



A novel way of detecting transient cavitation near a solid surface during megasonic cleaning using electrochemical impedance spectroscopy

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ABSTRACT

Megasonic energy assisted wet cleaning is traditionally used for removal of particulate contaminants from wafer and mask surfaces in semiconductor industry. One of the major issues associated with megasonic cleaning is the damage caused to fragile features due to transient cavitation. Development of a method to monitor transient cavitation events in solutions irradiated with sound energy will allow chemical formulators to fine tune the cleaning chemistry and acoustic field parameters for maximum cleaning efficiency without any feature damage. In this work, a method based on electrochemical impedance spectroscopy (EIS) measurements on a microelectrode has been found to be effective in detection of transient cavity collapses in solutions subjected to ~ 1 MHz sound field. Additionally, the technique also provides useful information about the diffusion boundary layer thicknesses in the presence and absence of megasonic field.

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1. Introduction

The use of megasonic energy for wafer and mask cleaning has been of interest to semiconductor industry for many years [1,2]. Although, megasonic cleaning offers the advantage of high particle removal efficiency (PRE), it has limited application due to feature damage. Two principle mechanisms, namely, acoustic streaming and cavitation are known to predominantly occur in solutions irradiated with sound field [3–5]. It is generally believed that both streaming and cavitation are instrumental in particle removal whereas cavitation is the main cause of damage to fragile features [3,6].

Two types of cavitation exist in solutions subjected to acoustic energy, stable cavitation and transient cavitation [7]. Stable cavitation, acting as a secondary sound source and leading to microstreaming, entails oscillations of bubbles about an equilibrium size for many acoustic cycles. Transient cavitation is characterized by large bubble size variations and eventual bubble collapse, which can be quite violent. This violent collapse, accompanied by extremely high temperature and pressure conditions, often leads to the formation of shock waves or liquid jets, depending on the distance between the collapsing cavity and the solid surface [8,9]. Both shock waves and liquid jets are believed to be responsible for feature damage [10,11]. In order to reduce damage while maintaining high PRE, it is important to significantly lower transient cavitation in clean-

ing solutions without affecting streaming forces. This can be achieved by monitoring transient cavitation events in solutions using a suitable in situ technique and tuning the sound field and liquid parameters that will minimize collapse of transient cavities.

Ashokkumar et al., used a multi-bubble sonoluminescence based technique for detection of stable and transient cavitation in aqueous solutions containing up to 100 mM of propanol or acetone irradiated with acoustic frequencies in the range of 20–440 kHz [12]. Their study revealed that stable cavitation is existent at low sound frequency of 20–37 kHz and transient cavitation can occur at high sound frequency of 440 kHz. In another study, high time resolution microelectrode based electrochemical (chronoamperometry) technique was used to characterize transient cavitation in aqueous solutions exposed to ultrasonic field (20–100 kHz) [13]. Measurement of reduction current of ruthenium (III) hexamine at a microelectrode (10 μm) was used to monitor transient cavitation. The results of this study showed that increasing the acoustic pressure amplitude from 0.8 to 1.7 atm at ~ 40 kHz of sound field increased the transient cavitation events from a few hundred to ~ 5000 events per second.

Keswani et al., measured frequency of transient cavitation events in DI water saturated with different dissolved gases (Ar, N₂, and CO₂) as a function of megasonic (~ 1 MHz) power density using cyclic voltammetry measurements on a 25 μm microelectrode [14]. It was reported that for Ar saturated solutions, the frequency of occurrence of transient cavitation (of certain collapse intensity) increased from ~ 5 to 65 in 10 s with increase in power density from 0.4 to 2 W/cm². Interestingly, when the experimental

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solution contained saturated levels of N_2 and CO_2 , respectively, the transient cavitation events reduced to 35 and 5 (in 10 s) at 2 W/cm^2 . A novel method based on measurement of cavitation noise using a hydrophone was shown to be effective in characterizing stable and transient cavitation at $\sim 1\text{ MHz}$ sound frequency generated in the power density range of $0.012\text{--}0.4\text{ W/cm}^2$ [15]. In this technique, the peak levels of $f/2$ and $2f$ harmonics in the cavitation noise spectrum were shown to be good indicators of stable cavitation while the cavitation noise power was representative of transient cavitation.

In this paper, an alternative method for detection of transient cavitation at $\sim 1\text{ MHz}$ of sound frequency is presented. The method is based on electrochemical impedance spectroscopy (EIS) measurements on a microelectrode in aqueous solutions containing an electroactive species such as potassium ferricyanide. Under reducing potentials for ferricyanide, when the applied AC frequency becomes comparable to the frequency of transient cavity collapses, the impedance values become unstable thereby revealing approximately the number of transient cavitation events occurring per unit time.

2. Materials and methods

Potassium ferricyanide ($K_3Fe(CN)_6$), and potassium chloride (KCl), were of high purity ($\geq 99.9\%$) and purchased from Sigma Aldrich. Platinum (Pt) wires ($\geq 99\%$ purity) were obtained from Goodfellow. Electrochemical Impedance Spectroscopy (EIS) measurements were conducted in aqueous solutions at $23 \pm 2^\circ\text{C}$ containing 0.1 M KCl and $0.05\text{ M K}_3\text{Fe(CN)}_6$ prepared using de-ionized (DI) water of resistivity $18\text{ M}\Omega\text{-cm}$. Prior to EIS measurements, the experimental solutions were de-oxygenated by bubbling with Ar gas ($\geq 99\%$ purity) for 30 min followed by keeping an Ar blanket over the surface of the solution. Removal of oxygen from solutions is necessary to prevent any interference with ferricyanide reduction and was confirmed by measuring the dissolved oxygen content using an oxygen sensor (Rosemount Analytical model 499A DO).

The three electrode set up used for EIS experiments consisted of $25\text{ }\mu\text{m}$ diameter disc as the working electrode (WE), and $500\text{ }\mu\text{m}$ diameter Pt wires 1 cm long as reference and counter electrodes (RE and CE). The three electrodes were enclosed in separate glass capillary tubes and arranged in a triangular manner. Pre-cleaning of Pt was done using reagent grade isopropyl alcohol (IPA) and flame heating to remove organic contaminants. Each of these steps was preceded by thorough DI water rinsing for 5 min and N_2 drying.

For electrochemical measurements, the electrode set-up was placed in a ProSys[®] cylindrical tank (volume $\sim 500\text{ ml}$) equipped with circular transducer (area 22.2 cm^2) that operates at $\sim 1\text{ MHz}$ sound frequency. The working electrode was positioned close to the center of the transducer at $\sim 2.0\text{ cm}$ above it. In cases of solutions exposed to megasonic energy, the transducer power density was set to 2 W/cm^2 and the mode of sound propagation was continuous, where the transducer was on for the entire measurement time. For cyclic voltammetry measurements, the potential was first scanned in the cathodic direction from open circuit potential (OCP) followed by reverse scan in the anodic direction and back to OCP at a rate of 20 mV/s . In chronoamperometry experiments, the working electrode was biased at -0.1 , -0.4 or -0.8 V potential and current was measured as a function of time at high sampling rate of 8 million samples per second. After about 0.5 s , transducer was switched on for $\sim 2\text{--}3\text{ s}$ at 2 W/cm^2 . The total time for measurement was about 4 s . National Instrument Labview 9.0 was used for acquisition of the data, which was processed for graphical output using DIAdem 2010. Single sine EIS experiments were

performed at -0.2 V overpotential bias by sweeping the frequency from 100 kHz to 0.1 Hz using an AC rms voltage of $\pm 10\text{ mV}$. The sampling rate was fixed at 10 points per decade of frequency, where number of cycles at each AC frequency ranged between 2 and 20 with more cycles at higher frequency. Average of impedance values collected for several cycles at each frequency was used. Commercially available software, ZView (Version 2.9c), was used to fit the data to an equivalent circuit and calculate values of the circuit parameters.

3. Results and discussion

Cyclic voltammetry experiments were first performed on Pt ($\sim 1\text{ cm}^2$) in deoxygenated 2 mM potassium ferricyanide solution to determine the redox potential of the ferricyanide/ferrocyanide couple. The results, in the form of a voltammogram, are shown in Fig. 1. As the potential is scanned from 0 V to negative values, ferricyanide species reduce to ferrocyanide and a reduction (cathodic) peak is observed at -0.26 V . During the reverse (oxidation) cycle, when the ferrocyanide oxidizes to ferricyanide, an oxidation (anodic) peak occurs at -0.16 V . A peak separation of 100 mV , which is larger than 59 mV difference typically seen for a reversible redox reaction, indicates the behavior of the ferricyanide/ferrocyanide couple to be quasi-reversible, as also reported in the literature [16]. The redox potential, calculated from the mean of peak cathodic potential and peak anodic potential, was found to be approximately -0.2 V .

Additionally, chronoamperometry experiments were also performed at various bias potentials of -0.1 , -0.4 V and -0.8 V . The microelectrode set up consisting of $25\text{ }\mu\text{m}$ Pt working electrode was used. The solution contained 50 mM potassium ferricyanide and 100 mM KCl , which was deaerated by bubbling Ar gas. The sequence of events was as follows. The microelectrode was subjected to a suitable potential for a total period of 4 s . During first 0.5 s of applied potential, no megasonic field was applied. After this time, the solution was irradiated with $\sim 1\text{ MHz}$ sound field at 2 W/cm^2 for $2\text{--}3\text{ s}$. Current was measured at 8 million samples per second for entire 4 s . The results are shown in Fig. 2. As can be seen in the case of applied potential of -0.8 V , the baseline current in the absence of megasonic field is $\sim 0.3\text{ }\mu\text{A}$. This current increases to $\sim 0.45\text{ }\mu\text{A}$ with current 'peaks' superimposed on it upon application of the megasonic field. The increase in baseline current has been attributed to enhanced diffusion due to acoustic streaming where as current 'peaks' are a result of transient cavitation. These have been discussed in detail elsewhere [14,17]. As the applied potential reduces to -0.4 V , there is no measurable difference in the baseline current or other features in the chronoamperometry

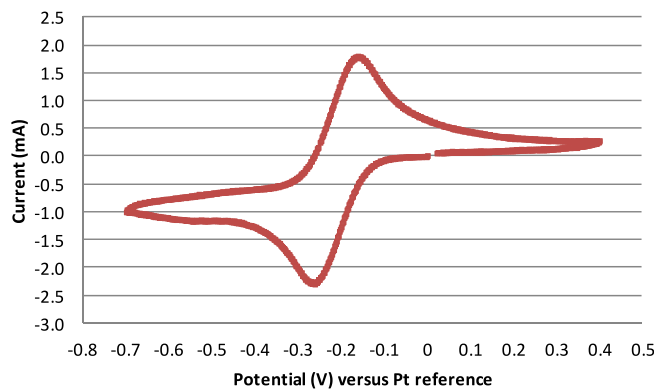


Fig. 1. Cyclic voltammetry on Pt ($\sim 1\text{ cm}^2$) in deoxygenated 2 mM potassium ferricyanide solution containing 0.2 M KCl solution at a scan rate of 20 mV/s . Pt used as the reference and counter electrode.

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