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Characterization of stable and transient cavitation in megasonically irradiated aqueous solutions ☆

Rajesh Balachandran [a], Mingrui Zhao [b], Petrie Yam [c], Claudio Zanelli [c], Manish Keswani [a,*]

[a] Materials Science and Engineering, University of Arizona, Tucson, AZ, USA
[b] Chemical and Environmental Engineering, University of Arizona, Tucson, AZ, USA
[c] Onda Corporation, Sunnyvale, CA, USA

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ABSTRACT

Megasonic cleaning is routinely used for removal of particulate contaminants from various surfaces in integrated circuit industry. One of the drawbacks of megasonic cleaning is that although it can achieve good particle removal efficiencies at high power densities, it also causes feature damage. The current paradigm is that damage is primarily caused by transient cavitation whereas cleaning is affected by streaming and stable cavitation. In order to develop a damage-free and effective megasonic cleaning process, it is essential to understand the acoustic bubble behavior and identify conditions that generate significant stable cavitation without any transient cavitation. In the current work, microelectrode based chronoamperometry, pressure measurements using a hydrophone and fluorescence spectroscopy studies were conducted under different acoustic frequencies (1–3 MHz) and power densities (2–8 W/cm^2) to fundamentally investigate the type of cavitation produced under these conditions and also establish a correlation to the generation of hydroxyl radicals for characterization of transient cavitation.

1. Introduction

Megasonic cleaning has been widely used in the integrated circuit (IC) industry as an intermediary step for surface preparation of processes such as thin film deposition, etching, chemical mechanical planarization (CMP), lithography and others [1]. As the technology node in the semiconductor industry moves towards smaller sizes, the demand for efficient megasonic cleaning processes that can effectively remove particles with minimum damage arises. Considerable work has been done on fundamentally characterizing the cavitation behavior at frequencies in the range of about 0.8–1 MHz [2–5]. Kumari et al. [2] conducted damage studies on two types of patterned substrates (array of lines of high k-metal gate stacks on silicon and poly-Si lines on silicon) at a frequency of about 0.925 MHz by varying the power density (0.15–2.94 W/cm^2) and amount of dissolved CO_2 (0.5–1035 ppm). For both structures, it was observed that there was significant damage observed in air saturated solutions while CO_2 saturated solutions (1035 ppm CO_2 in DI water) showed minimal damage. The authors hypothesized that CO_2 due to its higher solubility than air diffuses into the cavity in higher amounts and cushions the collapse, which significantly suppresses transient cavitation. In another study on investigating the role of various dissolved gases (Ar, N_2, CO_2) on transient cavitation at ~1 MHz sound field using high time resolution cyclic voltammetry studies, it was illustrated that the frequency of occurrence and intensity of transient cavitation was lowest in CO_2 containing aqueous solutions and highest in Ar saturated solutions [3]. Kang et al. [4] conducted particle removal and damage studies on patterned photoresist and polysilicon structures at operating frequency of ~0.8 MHz in DI water solutions containing different concentrations of dissolved gases (Ar, O_2, N_2 and H_2). The operating power was maintained constant at 70% of the maximum value. They showed that as the partial pressure of the dissolved gases increased, the particle removal efficiency and the number of damaged structures also increased. These studies emphasize the importance of dissolved gases on cavitation activity. It is generally believed [6] that the intensity of transient cavitation is much lower at higher acoustic frequencies and may offer a viable solution to damage-free and effective cleaning. Although there are several reported studies on particle removal, feature damage and the driving mechanisms at an acoustic frequency of ~1 MHz, there is little information available on cavitation behavior at higher frequencies (2–4 MHz).

In a study on the effect of megasonic frequency at ~3 MHz on cleaning efficiency, Kim et al. [1] developed a near-field megasonic waveguide consisting of a small cylindrical lead zirconate titanate

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* Corresponding author. Tel.: +1 (520) 270 4361.
E-mail address: manishk@email.arizona.edu (M. Keswani).

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(PZT) actuator for effective removal of nanoparticles from silicon wafers. The results revealed that the average maximum pressure values obtained from the new waveguide were about 35.6% lower with more uniform pressure field distribution compared to that from a traditional waveguide, indicating a possible decrease in the degree of transient cavitation and therefore pattern damage. Shende et al. [7–9] studied the effect of different dissolved gases (Ar, CO_2 and H_2) on the acoustic pressure, sonoluminescence and pattern damage on phase shift masks with aspect ratios in the range of 1:1 to 1.8:1 under different acoustic frequencies (1–4 MHz) and transducer powers. The effect of varying the frequency in the range of 1–4 MHz [8,9] was quite evident for DI water cleaning solution where the damage was lowest at 4 MHz suggesting a significant reduction of transient cavitation at this frequency.

Yasui [10] simulated the bubble behavior under different frequencies to understand the effect of controlling parameters behind cavitation. His work revealed that the range of the ambient bubble radius for sonoluminescing cavitation bubbles narrows as the ultrasonic frequency increases from 20 kHz to 1 MHz. Another study [11] indicated that the pressure amplitude of the megasonic wave must be in the range of about 100–400 kPa for stable cavitation to be dominant. It was reported in this work that effective particle removal with minimal damage could be achieved by maximizing the extent of stable cavitation and eliminating any occurrence of transient cavitation.

In this study emphasis has been laid on fundamentally understanding the cavitation behavior under applied acoustic frequencies of 1 and 3 MHz and transducer power densities of 2–8 W/cm^2, as estimated by the electrical power input from the generator and the area of the transducers. Primarily, cavitation investigations have been carried out by means of a microelectrode based electrochemical sensor in solutions containing ferricyanide as the electroactive species. Supporting pressure measurements were conducted using a hydrophone to confirm the extent of transient cavitation under different experimental conditions. Finally, fluorescence spectroscopy was performed to determine the rate of generation of OH radicals, which is further an indicator of the degree of transient cavitation.

2. Materials and methods

High resistivity de-ionized water (18 MΩ-cm) was used for all experiments. Potassium ferricyanide, potassium chloride, terephthalic acid and 2-hydroxy terephthalic acid were greater than 99% purity and purchased from Sigma Aldrich Inc. VLSI grade ammonium hydroxide (29%) was procured from Honeywell Inc. Megasonic experiments were performed in Mini-meg® tanks (PCT Systems Inc.) of volume ~4.5 l consisting of 125 cm^2 transducers affixed at the bottom with operating frequencies of 1 and 3 MHz. Chronoamperometry experiments were conducted with a microelectrode (12.5 μm radius) in 50 mM potassium ferricyanide ($K_3Fe(CN)_6$) solutions with 100 mM potassium chloride (KCl) as the supporting electrolyte. The solutions were saturated with argon gas for 30 min and a blanket was maintained to prevent diffusion of O_2 into the solution. The microelectrode set-up consists of three electrodes namely, working (25 μm diameter Pt disc), reference and counter (500 μm diameter Pt wires) placed in a triangular fashion with a spacing of 0.4 cm between them [12]. High sampling rates (4 million samples/s) were achieved by using an oscilloscope (NI USB 5133) in tandem with a potentiostat (Gamry Interface 1000). Labview® and Diadem® software (National Instruments) were used to acquire and analyze the high sampling rate data. Pressure measurements in the megasonic tank were achieved by means of a hydrophone (HCT-0310, Onda Corp.). The hydrophone consists of pressure sensitive tip (diameter ~1 mm) which is acoustically isolated from the rest of the probe to localize the measurement. Data was collected as a function of time at sampling rate of 50 million samples/s using a similar setup as that for the chronoamperometry experiments. Discrete Fourier Transform (DFT) applied to the voltage–time data transformed it to frequency domain, which was further adjusted using the hydrophone calibration. Subsequently, hydroxyl radical (OH·) measurement experiments were conducted in dilute (1:10,000 by volume) NH_4OH (29%):DI water solution (pH = 8.7) containing 75 μM terephthalic acid (TA) using fluorescence spectroscopy (FluroMax 4, Horiba Inc.) [13]. The alkaline pH of the solution was necessary to achieve complete dissolution of TA. In the presence of applied megasonic field, the terephthalic acid reacts with the generated OH· to form 2-hydroxyterephthalic acid which under a suitable excitation field (318 nm) undergoes emission (425 nm). The fluorescence intensity was related to amount of OH· released using a calibration curve (shown in Fig. 1) generated by measuring fluorescence from aqueous solutions containing known concentrations of 2-hydroxyterephthalic acid.

3. Results and discussion

3.1. Cavitation behavior at 1 MHz

Fig. 2(a) and (b) show current as a function of time at an operating frequency of 1 MHz and two different power densities of 2 and 8 W/cm^2, respectively. The current data in the presence and absence of megasonic field in each plot are marked appropriately. It may be noted that in the absence of applied megasonic field, a baseline current of about −0.4 μA was observed. This baseline current pertains to the reduction of ferricyanide to ferrocyanide as per the following reaction (R1):

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-} \quad (R1)$$

In the presence of megasonic field, current peaks (or actually inverse current peaks) were observed. These peaks have been attributed to transient cavitation events [3]. It could be seen that as the power density was increased from 2 W/cm^2 to 8 W/cm^2, the number of current peaks and their magnitude increased. This observation is in agreement with the fact that the number of transient cavities increase with increasing power density. Further, to better understand the behavior of the bubble, the expanded time scale of typical current peaks is shown in Fig. 2(c) and (d). The rise and fall in current correspond to the diffusion of electroactive species from the imploding cavity towards the microelectrode. The rise and fall times for a transient cavity at 2 W/cm^2 were measured

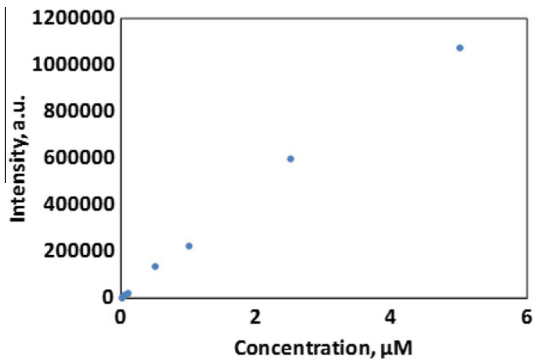

Fig. 1. Calibration curve for fluorescence intensity as a function of 2-hydroxyterephthalic acid concentration, excitation wavelength = 318 nm, emission wavelength = 425 nm, slit size = 2 nm.