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Electrochemical investigations of stable cavitation from bubbles generated during reduction of water

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ABSTRACT

Megasonic cleaning is traditionally used for removal of particles from wafer surfaces in semiconductor industry. With the advancement of technology node, the major challenge associated with megasonic cleaning is to be able to achieve high cleaning efficiency without causing damage to fragile features. In this paper, a method based on electrochemistry has been developed that allows controlled formation and growth of a hydrogen bubbles close to a solid surface immersed in an aqueous solution irradiated with ~1 MHz sound field. It has been shown that significant microstreaming from resonating size bubble can be induced by proper choice of transducer duty cycle. This method has the potential to significantly improve the performance of megasonic cleaning technology through generation of local microstreaming, interfacial and pressure gradient forces in close vicinity of conductive surfaces on wafers without affecting the transient cavitation responsible for feature damage.

1. Introduction

Megasonic cleaning is one of the common techniques used for removal of particles from wafer surfaces in semiconductor industry [1,2]. However, with the advancement of technology node to 22 nm and lower, the feature size is becoming increasingly small and fragile while the requirements for cleaning are becoming more stringent [3]. In order to be able to continue the use of megasonic technology for wafer cleaning, it is essential to identify new cleaning mechanisms that will allow high particle removal without causing damage to fine features.

During megasonic exposure of liquids, two primary phenomena/mechanisms are known to exist, namely, acoustic streaming and cavitation [4–6]. Acoustic streaming is the time independent motion of a fluid due to viscous attenuation and can be classified into four different types: Eckart streaming, Schlichting streaming, Rayleigh streaming, and Microstreaming [7]. In acoustic cavitation, bubbles form and grow in size by rectified diffusion or coalescence driven by either primary or secondary Bjerknes forces [8]. Some bubbles continuously oscillate for many acoustic cycles (stable cavitation) while others collapse (transient cavitation) typically in less than one cycle. Microstreaming, which is a consequence of large oscillations of stable bubbles, can cause significant fluid flow surrounding the bubbles [9]. It is generally believed that microstreaming plays an important role in removal of particles during megasonic cleaning of wafers while feature damage is primarily caused by transient cavitation [9,10]. Development of an effective megasonic cleaning process that can achieve high particle removal efficiency (PRE) with minimum damage is possible through enhancement of microstreaming, interfacial and pressure gradient forces [11] without affecting transient cavitation.

There have been several studies in the past that have focused on understanding the behavior of stable and transient cavities and their associated physical and chemical effects [12–15]. Birkin et al. investigated the growth of a 2 mm radius bubble due to rectified diffusion as well as mass transfer from microstreaming using an acoustoelectrochemical technique employing a 25 μm Pt microelectrode [15]. The bubble radius growth rate was determined to be ~0.03 μm/s in aerated potassium ferricyanide containing aqueous solutions irradiated with a sound field of 2.08 kHz at 51.74 Pa. In another study using a 25 μm Pt microelectrode, Maisonhaute et al. examined single bubble oscillatory behavior in aqueous solutions subjected to 500 kHz sound frequency at power density of 1.4 W/cm^2 [16]. The current transients consisting of ‘peaks’ with life times of a few milliseconds observed during high time resolution chronoamperometry measurements were attributed to flux of ferricyanide species towards the electrode surface from microstreaming resulting from oscillations of stable bubbles . At lower sound frequency of 20 kHz, bubbles of sizes up to 0.8 mm oscillating at harmonics of driving frequency were observed [17,18]. It was suggested that the shape of the bubbles was hemispherical

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rather than spherical and the bubbles exhibited transient as well as quasi-stable cavitation behavior. Other studies conducted using microelectrodes (6–25 μm) in the ultrasonic frequency range (20–100 kHz) have shown that mass transfer induced by transient cavitation is much higher than that by acoustic streaming [19,20]. Keswani et al. characterized transient cavitation under ~1 MHz sound field using high time resolution cyclic voltammetry and chronoamperometry techniques in aqueous solutions containing additives such as dissolved gases (Ar, N_2 or CO_2) or non-ionic surfactants (Triton X®-100 or NCW®-1002) [21,22]. Their results revealed that dissolved Ar and non-ionic surfactants increase the intensity of transient cavity collapses while dissolved CO_2 significantly reduces it.

As can be noticed from aforementioned studies, most of the work in literature has been directed towards understanding the role of acoustic cavitation and streaming during sonic exposure of liquids. In order to enhance the performance of megasonic processes for wafer cleaning, it is important to not only develop fundamental understanding of current cleaning mechanisms but also devise new methods that will likely improve cleaning. In the current work, electrochemical investigations of microstreaming in aqueous solutions have been carried out using a Pt microelectrode *at potentials where water reduction occurs*. Under these conditions, significant microstreaming from oscillating hydrogen bubbles (depending on the transducer percent duty cycle) was observed as indicated by current 'transients' during chronoamperometry measurements. This technique can benefit the semiconductor industry through its further development for improved megasonic cleaning of conductive surfaces. Although, the micro-electrode based electrochemical set-up used in our experimental investigations offers the major advantage of detecting single bubble activity in a multi-bubble environment, it can't be used for monitoring multiple bubbles at the same time (which requires an array of micro-electrodes).

2. Materials and methods

High purity (99.9%) chemicals (potassium ferricyanide ($K_3Fe(CN)_6$) and potassium chloride (KCl)) were purchased from Sigma Aldrich. Platinum wires (99%) were procured from Goodfellow. The electrode set up, pre-cleaning procedures and placement of electrodes in the megasonic system used for the experiments have been described elsewhere [21]. The electrodes were positioned facing down parallel to the transducer surface. The transducer power density was fixed at 2 W/cm^2 while percent duty cycle was varied between 10% and 100% for 5 ms pulse time [22]. Aqueous solutions containing 0.1 M KCl with and without 50 mM ($K_3Fe(CN)_6$) were prepared using high purity de-ionized (DI) water of resistivity 18 Mohm-cm. Ferricyanide, being an electroactive species, is used as an electrochemical probe in this study to monitor the bubble behavior. The experimental solutions were saturated with Ar gas by bubbling for 30 min and keeping the Ar blanket over the liquid surface during the measurements. The removal of dissolved O_2 was confirmed by measuring the oxygen level using an oxygen sensor (Rosemount 152 Analytical model 499A DO).

Chronoamperometry experiments were conducted using a function generator Agilent 33250A with a custom built potentiostat equipped with positive feedback ohmic drop compensation (constructed by Mike Read, ChIEF, University of Arizona) described in [23]. Measurements were performed with and without application of potential at −2 V (*versus Pt reference or −1.4 V versus standard hydrogen electrode (SHE)*) in the absence and presence of megasonic field at ~1 MHz. The data were acquired at a high sampling rate of 8 MHz using an oscilloscope (NI USB-5133). NI LabVIEW 9.0 and DIAdem™ 2010 were used for data acquisition and graphical processing, respectively.

3. Results and discussion

A first set of experiments was carried out using Ar saturated aqueous solutions containing 0.1 M potassium chloride and no ferricyanide. The results are shown in Fig. 1(a) where the *y*-axis represents current and *x*-axis depicts time. The first 0.5 s of data was collected without any applied potential and megasonic energy. During this time, no current was measured. After 0.5 s, a potential of −2.0 V (*versus* Pt) was applied to the working electrode (25 μm) at which time the current shoots up to a steady or limiting value of 20–25 μA. Since the applied potential is far more negative than the standard reduction potential of water (−0.83 V), the limiting current may be attributed to reduction of water to hydrogen gas and hydroxyl ion. Upon application of megasonic field at 100% duty cycle (DC) after 1 s of applied potential, the limiting current shows 'valleys' superimposed on it.

Fig. 1(b) displays examples of these current 'valleys' with expanded time scale. The fall or dip times of 'valleys' range from 8 μs to 0.3 ms with majority of them occurring between 0.1 and 0.3 ms time scale while the rise was found to vary from 0.1 to 0.3 ms. We interpret the fall in current as possibly due to the formation and growth of hydrogen bubbles in the close vicinity of the electrode surface. Due to continuous generation of hydrogen gas at the electrode surface, there is enough gas available to form and grow oscillating bubbles by rectified diffusion [24]. It is to be noted that the bubble may not be composed of only hydrogen gas but may also partly contain the gas that is dissolved in the liquid as will be evident from the results in the later sections. As the bubbles grow, they mask the electrode surface, which causes the current to fall. After some time, bubbles have grown to sizes that exceed the acoustic boundary layer thickness and are swept away from the electrode surface due to the liquid flow from acoustic streaming and the current recovers to the limiting value. After the megasonic field is switched off at ~3.5 s, the current 'valleys' no longer appear on the limiting current. When the megasonic field is applied at 10% duty cycle, the current–time data, illustrated in Fig. 1(c), shows mostly noise in current and hardly any current 'valleys'. At 10% duty cycle, the screening of the electrode due to hydrogen bubbles may not be efficient enough due to the formation of (a) a smaller number of bubbles close to the electrode surface and (b) not enough time for the bubbles to grow beyond the resonating size (~3.8 μm radius at ~1 MHz sound frequency) by rectified diffusion. In this case, since the area blocked by few small bubbles is much smaller than the electrode area, it does not lead to any measureable drop in current.

Fig. 2(a) through (f) show the effect of addition of potassium ferricyanide on the measured current at different percent duty cycle (for fixed pulse time of 5 ms) for Ar saturated aqueous KCl solution irradiated with megasonic field. In all these cases, the working electrode was biased at −2.0 V (*versus* Pt reference) throughout the experiment. Firstly, the current is measured in the absence of megasonic field for <1.6 s, then the megasonic field is turned on for 2 s followed by last ~0.5–1 s of current measurement again in the absence of megasonic field. The limiting current in the absence of megasonic field was approximately constant at 20–25 μA, as in the previous case with no ferricyanide, indicating that the current due to ferricyanide reduction (measured to be 0.3 μA in [22]) is negligible compared to that due to water reduction.

At 10% duty cycle, corresponding to the transducer on and off times of 0.5 and 4.5 ms, respectively, the results shown in Fig. 2(a) and (b) indicate current 'peaks' riding on the limiting current. These current 'peaks' exhibit a rise time of 0.5 ms (same as the transducer on time) and fall time of <1 ms. The maximum current reached by peaks is ~85 μA with many peaks