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

Authors	Acoustic Frequency	Acoustic Power	Liquid medium	Equipment Used	Peaks (nm) in the emission spectra	Comments
Didenko et al. (16)	22 kHz, 337 kHz and 1.1 MHz	10, 4 and 22 W/cm^2	De-ionized water (Ar saturated)	MDR-23 monochromator (Russia, LOMO) and FEU-100 PMT	270, 280, 310 and 340	Peaks due to OH radicals
Beckett et al. (17)	205, 358, 618 and 1071 kHz	5.1 W/cm^2	Ultra-pure water (Ar saturated)	Cornerstone 130 monochromator and PMT (Oriel Instruments)	310	Maximum intensity at 358 kHz
Pflieger et al. (18)	20, 200 and 607 kHz	0.17 W/ml	Ar, Kr or Xe containing DI Water	SP 2356i spectrometer and SPEC10-100BR liquid-nitrogen cooled CCD camera (Roper Scientific)	~240 and 310	Due to OH radical formation
Hayashi et al. (19)	116 kHz and 1.0 MHz	1.8, 7.3 and 15.5 W for 116 kHz; 2.0, 7.4 and 16.1 W for 1.0 MHz	Ar saturated DI water	Monochromator (Nikon, P250) and PMT (Hamamatsu, C3866)	290, 310 and 340	Very weak emission at 1.0 MHz

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 cm^3 in volume, is light tight and equipped with a transducer (~0.73 cm^2) 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/cm^2.

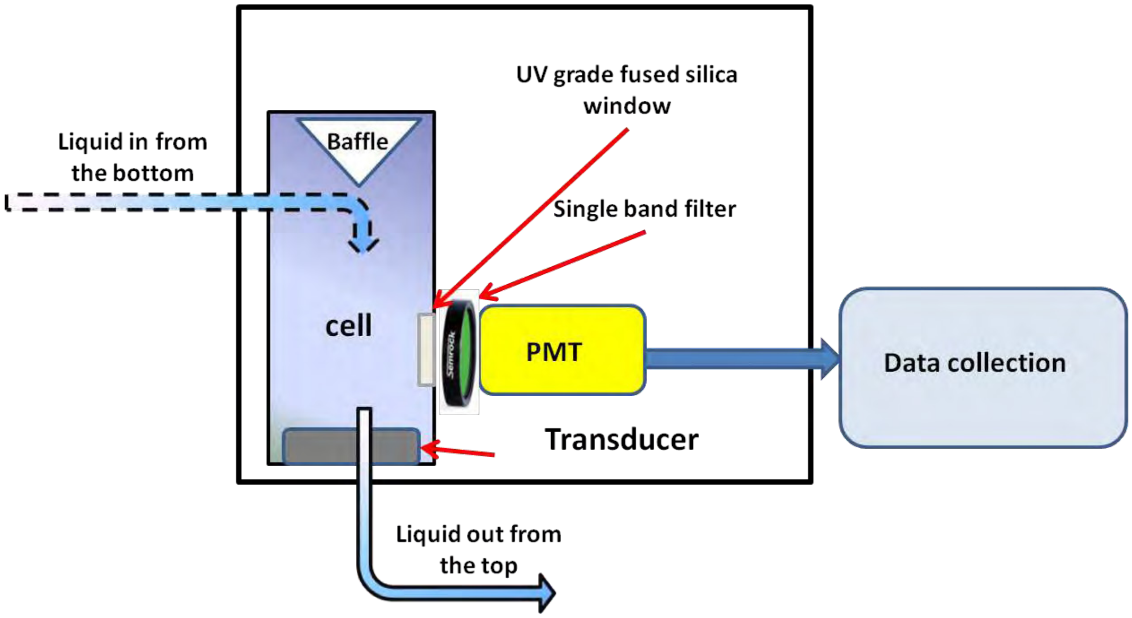
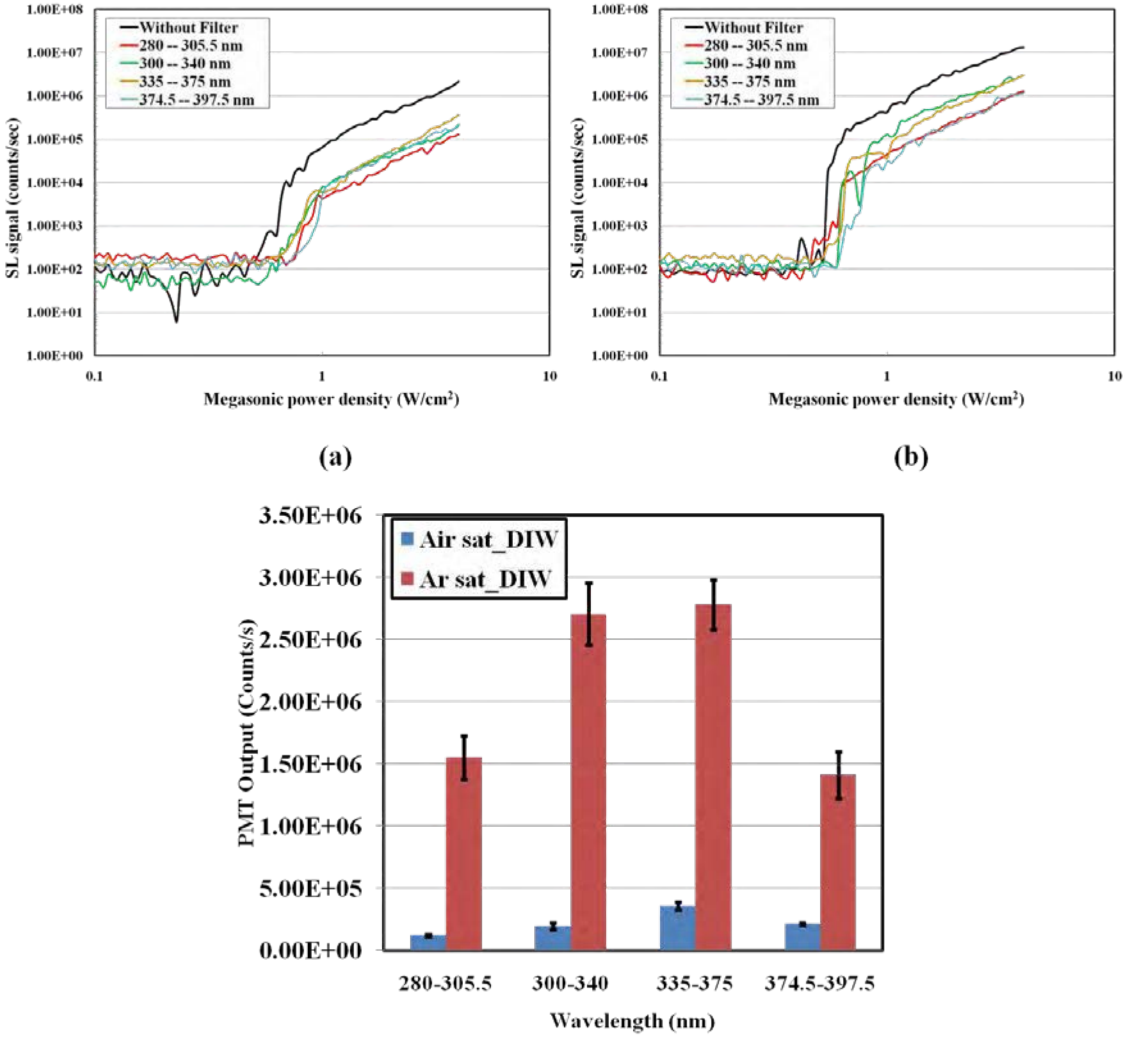


Figure 1: Schematic of CT cell (top view) with a single band filter sandwiched between the PMT and UV grade fused silica window.

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/cm^2, 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.



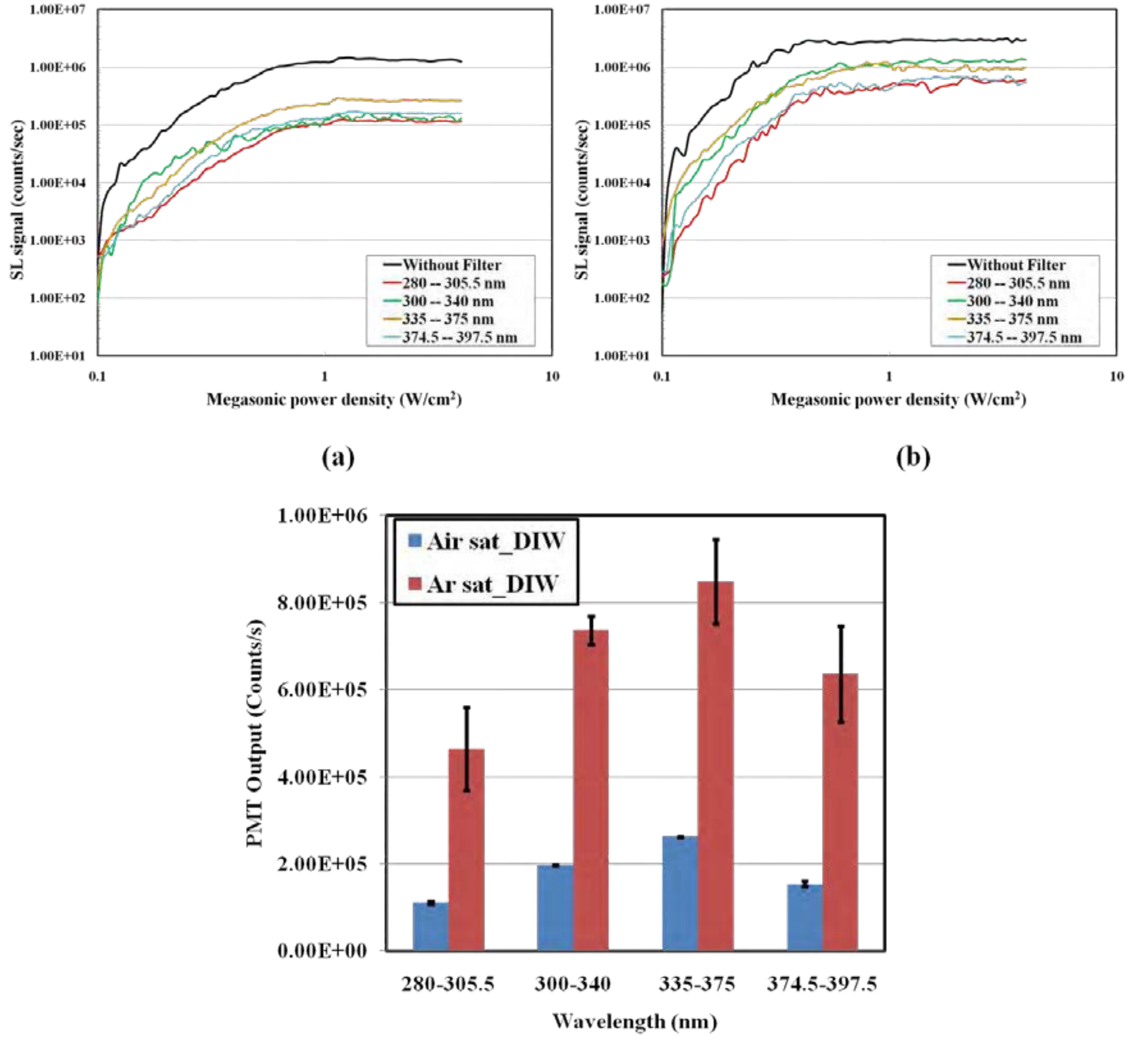
(a) (b)

(c)

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%.



(a) (b)

(c)

Figure 3: SL signal from air (a), Ar (b) containing DI water at 10% duty cycle and the comparison at 4 W/cm^2 (c).

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/cm^2) 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/cm^2 in each wavelength 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.

An area of interest to researchers involved in sonic cleaning techniques is correlation between SL signal and hydroxyl radical concentration in ammoniacal solutions that are used for cleaning. Very recently, using a fluorescence technique that works on the capture of hydroxyl radicals ($OH^\bullet$) by terephthalic acid, Keswani et al. (21) reported the generation rate of these radicals (~ 0 to 0.2 μM/min) in ammonium hydroxide solutions irradiated with megasonic waves. The generation rate of $OH^\bullet$ 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 $OH^\bullet$ 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 NH_3 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.

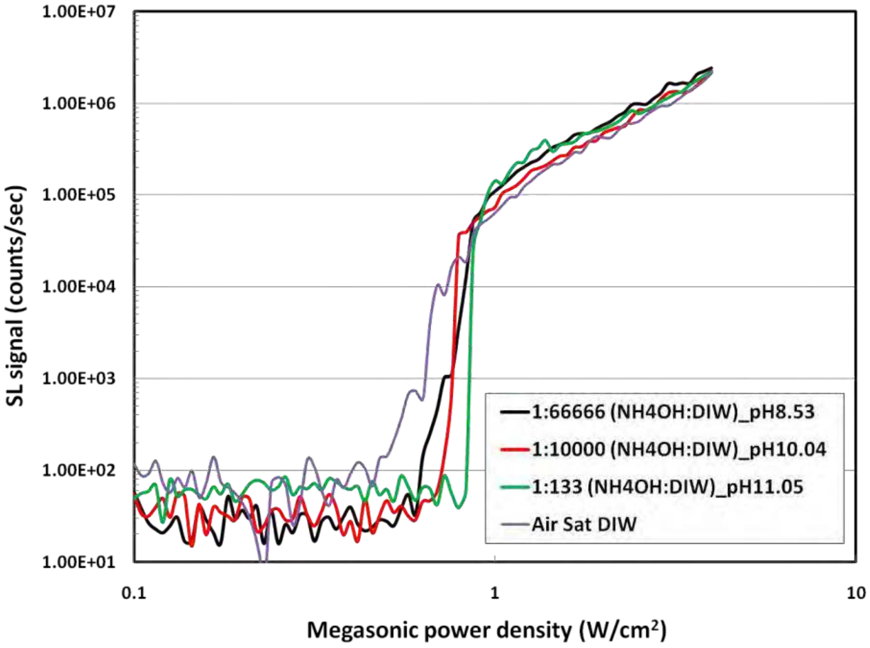


Figure 4: SL signal from NH_4OH solutions at 100% duty cycle.

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/cm^2, 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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