sonoluminescence in Carbon Dioxide Containing DI Water at Near Neutral pH Conditions

Sangita Kumari[1, a], Manish Keswani[1,b], Satish Kumar Singh[2, c], Mark Beck[3, d], Eric Leibscher[3, e], Pierre Deymier[1, f] and Srini Raghavan[1,g]

[1] Department of Materials Science and Engineering, The University of Arizona, Tucson, Arizona 85721, USA

[2] Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721, USA

[3] Product Systems Incorporation, Campbell, California 95008, USA

[a]sangitak@email.arizona.edu, [b]manishk@email.arizona.edu, [c]satish@email.arizona.edu, [d]mjb@prosysmeg.com, [e]egl@prosysmeg.com, [f]deymier@email.arizona.edu, [g]srini@email.arizona.edu

Keywords: Megasonic cleaning, Damage, Sonoluminescence, Carbon Dioxide.

Abstract. Light emission in sound-irradiated liquids, known as Sonoluminescence (SL), is associated with the phenomenon of cavitation that affects wafer damage during megasonic processing of wafers. It has been shown that the intensity of SL can be substantially decreased through the dissolution of carbon dioxide in deionized water. However, such dissolution decreases the pH to roughly 4.0, which is not very desirable for the removal of contaminant particles. This paper reports two chemical systems that are capable of taking advantage of the effect of CO_2 while allowing the use of slightly higher pH values. Specifically, NH_4OH/CO_2 and NH_4HCO_3/dilute HCl systems have been shown to be capable of well controlled reduction in SL at pH 5.7 or 7.0. In order to test whether the free radical scavenging ability of CO_2 may be responsible for its strong SL-inhibitory effect, the effect of a well known free radical scavenger, dimethyl sulfoxide (DMSO), on SL produced in DI water has been investigated.

Introduction

Megasonic irradiation of aqueous solutions of NH_4OH and H_2O_2 is routinely used in the semiconductor industry for particle removal from wafer surfaces [1, 2]. Acoustic streaming and cavitation are known to be the primary particle removal mechanisms during megasonic cleaning. Unfortunately, cavitation arising from imploding transient cavities also results in wafer damage [3, 4]. Transient cavitation is strongly associated with the release of light, a phenomenon known as sonoluminescence (SL) [5]. Conditions that generate high SL appear to lead to increased pattern damage [6, 7] and thus there is a growing interest in identifying conditions that would reduce SL without reducing the particle removal efficiency. It is well known that particle removal is a strong function of pH of cleaning solution and therefore identifying conditions that would reduce SL and also maintain the solution pH at a desired value, can be key to damage-free wafer cleaning.

The authors of this paper recently described the development of a portable, UV light tight cavitation threshold (CT) cell allowing measurement of SL under precisely controlled conditions. Using the CT cell, they established that dissolved CO_2 in the hydrated form [CO_2(aq)] strongly inhibits SL generation in water, even in presence of other dissolved gases [8]. To demonstrate the inhibitory effect of CO_2(aq), a novel method for *in situ* release of CO_2 from NH_4HCO_3 by a pH-induced shift in the carbonic acid equilibria was developed. The method required a decrease in pH to induce release of CO_2. Decrease in pH may however adversely affect particle removal efficiencies. In this paper, a method for generating varying levels of CO_2(aq) (and thus SL inhibition) at neutral to near neutral pH values is reported. Specifically, the usefulness of two different chemical systems, NH_4OH/CO_2 or NH_4HCO_3/dilute HCl has been investigated.

Additionally, the hypothesis that SL may be inhibited through scavenging of free radicals has been tested using dimethyl sulfoxide (DMSO), a well known free radical scavenger [9]. The mechanism by which DMSO acts as a scavenger in an aqueous solution has been attributed to quenching of $OH^\bullet$ radical by the $CH_3^\bullet$ radicals that are generated upon thermolysis of DMSO inside hot, cavitating bubbles [10].

Experimental Methods

SL data were collected in a clean room environment using a CT cell as previously described [11]. In brief, solutions were flown through the CT cell at a flow rate of 130 ml/min and exposed to 0.93 MHz megasonic field in either continuous (100% duty cycle, 50 ms pulse period) or pulse mode (10% duty cycle, 5 ms pulse period) over a power density range of 0.1 to 4.0 W/cm^2. Water samples with varying concentrations of CO_2(aq) at a constant pH were generated using two different systems, a) NH_4OH/CO_2 and b) NH_4HCO_3/dilute HCl. In the NH_4OH/CO_2 system, suitable amount of NH_4OH and CO_2 saturated (1500 ppm) DI water were added to air saturated deionized (DI) water to generate a desired equilibrium concentration of CO_2(aq) at a constant pH of 5.7. The initial concentrations of NH_4OH and total dissolved inorganic carbon required to generate a desired concentration of CO_2(aq) at equilibrium and at a given pH, were numerically calculated using the equations of ionic equilibria and the laws of mass and charge conservation, yielding Eq. 1 through Eq. 8, as shown below [8].

$$\frac{[H_2CO_3]}{[CO_2]} = K_h = 1.7\times10^{-3} \tag{1}$$

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]} = K_{a1} = 2.5\times10^{-4}M \tag{2}$$

$$\frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = K_{a2} = 5.61\times10^{-11}M \tag{3}$$

$$[OH^-][H^+] = K_w = 10^{-14}M^2 \tag{4}$$

$$[NH_4^+]+[H^+] = [OH^-]+[HCO_3^-]+2[CO_3^{2-}] \tag{5}$$

$$[NH_4^+]+[NH_3] = B_0 \tag{6}$$

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = K_b = 1.8\times10^{-5}M \tag{7}$$

$$[CO_2(aq)]+[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}] = C_i + C_0 \tag{8}$$

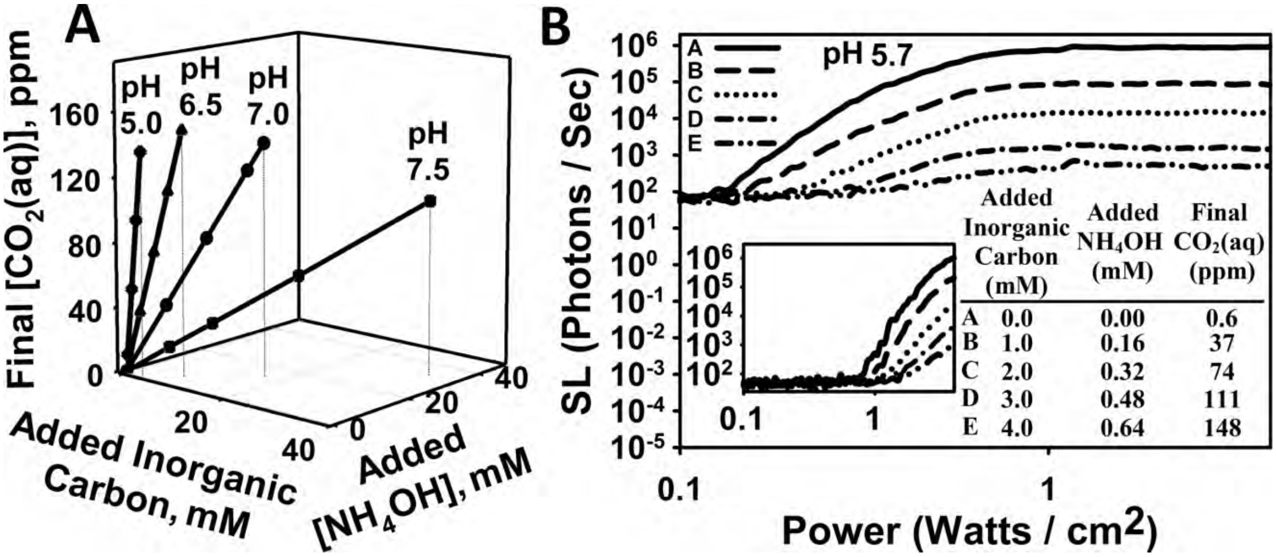
Here, C_0 = added dissolved inorganic carbon , B_0 = added $[NH_4OH]$ and C_i = dissolved inorganic carbon initially present in DI water (~) $1.4\times10^{-5}M$. For the NH_4HCO_3/dilute HCl system at pH 7.0, the initial concentrations of NH_4HCO_3 and HCl required were calculated using Eqs 1 to 8 with two minor modifications; B_0 = added $[NH_4HCO_3]$ and charge balance equation (Eq. 5) was modified to include added HCl concentration as shown in Eq. 9.

$$[NH_4^+]+[H^+] = [OH^-]+[added\ HCl\ ]+[HCO_3^-]+2[CO_3^{2-}] \tag{9}$$

SL measurements on DMSO - water mixtures were made by mixing DMSO and air saturated DI water at different volume percentages and allowing them to equilibrate to room temperature before data collection.

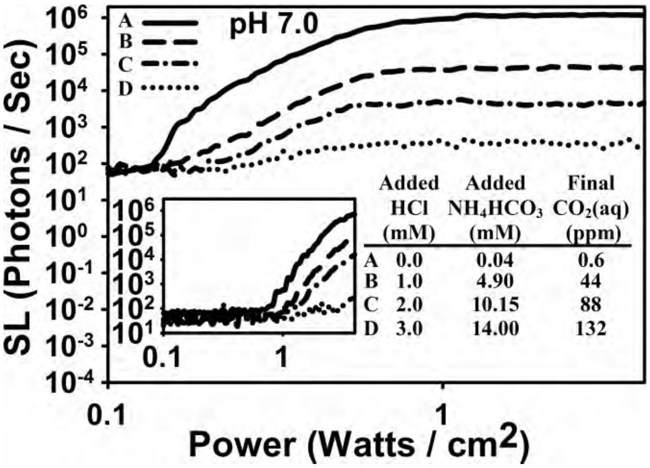
Results and Discussion

Fig. 1A shows a theoretical plot of required initial concentrations of total dissolved inorganic carbon and NH_4OH for generating varying concentrations of CO_2(aq) at equilibrium, at pH: 5.0, 6.5, 7.0 and 7.5. Data for the plot were generated from the numerical solution of Eqs. 1 through 8. Fig. 1B displays the SL data collected on NH_4OH/CO_2 system at a constant pH 5.7. The CO_2(aq) content was varied by changing the total added inorganic carbon. The data show a well controlled decrease in SL with increasing CO_2(aq) concentration. SL is almost completely suppressed in both the pulse and continuous modes at an equilibrium CO_2(aq) concentration of ~150 ppm. This compares well with the value of 130 ppm that was previously shown to be minimally neccessary for complete suppression of SL in air saturated DI water at a pH 4.2 [8]. It may also be noted that the threshold power density necessary to produce detectable SL increases with increase in concentration of CO_2(aq), suggesting that higher concentration of CO_2(aq) suppresses the initiation of transient cavity callapse. Control of SL has also been demonstrated at neutral pH 7.0 in the NH_4HCO_3/dilute HCl system (Fig. 2). Here too, a near complete suppression of SL is achieved at an equilibrium concentration of ~130 ppm CO_2(aq).



	Added Inorganic Carbon (mM)	Added NH_4OH (mM)	Final CO_2(aq) (ppm)
A	0.0	0.00	0.6
B	1.0	0.16	37
C	2.0	0.32	74
D	3.0	0.48	111
E	4.0	0.64	148

Fig. 1. **(A)** Plot of the added inorganic carbon and NH_4OH concentrations required to generate a desired final concentration of CO_2(aq) at pH 5.0, 6.5, 7.0 and 7.5. **(B)** Pulse and continuous mode (inset) SL intensity as a function of power density for the NH_4OH/CO_2 system, at a constant pH 5.7.



	Added HCl (mM)	Added NH_4HCO_3 (mM)	Final CO_2(aq) (ppm)
A	0.0	0.04	0.6
B	1.0	4.90	44
C	2.0	10.15	88
D	3.0	14.00	132

Fig. 2. Pulse and continuous mode (inset) SL intensity as a function of power density for the NH_4HCO_3/dilute HCl system at pH 7.0.

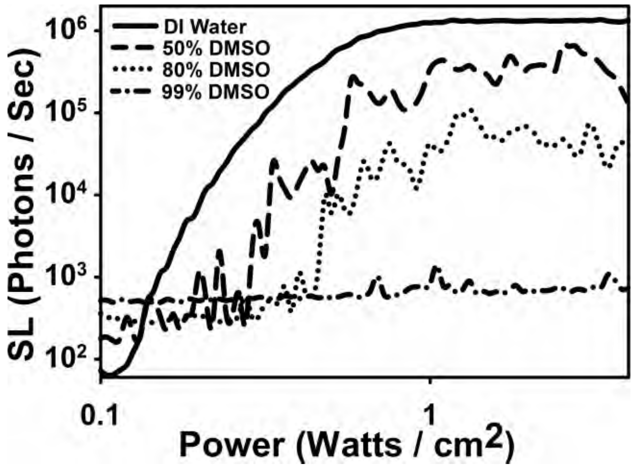


Fig. 3. Pulse mode SL intensity as a function of power density for varying concentrations of DMSO mixed with air saturated DI water.

One plausible method by which CO_2 may reduce SL is by scavenging free radicals that recombine and emit light [8]. To test this hypothesis, the effect of a chemical that is a well known free radical scavenger on SL was investigated. Dimethyl sulfoxide (DMSO) was chosen for these investigations. Solutions containing different volume percentages of DMSO in air saturated DI water were prepared and characterized using the CT cell. Fig. 3 presents experimental data collected on different DMSO-water mixtures. The data clearly shows that increasing concentration of DMSO decreases SL generation, indicating that free radical scavenging could indeed lead to reduction in SL intensity.

Various radicals such as $CH_3SO^\bullet$, $CH_3SO_2^\bullet$, $CH_3SOCH_2^\bullet$ and $CH_3^\bullet$ are generated during thermolysis of DMSO and being free radicals themselves, they may act as excellent scavengers of $OH^\bullet$ radical generated from water vapor inside the cavitation bubbles [10]. DMSO reacts with $OH^\bullet$ with a rate constant of 6.6×10^9 $L.mol^{-1}s^{-1}$. Similarly, $OH^\bullet$ radical can also be scavenged by both CO_2 (rate constant of reaction = 1.0×10^6 $L.mol^{-1}s^{-1}$) and the products of its interaction with water, namely, HCO_3^- (rate constant 8.5×10^6 $L.mol^{-1}s^{-1}$) and CO_3^{2-} (rate constant 3.9×10^8 $L.mol^{-1}s^{-1}$) [12]. Therefore, ability to scavenge luminescent free radicals may explain the SL inhibitory effect of both $CO_2(aq)$ and DMSO.

Summary

Methods to suppress the SL generation in DI water to any desired extent while holding the pH constant in the range 5.0 to 7.5 have been demonstrated using two chemical systems, NH_4OH/CO_2 and NH_4HCO_3/HCl. The hypothesis that $CO_2(aq)$ may inhibit SL through free-radical scavenging has been tested using another potent $OH^\bullet$ radical scavenger, DMSO.

References

[1] Gale GW and Busnaina AA (1999) *Particul Sci Technol* **17,** pp. 229-238.

[2] Kapila V, Deymier PA, Shende H, Pandit V, Raghavan S and Eschbach FO (2006) *Proc SPIE-Int Soc Opt Eng* **6283,** pp. 628324/1-12.

[3] De Marco C, Wostyn KL, Bearda T, Sano K-I, Kenis K, Janssens T, Leunissen LHA, Eitoku A and Mertens P (2007) *ECS Transactions* **11,** pp. 87-93.

[4] Vereecke G, Holsteyns F, Arnauts S, Beckx S, Jaenen P, Kenis K, Lismont M, Lux M, Vos R, Snow J, *et al*. (2005), eds. Mertens P, Meuris M and Heyns M, **103-104**, pp. 141-146.

[5] Negishi K (1961) *J Phys Soc Jpn* **16,** pp. 1450-1465.

[6] Muralidharan K, Keswani M, Shende H, Deymier P, Raghavan S, Eschbach F and Sengupta A (2007) in *Emerging Lithographic Technologies XI* (SPIE, San Jose, CA, USA), **6517**, pp. 65171E/1-13.

[7] Helbig S, Urban S, Klein E and Singh S (2008) in *Photomask Technology 2008* (SPIE, Monterey, CA, USA), **7122**, pp. 712210/1-10.

[8] Kumari S, Keswani M, Singh SK, Liebscher E, Beck M, Deymier P and Raghavan S (2010) Accepted for Publication in *Microelec Eng*.

[9] Klein SM, Cohen G and Cederbaum AI (1981) *Biochemistry-US* **20,** pp. 6006-6012.

[10] Kondo T, Kirschenbaum LJ, Kim H and Riesz P (1993) *J Phys Chem-US* **97,** pp. 522-527.

[11] Kumari S, Keswani M, Beck M, Liebscher E, Liang T, Deymier P and Raghavan S (2009) *ECS Transactions* **25,** pp. 295-302.

[12] Buxton GV, Greenstock CL, Helman WP and Ross AB (1988) *J Phys Chem Ref Data* **17,** pp. 513-886.