A Sono-Electrochemical Technique for Enhanced Particle Removal from Tantalum Surfaces

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Low power megasonics is of interest to semiconductor cleaning community due to minimal feature damage. In this work, megasonic field at low power density in conjunction with electrochemistry is used for enhanced removal of silica particles from tantalum wafers. Cleaning studies were conducted in air or argon saturated aqueous solutions at $0.5\,W/cm^2$ in the absence and presence of applied potentials of $-1.5\,V$ or $-2.0\,V$ to tantalum (vs Ag/AgCl). The improvement in particle removal efficiency is attributed to oscillating hydrogen bubbles formed from water reduction in vicinity of tantalum surface and grown to a resonant size under suitable acoustic conditions.
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Moore's law dictates that the number of transistors on a chip should double every two years. As the demand for number of transistors on the chip increases, the cleaning requirements become more and more stringent due to the decreasing size of the features. With the advent of megasonic cleaning processes in the late 70's, researchers at RCA labs[1,2] created a breakthrough in identifying a new and powerful technique that could meet the growing cleaning requirements. The principle behind using a megasonic field was that it could significantly enhance particle removal by means of physical forces generated as a result of acoustic streaming and cavitation. Acoustic streaming refers to a steady flow of fluid generated by viscous attenuation of the sound waves whereas cavitation is the phenomenon in which bubbles either oscillate over several cycles (stable cavitation) or collapse typically in less than a few cycles (transient cavitation). Although, both stable and transient cavitation aid in the removal of particles through microstreaming and shock waves/microjet formation respectively, the disadvantage of exploiting transient cavitation for cleaning is that it causes significant damage to thin and fragile features. Over the years, megasonic cleaning processes in semiconductor industry have constantly evolved through investigations of various parameters such as cleaning chemistries, dissolved gases,[3] sound field frequency,[4] transducer power density, particulate contaminant size and aspect ratio of trenches[5,6] on particle removal efficiency.

Karimi et al.[5] studied the removal of polystyrene latex (PSL) nanoparticles from micrometer and sub-micrometer size trenches with aspect ratio of 1, by varying the megasonic power and cleaning time. It was shown that at $\sim1\,MHz$ sound frequency and $8\,W/cm^2$ of megasonic power density, the removal efficiency of polystyrene latex particles reduced from ~95 to 25% as the trench width decreased from 2 to $0.2\,\mu m$. The results also indicated that particle removal efficiency was more sensitive to megasonic power density than cleaning time and decreased significantly as megasonic power was reduced. Although, by using elevated levels of megasonic power density, significant particle removal can be achieved, higher power density also results in damage to fragile features.[9]

From the use of traditional ammonia-peroxide mixture (APM)[1] for particle removal to chemistries employing salts, dissolved gases, surfactants and solvents have been discussed in detail by researchers till date.[5–8] Keswani et al.[8] have shown that the presence of a simple electrolyte such as KCl could enhance PRE in a megasonic field. This enhancement in PRE was attributed to a combined effect of electroacoustic forces and increased cavitation generated due to the propagation of sound waves in an ionic solution. It was shown that electroacoustic forces dominated at lower concentrations of KCl ($\leq0.01\,M$) while at higher concentrations, forces due to cavitation in addition to electroacoustic forces aided in particle removal.

Other authors have established that the presence of dissolved gases assists in not only increasing the particle removal efficiency but also in reducing damage caused to the small features.[3,9] Hagimoto et al.[3] showed that cleaning efficiency and damage depends on concentrations of dissolved gases such as N_2, O_2 and CO_2 in conventional APM mixtures. At transducer powers of 200 and 600 W, a significant number of pattern collapses (~200 counts) and lower PRE ($<50\%$) was measured for low concentrations of dissolved N_2 (2 ppm) and O_2 (5 ppm). When higher concentrations of N_2 (16 ppm) and O_2 (20 ppm) were used, negligible pattern collapses and higher PRE ($>70\%$) were observed. They attributed enhanced cleaning and reduced damage to the cushioning effect provided by dissolved gases at higher concentrations. Kumari et al. conducted a systematic study on damage to high-k metal gate test structures (consisting of HfO_2/AlO, TiN and Si layers) in air or CO_2 containing DI water for a range of transducer power densities (0–3 W/cm^2) at 0.93 MHz of megasonic frequency.[9] The study revealed that breakage of lines was a strong function of power density and type of gas dissolved. Other studies have directed their efforts on optimizing the megasonic process for maximum cleaning performance and lowering damage by controlling the amount and type of dissolved gas in the cleaning solution and modulating the power density.[10,11] In order to be able to continue the use of megasonic technology for wafer and mask cleaning, it is essential to identify new cleaning mechanisms that will allow enhanced particle removal at lower power densities from different surfaces used in silicon industry.

Although various megasonic cleaning methods have exploited optimization of parameters like cleaning chemistries and use of electrolyte/dissolved gases,[9] they all demand high power densities of up to 5 W/cm^2 for achieving effective particle removal. Unfortunately, use of high power densities also causes damage to features. Therefore, there still exists a need for a megasonic cleaning technology that can achieve high particle removal at low power densities. In the current paper, a novel sono-electrochemistry based technique has been shown to be effective in improving the removal of silica particles from tantalum surface at a low power density of $0.5\,W/cm^2$. The choice of percent duty cycle of 10% for pulse time of 5 ms and megasonic frequency of $\sim1\,MHz$ was based on the previous work of the authors where it was shown that stable hydrogen bubbles of resonating size oscillating with high amplitude and generating strong microstreaming forces are formed in close vicinity of a solid conductive surface under suitable electrochemical and megasonic conditions.[12] Microstreaming force in the vicinity of surfaces can be extremely beneficial in removing particulate contamination and achieving high cleaning efficiency at low megasonic power densities.

Materials and Methods

Deionized water of 18 MΩ-cm resistivity was used for all experiments. Semiconductor grade isopropyl alcohol (IPA) was purchased from Sigma Aldrich Inc. VLSI grade ammonium hydroxide (NH_4OH), hydrogen peroxide (H_2O_2) and hydrofluoric acid (HF) were purchased

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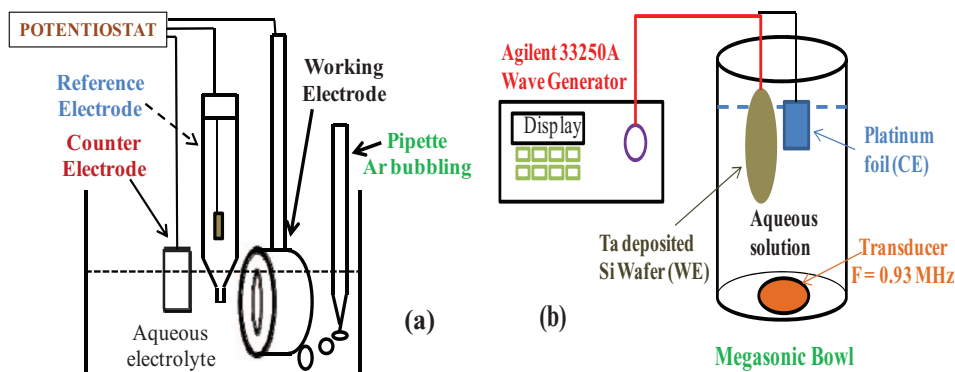
Figure 1. Experimental setup for (a) electrochemical measurements and (b) cleaning experiments.

from Honeywell Inc. BioXtra grade (>99%) potassium chloride was procured from Sigma Aldrich Inc. Silica microspheres (10%, wt.) of mean size 300 nm were obtained from Polysciences Inc. Tantalum films (400 nm) deposited onto 2″ p-type doped blanket silicon wafers (5–10 mΩ-cm) were procured from Addison Engineering Inc. Platinum foil (99.999%) used as counter electrode was purchased from Alfa-Aesar. Standard Ag/AgCl (sat KCl) electrode was used as reference. Ultra high purity argon (99.999%) gas was used to deoxygenate the DI water/KCl solutions used in experiments.

Pre-cleaning of the Ta films was performed using IPA for 1 min, followed by SC-1 (1: 1: 50) and HF (1:100) treatments for about 5 min and 30 seconds, respectively. For the electrochemical experiments, the Ta samples were diced into 1×1 cm size to accommodate them in the dip cell made of Teflon, as shown in Figure 1a. The electrochemical setup consisted of a glass vessel (∼250 mL) sealed with a rubber stopper with provision for inserting the electrodes (Fig. 1a). The working electrode, reference electrode (Ag/AgCl, sat KCl), counter electrode (Pt foil) and the pipette (for Ar bubbling) were inserted through the holes in the rubber stopper. Contact to the Ta face was established by means of gallium-indium eutectic coating on the silicon side. The Ar bubbling was performed for 30 min to remove dissolved oxygen and a blanket of the gas was maintained above the liquid surface just prior to the experiment. Electrochemical experiments were performed using a potentiostat Gamry Interface 1000. Cathodic polarization experiments were carried out at a scan rate 1 mV/sec.

For cleaning experiments, the Ta surface was contaminated by dispensing 1 mL of the sonicated 300 nm silica microsphere (0.001%, wt.) dispersion of pH 5.8 onto the rotating sample. Zetasizer nano ZS (Malvern Instruments) was used to determine the mean particle size and zeta potential of SiO_2 particles in DI water. The measured particle size and zeta potential were about 293 ± 25 nm and -51.2 mV, respectively. The blanket Ta wafer was viewed and imaged under the microscope (Leica DM 4000 M) before and after contamination and after cleaning. The particles were counted by using ImageJ software. After counting the number of particles deposited, the samples were aged for about 24 hours. PRE studies were then conducted the following day by varying the different process parameters for constant cleaning time of 60 s. Figure 2 shows an example of microscope im-

ages of Ta surface at 500x magnification before contamination, after contamination and after cleaning under specific condition. The number of particles as counted using the ImageJ was zero, 150 and 65, respectively on the measured area of 0.02 (0.14 × 0.14) mm^2.

The setup for PRE experiments is shown in Figure 1b. For all megasonic experiments, the power density, duty cycle and pulse period were fixed at 0.5 W/cm^2, 10% and 5ms, respectively. The values for these parameters were adjusted based on the settings provided by the megasonic tool manufacturer. The sound field was assumed to be uniform across the entire sample surface during cleaning. The electrochemical potential was applied by means of Agilent 33250 A wave generator shown in Figure 1b.

Results and Discussion

In the first step, cathodic polarization experiments were performed to identify the range of potential where water reduction occurs to form hydrogen gas. Based on these measurements, a suitable potential condition was identified and used later in megasonic cleaning experiments to determine its effect on removal of particles from Ta surface.
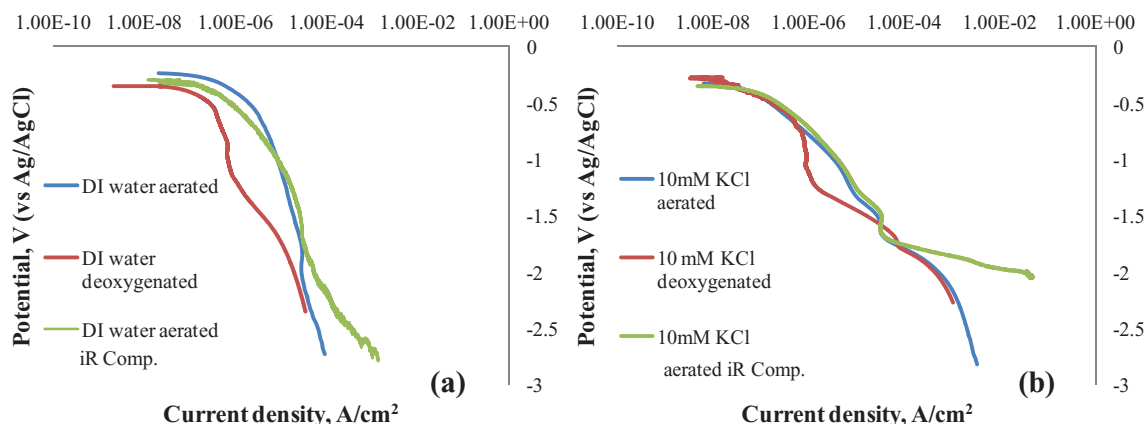
Cathodic polarization.— In Figure 3, the cathodic polarization of Ta film in deoxygenated DI water and 10 mM KCl solution is displayed. From this plot, it can be seen that the open circuit potential of Ta in either of the solutions was about -0.35 V (vs Ag/AgCl). As the potential is scanned in the negative direction for deoxygenated solutions, the current density initially increases slowly and then attains a limiting value in the potential range of -0.5 and -1.0 V. This limiting current density was not observed for aerated solutions. After about -1 V (vs Ag/AgCl) the current density increases more prominently until about -2 V (vs Ag/AgCl) possibly indicating the reduction of water according to the following reaction,

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2OH^-_{(aq.)}; \qquad E^\circ = -0.83\,V$$
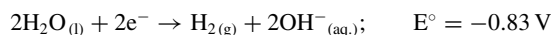
It can also be seen that in the potential range of -1 to -2 V, the slope of the current density curve for 10 mM KCl solution is greater than that for pure DI water. This is indicative of the fact that there
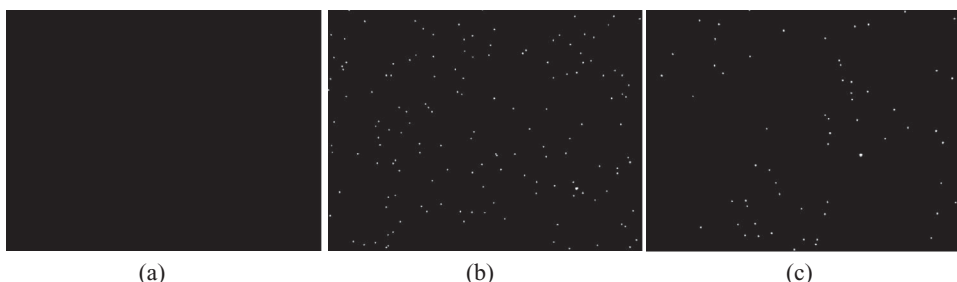
Figure 2. Microscope images of Ta sample (a) before contamination with SiO_2 particles, (b) after SiO_2 contamination (∼150 particles) and (c) after cleaning (∼65 particles).

Figure 3. Cathodic polarization plots for Ta deposited Si wafers in (a) deoxygenated and aerated DI water and (b) deoxygenated and aerated 10 mM KCl solution, Scan rate = 1 mV/sec.

is likely a greater generation of H_2 owing to the greater conductivity of the KCl solution. Therefore, from the cathodic polarization plot, the favorable conditions for performing particle removal studies were considered to be in the potential range of −1 to −2 V (vs Ag/AgCl). Further, since no significant difference in current density was measured in −1 to −2 V potential range for aerated solutions with and without iR compensation, all cleaning experiments were conducted without any iR compensation.

Particle removal studies.— The SiO_2 contaminated Ta wafers were subjected to a series of cleaning experiments wherein the effect of various parameters such as dissolved gases (Ar and air), power density $(0.5 \, W/cm^2)$ and applied potential (−1.5 V and −2 V, vs Ag/AgCl) were investigated and the results obtained are discussed below.

Figure 4a shows a plot of particle removal efficiency under different cleaning conditions. The power density was fixed at a low value of $0.5 \, W/cm^2$ and the applied potential was −1.5 V (vs Ag/AgCl). The reason for having the duty cycle of only 10% at 5 ms was two fold. The first reason is based on our previous experiments where it was shown that under these conditions of applied negative potential and duty cycle, hydrogen bubbles that are formed close to the conductive surface grow to a resonant size of 7 μm and generate significant microstreaming forces.[12] Secondly, low duty cycle of 10% for pulse time of 5 ms significantly reduces the occurrence of transient cavitation that is known to cause damage to features during megasonic cleaning.[13] From Figure 4a, it can be seen that for Ta wafers in the presence of a megasonic field, the PRE in the absence and presence of an applied potential was about 55% and 75%, respectively in Ar saturated DI water. This increase in PRE can be explained as follows. When a potential of −1.5 V (vs Ag/AgCl) is applied to the Ta surface, hydrogen gas is generated in-situ due to the reduction of water. In the

presence of megasonic field, hydrogen gas is stabilized in the form of oscillating bubbles in close vicinity of the Ta surface. The higher PRE is most likely an effect of significant microstreaming resulting from these oscillating hydrogen bubbles. The same effect was observed in the case of DI water saturated with air.

In may also be noticed from Figure 4a that the PRE in Ar saturated water was higher by 25% than that in air saturated water under the applied potential condition. It is known that intensity of transient cavity collapse is higher in Ar saturated solution than that in air saturated solution.[14] This is because of the higher value of the polytropic index (ratio of specific heat at constant pressure to that at constant volume) of argon (1.67) compared to that of air (1.4). The increase in PRE may possibly be attributed to slightly higher intensity of transient cavitation in Ar saturated solution, which adds to the removal of particles due to the microstreaming effect. When the experiments were carried out in megasonic irradiated 10 mM KCl solutions saturated with Ar, the PREs in the absence and presence of applied potential of −1.5 V (vs Ag/AgCl) were ∼75 and 95%, respectively. The enhanced particle removal is likely due to the electro-acoustic effect[8] that originates in the presence of an electrolyte and higher generation of hydrogen gas (compared to that in DI water) when the potential (−1.5 V) is applied.

Figure 5 shows the comparison of particle removal efficiencies in Ar saturated DI water when a more negative potential of −2 V (vs Ag/AgCl) was applied both in the absence and presence of a megasonic field ($0.5 \, W/cm^2$, 10% duty cycle). Particle removal efficiency as high as 98% was achieved in the presence of applied potential of −2 V (vs Ag/AgCl) and low energy megasonic field clearly demonstrating the usefulness of this work in cleaning of patterned wafers. The reason for increase in PRE with increase in applied potential from −1.5 to 2.0 V (vs Ag/AgCl) for Ar saturated (deoxygenated) DI water is due to higher generation of hydrogen gas (and the corresponding
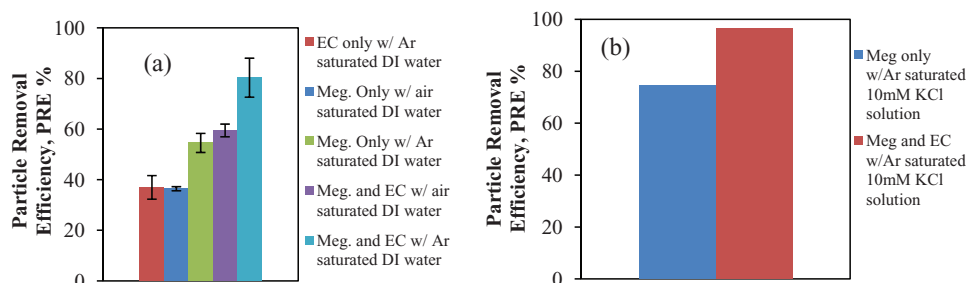
Figure 4. Particle removal efficiency of SiO_2 particles from tantalum blanket wafers in deoxygenated (a) DI water and (b) 10 mM KCl solution; Power density = $0.5 \, W/cm^2$ at 10% duty cycle, electrochemical potential = −1.5 V (vs Ag/AgCl).
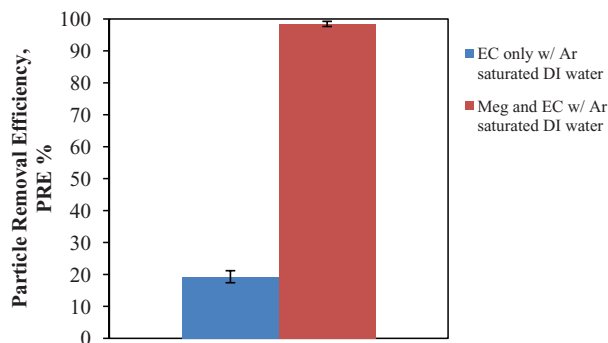
Figure 5. Effect of higher applied potential (-2 V, vs Ag/AgCl) on PRE, Power density $= 0.5$ W/cm^2, Duty cycle $= 10\%$, Ar saturated DI water.

level of microstreaming) as indicated by an order of magnitude higher current at -2.0 V compared to that at -1.5 V (Figure 3a).

Conclusions

A novel sono-electrochemistry based technique was found to be effective in enhanced removal of silica particles from tantalum deposited silicon wafers. Particle removal efficiency of $\sim$98% was achieved in Ar saturated DI water irradiated with low megasonic power density and duty cycle of 0.5 W/cm^2 and 10% respectively under applied potential of -2.0 V (vs AgCl). The technique will be of significant advantage in megasonic cleaning of conductive surfaces on patterned wafers without any feature damage.

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