Chemically controlled megasonic cleaning of patterned structures using solutions with dissolved gas and surfactant

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A B S T R A C T

Acoustic cavitation is used for megasonic cleaning in the semiconductor industry, especially of wafers with fragile pattern structures. Control of transient cavitation is necessary to achieve high particle removal efficiency (PRE) and low pattern damage (PD). In this study, the cleaning performance of solutions with different concentrations of dissolved gas (H2) and anionic surfactant (sodium dodecyl sulfate, SDS) in DIW (DI water) on silicon (Si) wafers was evaluated in terms of PRE and PD. When only DIW was used, PRE was low and PD was high. An increase in dissolved H2 gas concentration in DIW increased PRE; however, PD also increased accordingly. Thus, we investigated the megasonic cleaning performance of DIW and H2-DIW solutions with various concentrations of the anionic surfactant, SDS. At 20 ppm SDS in DIW, PRE reached a maximum value and then decreased with increasing concentration of SDS. PRE decreased slightly with increasing concentrations of SDS surfactant when dissolved in H2-DIW. Furthermore, PD decreased significantly with increasing concentrations of SDS surfactant under different chemical conditions. We developed a hypothesis to explain the change in bubble characteristics under different chemical environmental conditions.

1. Introduction

Numerous methods including laser-induced shockwave cleaning, carbon dioxide (CO2) snow cleaning, wet cleaning, megasonic cleaning, etc to remove particles from wafer surfaces during the manufacture of semiconductor devices have been developed [1–3]. As the size of the particles decreases, it becomes more difficult to remove them using any of these methods. In general, as particle size decreases, the distance between the particle and substrate decreases, this causes the increasing in adhesion force. Therefore, it significantly affects the particle removal efficiency (PRE). Hence to remove nanoparticles usually physical methods are used, however they cause excess material loss due to undercut and so not preferred for semiconductor process. Physical forces such as megasonics are preferable. However, if the particles are too small, some chemical effect is required in combination with physical forces. Hence removing the nano particles is a challenging to find suitable conditions for megasonics. This is further complicate to remove them from delicate and nanometer-scale patterned structures and 3D printing objects [4]. Any kind of physical contact would cause the damages to the structures. Megasonic cleaning is a non-contact cleaning process that can remove particles, even from trenches. However, control of pattern damage is also necessary due to the strong physical force, i.e. cavitation, induced during megasonic cleaning of patterned structures. Various parameters including megasonic power, frequency, and ultrasound pulses affect the cavitation phenomenon and therefore influence the characteristics of bubbles and their sizes [4]. Regardless of whether low-frequency or high-frequency ultrasound is irradiated, cavitation; bubbles can oscillate either in a stable manner (with microstreaming [5]...
or transient manner (with violent collapse, re-entrant jet formation and bubble fission). The difference caused by the ultrasound frequency is the size of bubbles under resonance [6] the bubble size for the case of megasonic waves is on the order of microns, while that for the case of lower-frequency (0–10 kHz) ultrasound is on the order of sub-millimeters. If water contains heterogeneous bubble nuclei of sub-millimeter size, low-frequency ultrasound can trigger cavitation bubble nucleation more easily. For the case with transient cavitation, violent bubble collapse (often with re-entrant jet formation) will give rise to surface damage. This is why the use of deagassed water is recommended for low-frequency ultrasonic cleaning, traditionally speaking; however, this will give rise to low cleaning efficiency [7]. The similar scenario may hold for the case of megasonic cleaning. In the case of higher frequency, the resonant size of bubbles gets smaller with thermal and viscous dampings being more effective [8]. This will contribute to more stable oscillations and thus to less erosive surface cleaning. In the context of silicon wafer cleaning, megasonic cleaning with minimal cavitation erosion is favoured. However, these parameters influence physical forces in the same manner such that both PRE and PD are affected. The exact mechanism of cleaning by cavitating bubbles is still under discussion. Some key factors such as dissolved gases, surfactants, and solutes are thought to play key roles in cavitation [2,3,9,10].

It is well known that overcoming adhesive forces, mainly the van der Waals force, electrostatic, and covalent forces between the surface and contaminants results in physical cleaning [11,12]. Formation of gas bubbles in liquid and the removal of contaminants from surfaces by acoustic cleaning have been studied extensively. The cleaning process that occurs as a result of acoustic cavitation determines megasonic cleaning performance [13]. This can be achieved by controlling the bubble dynamics to cause stable cavitation and transient cavitation. Stable cavitation could produce particle removal forces, whereas transient cavitation could produce damaging forces. Some researchers suggest increasing the bubbles near the objects to be cleaned by the physical methods such as reducing frequency [4]. However, modifying the chemical environment is more preferable, because adding chemical components (dissolved hydrogen and surfactant) could make the bubbles more stable maintain the required frequencies. And also, optimizing the chemistry is easier than the optimization of physical parameters of megasonic systems. It has been reported that the cavitation intensity can be greatly intensified with the addition of dissolved gases and in our previous experimental results also it was observed that the addition of H₂ gas to DIW improved the cavitation intensity greatly [14,15]. To reduce this higher cavitation, we utilized the characteristics of surfactants to reduce the cavitation. These may also cause a reduction in surface tension to improve acoustic streaming, however, but this effect is less significant compared to the cavitation effect. The sound field created during megasonic cleaning has a direct relation to the interaction between cavitating bubbles and residue particles attached to the surface [16]. However, the exact mechanism of particle removal due to acoustic forces is not yet clear [17]. Water is usually used as a cavitating medium. A variety of surfactants have also been proposed to be effective for the megasonic cleaning process. Lee et al. studied the effect of the addition of surface-active solutes on the coalescence and clustering of bubbles. They focused mainly on the dynamic behavior of bubbles under the influence of SDS surfactant using a high-speed camera [18]. Furthermore, the size variation and stability of bubbles in response to the addition of surface-active solutes (SDS) and electrolytes (sodium chloride) were discussed [19]. When the concentration of SDS was increased, the size of bubbles decreased. Anionic surfactants like SDS generally enhance the stability of microbubbles. However, the stability of microbubbles also depends on the composition and physiochemical properties of the aqueous solution of SDS. Similarly, the agglomeration of bubbles as a function of surface-active solutes during ultrasonication was studied by a visualization technique [20]. The size of bubbles and their agglomeration play key roles in megasonic cleaning. The effects of surface-active solutes, aliphatic alcohols, amines, and carboxylic acids on the growth of bubbles exposed to ultrasound have also been investigated [21]. Two main mechanisms, viz. rectified diffusion and Bjerknes forces affect the rate of acoustic bubble growth. Rectified diffusion involves the exchange of mass between gas and the interface of the bubble, which determines the growth of bubbles [22–24]. Crum proposed the first equation to describe the rectified diffusion process and demonstrated its validity under isothermal and adiabatic conditions [25,26]. In addition to the rectified diffusion process, various forces also act on bubbles in a sound field, which are referred to as primary Bjerknes forces. In addition to primary Bjerknes forces, secondary Bjerknes forces that appear between neighboring oscillating bubbles are also important, as they cause oscillation of bubbles and thus a change in bubble size and distribution. These Bjerknes forces attract and repulse individual bubbles at antinode positions in addition to mutual attraction and/or repulsion of air bubbles [27]. In addition to surfactants, the influence of various gases dissolved in water such as H₂, N₂, Ar, etc. on the growth of bubbles under megasonic and ultrasonic waves has been reported [15,28]. The concentration of gas dissolved in DIW plays a dominant role in determining cavitation type and the intensity of cavitation.

Several recent studies have demonstrated undesirable damage to nano-sized pattern structures during cleaning [16,29]. Kim et al. investigated the mechanism of particle removal from solid surfaces by the oscillation of microbubbles during megasonic cleaning using a direct visualization process. They observed that not only particles were removed during the cleaning process, but pattern damage (PD) also occurred. The involvement of transient and inertial bubbles on the surfaces of wafers in PD therefore requires further investigation. However, our understanding of the growth of bubbles in dissolved gases mixed with DIW is insufficient to analyze the relationship between cavitation intensity and the types of Bjerknes force between bubbles [7]. Thus, it is necessary to further study the characteristics of cavitation, which plays a key role in determining both PRE and PD. In addition to the size of bubbles, the effects of different concentrations of surfactant on cleaning efficiency and pattern damage need to be studied in more detail. Several researchers have attempted to enhance PRE using dissolved gases. Vereecke et al. studied the effect of the addition of gases such as O₂ and N₂ into SC-1 solution on megasonic cleaning using controlled cavitation, but did not report control of PD that occurred via cavitation. Various gases such as H₂, N₂, and Ar dissolved in DIW have been proposed to induce cavitation, which not only enhances the removal efficiency of particles but also causes unstable microbubble motion [31,32]. Therefore, more fundamental research is required to determine the roles of surfactant and dissolved gases in DIW on PRE and PD during acoustic cavitation.

The main focus of this study is to understand the basic cleaning mechanisms to control it chemically to improve PRE and PD simultaneously. In the actual semiconductor industrial process, the magnitude of contamination is very low. However, removing this contamination from the delicate patterns is challenging. During megasonic cleaning acoustic streaming and cavitation play a key role. However, cavitation mechanism is dominant in surface cleaning [12]. Since our focus is on removing particles from pattern structure, we focused on controlling the cavitation chemically. To evaluate PRE variation, we used silicon nitride particles as model contamination particles since they have strong adhesion forces and are difficult to remove during semiconductor cleaning. We evaluated the cleaning performance of DIW solutions as a function of surfactant (SDS) and dissolved H₂ concentration under cavitation by focusing on the PRE of Si wafers and the PD of polysilicon line pattern structures. To our knowledge, no studies are available combining these two factors such as surfactant and dissolved gas together. In this work, we have used flat surfaces (non-patterned structured wafers) and pattern structured wafers. In this case, we can reduce the boundary layer thickness and expose even sub-micron particles to the streaming flow to achieve higher particle removal. The effects of surfactant addition on the size, population of bubbles, and
adsorption at the air-liquid interface were observed using a visualization technique. Finally, we proposed a hypothesis for PRE and PD that describes the characteristics of bubbles as a function of size, density, agglomeration, coalescence, and rectified diffusion in the presence of surfactant and dissolved gases.

2. Experimental

2.1. Materials

8-inch bare Si (100) wafers (resistivity: ~8 Ω cm, SK Siltron, Korea) and polysilicon line pattern wafers (width: 70 nm, height: 250 nm, aspect ratio: 3:6) were used in the cleaning experiments in this study. Polysilicon patterns were fabricated at imec (Leuven, Belgium) and directly used for the experiments. As the adhesion forces have a strong influence on cleaning efficiency [33], we tried to obtain the strength of the patterns. It could be 34 μN or higher obtained from the pattern collapse force measurement performed in our previous works [34,35]. Wafers were cut into small coupons with a size of 20 mm × 20 mm to evaluate PRE and PD. Si₃N₄ particles (100 nm, NIST), sodium dodecyl sulfate (SDS, Sigma Aldrich), NH₄OH (ammonium hydroxide, 25 wt%, electronic grade), and H₂O₂ (hydrogen peroxide, 25 wt%, electronic grade).
grade) were all used as-received without further purification.

High purity hydrogen gas (99.999%, H₂) was dissolved in DIW (H₂-DIW). H₂-DIW was prepared using a gas injection method as described previously [15]. For the experimental process, a commercial gas controller (PHasor II, Entegris) was used to dissolve the H₂ gas in DIW. The concentration of H₂ gas in DIW was controlled and detected by an electrochemical dissolved gas analyzer (DHD1-1, DKK-TOA Corporation, Japan).

2.2. Evaluation of PRE and PD

Cleaning experiments were performed using a rod-type single wafer megasonic system (0.83 MHz, Akrion Systems, USA). This single megasonic cleaning system comprises a megasonic generation module and a single wafer cleaning system as shown in Fig. 1(a). Schematics of the rod-type megasonic system and megasonic wave generation mechanism are shown in Fig. 1(a). The megasonic assembly had a piezoelectric transducer attached to the endplate of a quartz rod. The rod was placed slightly above a horizontally positioned wafer in the chamber so that the generated sound energy transfer occurred through a liquid meniscus between the wafer and rod. Fig. 1(b) and (c) provide top and side views of the megasonic system, respectively.

To deposit particles, Si wafer coupons with dimensions of 2 × 2 cm² were treated with SC1 solution (a mixture of NH₄OH, H₂O₂, and DIW at a ratio of 1:1:5) at 70 °C for 10 min to remove any traces of organic and particle contaminants present on the wafer surface. First, 12 ppm Si₃N₄ (0.006 g/500 ml) particles were dispersed in DIW to prepare a solution for particle contamination. After ultrasonication, the mono-size distribution of particles with an average size of ~350 nm was observed. Then the prepared solution was dropped on a 2 cm × 2 cm² Si wafer coupon and left for 5 min. After 5 min, each coupon was dried using a UV ozone cleaner (UVC-30) for 15 min. The optimal cleaning process time for megasonic cleaning was determined to be 10 sec. The power of the megasonic cleaning system was optimized at 5 W to remove particles by cavitation in DIW or H₂-DIW solutions with or without surfactant. Using the dark field mode of an optical microscope (LV 100 D, Nikon, Japan) with a Hg lamp with 130 W power, PRE was quantitatively evaluated. Image J analysis software (Image-pro plus, Media Cybernetics, USA) was used to count particles on coupons before and after cleaning, and PRE was then calculated using Eq. (1) [1,36]:

\[
PRE(\%) = \frac{n_i - n_f}{n_i} \times 100(\%)
\]

where \(n_i\) is particle count before cleaning and \(n_f\) is the particle count after cleaning.

To evaluate PD, the same quartz rod type single wafer megasonic system (0.83 MHz, Akrion systems) was employed. Small coupons with polysilicon line patterns (width: 70 nm, height: 250 nm, aspect ratio: 3:6) sized 20 mm × 20 mm were used. Wafer rotational speed and megasonic cleaning time were optimized at 18 rpm and 10 sec, respectively. It is not possible to maintain the same power for the PD evaluation study as used for PRE (i.e., 5 W) study as no damage to the patterns was observed. Though industry uses the same power in estimating PRE and PD, to perform the academic study to understand the fundamentals it is not possible to use the same power for both PRE and PD estimation. Hence megasonic power for pattern damage tests was optimized at 90 W. A field electron microscope (MIRA3, TESCAN, Czech Republic) was employed to measure the magnitude of PD. Pattern damage that occurred as a result of cavitation during megasonic cleaning was evaluated quantitatively using Image J software after adjustment of brightness and white balance. Practically the estimation of the area is only possible, but not the number of lines for this study. The percentage pattern damage area was calculated as shown in Eq. (2):

\[
PD(\%) = \frac{\text{Damaged line area}}{\text{Initial line area}} \times 100
\]

2.3. Observation of bubble streaming in the megasonic-standing wave field

A schematic of the experimental setup used to observe bubbles and streaming under acoustic cavitation in the ultrasonic field is provided in Fig. 2. As shown in Fig. 2(a), a transparent acrylic bath with a length and width of 110 mm and height of 240 mm was attached to a square stainless steel plate with a thickness of 20 mm. The bath was filled with a solution of 1 L reaching a height of 120 mm for each experiment. A transducer with a resonance frequency of 0.96 MHz was placed at the bottom of the steel plate. An ultrasonic power generator was connected to the transducer and a power of 20 W (maximum limit of the instrument) was maintained to visualize the bubbles more clearly. Though the power used for bubble observation (20 W) different that used for PRE (5 W) and PD (90 W) measurement, it will not change the overall phenomenon with respect to change of chemical conditions. The oscillation of micro-bubbles in the steady acoustic standing wave is illustrated in Fig. 2(b). As shown in Fig. 2(b), nodes and antinodes formed at a wavelength of 1.56 mm along the Z-axis when irradiation of the whole acrylic bath with a megasonic field created a standing wave [21]. Since the wavelength of 0.96 MHz is 1.56 mm, this represents sinusoidal waves associated with sound propagation. The size of oscillating bubbles (or the amount of gas contents inside them) can vary over time due to rectified mass diffusion, bubble coalescence via secondary Bjerknes forces, and fission of collapsing bubbles. Depending on bubble size relative to resonant size, bubbles keep moving between pressure nodes and antinodes. When the bubbles are smaller than the resonance size, they move from the node to the antinode. Similarly, when bubbles are larger than the resonance size, they move from the acoustic antinode to the acoustic node [6], resulting in a standing wave-like acoustic field inside the acrylic bath. Similar observations were made by Ando and co-authors [37,38]. To gain insight into the coalescence and agglomeration behavior of bubbles, we recorded the input power and corresponding output power while bubbles were streaming in the ultrasonic standing wave field. A high-speed camera (Phantom, VEO 710L, USA) system along with an LED light source were connected to the experimental setup. Using a high-speed video camera (HSC set-up), Movies of the acoustic cavitation of bubbles that occur in the standing wave of a megasonic wavefield were captured at a height of 7 cm from the bottom of the tank. For this purpose, 10,000 fps was used to record the evolution of acoustic phenomena for 1 μs. Movies were analyzed frame by frame and certain frames were selected to further understand the coalescence and clustering behavior of bubbles in solution. All these experiments were repeated several times and all megasonic wavefield experiments were conducted at a liquid temperature of 24 ± 2 °C. As the estimation of bubbles quantitatively was extremely hard, all the analysis was done with qualitative comparison. In real conditions of the phenomenon, the movement of bubbles is very instantaneous and random. Though we can get a number by capturing the images may not be correct as the deviation is too high than the average value. However, we tried to provide the possible number for more clarification of the qualitative bubble estimation within the measured area of 32 × 20 mm².

3. Results and discussion

3.1. Effect of DIW on cleaning performance

As shown in Fig. 3(a), a PRE of 43% and PD of 51% were obtained when using DIW alone in the single wafer megasonic cleaning system. Fig. 3(b) demonstrates the number of particles that remained on the Si wafer after megasonic cleaning. Although the number of particles on the Si wafer decreased after megasonic cleaning, this decrease was not significant. SEM images of the wafer surfaces revealed the number of pattern lines before and after megasonic cleaning (Fig. 3(c)). Observed PRE and PD performance values were much lower than those required in the semiconductor wet cleaning process. DIW with dissolved gases can...
improve cavitation intensity, and \( \text{H}_2 \) is the most promising gas for this purpose [15]. Hence, we dissolved \( \text{H}_2 \) in DIW to obtain a higher PRE.

3.2. Effect of \( \text{H}_2 \)-DIW on cleaning performance

PRE and PD were measured after megasonic cleaning using DIW solutions with different concentrations of \( \text{H}_2 \) gas. When a liquid containing dissolved gases undergoes acoustic cavitation, a high number of bubble nucleates are formed due to the high diffusivity of gases in the solution as it causes fluctuation in pressure in the solution, which leads to creating new bubble nucleates. Generally, the cohesive forces between water molecules are much greater than the adhesion forces between water molecules and other materials. Heterogeneous nucleation is substantially easier than homogenous nucleation and takes place at lower saturation pressures. The rate of nucleation can be expressed as shown in Eq. (3) [39,40]:

\[
J = C \exp \left( -\frac{\Delta G}{kT} \right)
\]  

(3)

where \( J \) is the rate of nucleation, \( \Delta G \) is the change in free energy of the heterogeneous nucleation of bubbles in the solution, \( T \) is temperature, \( k \) is the Boltzmann constant, and \( C \) is a pre-exponential constant.

Due to dissolved \( \text{H}_2 \) gas in the DIW solution, the free energy of the solution changes. As per Eq. (3), free energy affects the nucleation rate. The cavitation inception threshold value for the formation of bubbles is reduced, which leads to the formation of more bubbles. During cavitation, nuclei start forming at these dissolved gases as per heterogeneous nucleation theory. Because the diffusivity of \( \text{H}_2 \) gas is very high in DIW it causes fluctuation in pressure in the solution, which leads to creating new bubble nucleates and hence the number of bubbles as explained above. Thus, a higher number of bubbles are produced than when using DIW only, which enhances microstreaming and cavitation intensity [15].

As shown in Fig. 4(a), PRE gradually increased with an increase in dissolved \( \text{H}_2 \) gas concentration. A small increase in \( \text{H}_2 \) concentration resulted in higher cleaning efficiency. The addition of 0.4 ppm of \( \text{H}_2 \) gas concentration increased the PRE from 43% obtained with DIW only to 54%. Furthermore, megasonic cleaning of Si wafers with DIW with 0.8
ppm H$_2$ increased the PRE to $\sim$ 71%. Dark field optical microscopy micrographs of particles before and after cleaning using H$_2$-DIW are shown in Fig. 4(b). As the H$_2$ gas concentration in DIW increased, so did the intensity of cavitation, resulting in the formation of a higher number of bubbles. Removal of particles from Si wafers during megasonic cleaning is directly attributable to the number of bubbles that participate in the cleaning process. PD in response to megasonic cleaning using different concentrations of H$_2$ gas dissolved DIW is shown in Fig. 4(a). Pattern damage test results for DIW and H$_2$-DIW solutions are presented in Fig. 4(c). The percentage density of the damage pattern increased from 51% to 65% with an increase in the concentration of H$_2$ gas from 0 to 0.8 ppm in DIW, as shown in Fig. 4(a). A higher H$_2$ gas concentration in liquid results in larger transient cavitation due to uncontrolled acoustic bubble growth by rectified diffusion and coalescence [15]. In previous studies, we evaluated PRE and PD after cleaning wafer surfaces with DIW containing different gases such as Ar, O$_2$, N$_2$, and H$_2$ as a function of pressurized level [28]. There also, H$_2$-DIW showed the best cleaning efficiency regardless of concentration compared to the other dissolved gases. Higher cleaning performance might be due to the transformation in size of bubbles from nuclei size to resonant bubble size due to the high diffusivity of hydrogen in DIW. However, this also increases PD. Hence to achieve a high PRE and low PD, we further studied the cleaning of nanopattern structures by DIW and H$_2$-DIW solutions containing surface-active solute. We used SDS as an anionic surfactant as it has been shown to influence the characteristics of bubbles formed in an ultrasonic field.

### 3.3. Effect of SDS concentration in DIW & H2-DIW on PRE and PD under megasonic cleaning

Fig. 5(a) shows the PRE and PD values obtained for DIW solutions containing various concentrations of SDS (0 to 100 ppm). As shown in Fig. 5(a), PRE increased with the addition of SDS to 20 ppm and then decreased drastically with a further increase in SDS concentration and was only 7.8% at 100 ppm. Pattern damage decreased gradually with the addition of SDS; at the highest SDS concentration of 100 ppm, the percentage PD was less than 20%. Based on both PRE and PD, 20 ppm SDS is used as an optimal concentration to this study to simultaneously achieve relatively a high PRE and low PD.

Fig. 5(b) shows the cleaning performance of H$_2$-DIW solutions with different concentrations of SDS surfactant.

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**Fig. 3.** (a) PRE and PD after cleaning with DIW solutions using a single wafer megasonic cleaning system. (b) Darkfield optical microscope images of particles on a Si wafer before and after cleaning in DIW, and (c) Field-emission scanning electron microscope images of a polysilicon line pattern before and after cleaning in DIW.

**Fig. 4.** (a) Evaluation of PRE and PD after cleaning with DIW solutions contain different concentrations of dissolved H$_2$ and (b) darkfield optical microscope images of particles on Si wafer before and after megasonic cleaning in H$_2$-DIW, and (c) Field-emission scanning electron microscopy (FESEM) images of polysilicon line patterns before and after cleaning in H$_2$-DIW (0.8 ppm).

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cleaning. When 5 ppm SDS was added, PRE increased slightly and when 20 ppm SDS was added, PRE increased to 82%. However, PRE at 50 ppm and 100 ppm SDS was reduced slightly, 76% and 77%, respectively. A higher concentration of surfactant could help in reducing bubble formation. Fig. 5 (b) demonstrates the effect of SDS concentration on pattern damage. The number of stable small bubbles increased with increasing SDS concentration, preventing transient cavitation. Pattern damage of the Si wafers decreased dramatically to below 20%, as the concentration of SDS surfactant increased to 100 ppm, as the transient bubbles reduced with increased surfactant. We tried to measure the size of the bubbles and in most of the cases, it varied from 50 µm to 150 µm.

3.4. Effect of surface tension on cleaning performance

Surface tension can also affect cavitation [1,41]. Fig. 6(a) shows static surface tension (SST) as a function of SDS concentration (0 – 4000 ppm). SST decreased gradually with an increase in SDS concentration. The lowest surface tension (30 mN/m) was obtained at around 2000 ppm SDS, representing the critical micelle concentration (CMC) [34,35]. Fig. 6(b) demonstrates the SST for SDS concentrations up to 100 ppm in the mixed solution. SST decreased slightly with increasing concentration of surfactant up to 100 ppm. Since PRE and pattern damage decreased with increasing SDS concentration, we concluded that surface tension value did not play a significant role in our system. To further investigate the effect of the surfactant on cleaning performance, we visually observed the characteristics of bubbles in megasonic standing waves using a high-speed camera setup.

3.5. Effect of SDS surfactant on bubble characteristics under a megasonic standing wave

To investigate changes in bubble behavior with an increase in surfactant concentration, the high-speed camera set-up described in Fig. 2 was used. Changes in bubble characteristics with an increase in surfactant concentration at a megasonic frequency (0.96 MHz) are presented in Fig. 7 (see Supplementary Information, Movies S1-S5 (DIW), Movies S6-S10 (H2-DIW), Movie for cleaning mechanism S11). As the concentration of SDS in DIW increased up to 20 ppm, the number of bubbles in the solution increased, and clusters of bubbles were observed (Fig. 7(a)). Coalescence of bubbles was observed for DIW and for DIW containing 5 ppm SDS. Addition of 20 ppm SDS surfactant resulted in clustering or agglomeration of bubbles. This could explain the improvement in PRE observed for DIW with 20 ppm SDS. Bubble cluster dynamics play an important role in medical applications of ultrasound-induced cavitation, for example breaking of kidney stones [44]. We observed that clustered bubbles produced microstreaming. Thus bubble clustering without bubble coalescence plays a major role in effective cleaning. The reduction in PRE to 56% and 7.8% for SDS concentrations of 50 and 100 ppm, respectively, is due to the fact that the number of resonant bubbles in DIW with SDS decreased. With an increase in concentration of surfactant, increased adsorption of surfactant occurred at the bubble–liquid interface, which likely prevented the growth of bubbles after bubble nuclei were generated, resulting in a reduction in cavitation. To further investigate how the surfactant influenced bubble behavior and megasonic cleaning performance, we studied the coalescence and clustering of bubbles according to SDS concentration in the cleaning solution as shown in Fig. 8(a). If the concentration of surfactant increased at the air–liquid interface, the mass transfer from liquid to bubble decreases, which reduces the size of the bubbles. Changes in bubble behavior...
according to surfactant concentration in H$_2$-DIW at a megasonic frequency (0.96 MHz) are presented in Fig. 7(b). As shown in Fig. 7(b), the population density of bubbles in the H$_2$-DIW solution was greater than that in the DIW solution. Cleaning with a 20 ppm SDS in H$_2$-DIW solution created more bubbles than cleaning with 20 ppm SDS DIW solution. We attributed this to the diffusion of hydrogen gas in the solution, which facilitated acoustic cavitation. The dynamics of clusters of bubbles in H$_2$-DIW according to SDS surfactant concentration are illustrated schematically in Fig. 8(b).

Snapshots of changes that occurred in bubble behavior including coalescence and agglomeration/clustering in a megasonic field are provided in Fig. 9(a-e). In the DIW only case (Fig. 9(a)), bubble coalescence was high, resulting in the formation of a single large bubble. When 5 ppm SDS was added to DIW, coalescence was reduced, but not completely inhibited (Fig. 9(b)). The oscillating bubbles shown in Fig. 9(c) confirm the agglomeration of bubbles with a further increase in surfactant concentration to 20 ppm. However, the coalescence of bubbles decreased significantly with an increase in SDS concentration from 0 to 20 ppm. Furthermore, bubbles formed clusters instead of coalescing as the concentration of surfactant was increased further to 50 ppm, as shown in Fig. 9(d). However, the bubbles were small. These observations indicate that the adsorption of SDS on the bubbles prevented coalescence of multi-bubbles and reduced the rectified diffusion of single bubbles to resonant bubbles, which triggers cavitation. When the surfactant concentration was increased to 100 ppm, cavitation was almost completely inhibited with only a few small bubbles present, as shown in Fig. 9(e). The effect of SDS on cavitation has been discussed by several researchers [45–47]. They reported that bubble–bubble electrostatic repulsion is related to the adsorption of charged surfactant to bubbles. According to these researchers, electrostatic repulsion between bubbles prevents coalescence, resulting in the formation of smaller bubbles at higher concentrations of surfactant. We propose that bubbles formed at a moderate amount of surfactant (20 ppm of SDS) could be more stable and active in cluster formation, resulting in higher microstreaming.

The characteristics of bubbles generated in SDS H$_2$-DIW solution at a
A megasonic frequency of 0.96 MHz are demonstrated in Fig. 10. In the H\textsubscript{2}-DIW case (Fig. 10(a)), more bubbles formed due to stronger transient cavitation than in the DIW case. Furthermore, a greater number of bubbles participated in agglomeration in the H\textsubscript{2}-DIW case than the DIW case. As shown in Fig. 10(b), two bubbles coalesced to form one large bubble despite the addition of 5 ppm of surfactant to the H\textsubscript{2}-DIW solution, indicating that coalescence still occurs (Fig. 10(c)). The density of microbubbles was much higher in 20 ppm SDS added H\textsubscript{2}-DIW solution than 20 ppm SDS added DIW solution. The addition of surfactant (50 ppm) resulted in the stable suspension of microbubbles and facilitated the clustering of bubbles, as shown in Fig. 10(d). Furthermore, the addition of 100 ppm SDS in H\textsubscript{2}-DIW resulted in stronger cavitation. As shown in Fig. 10(e), cavitation still occurred in 100 ppm SDS added H\textsubscript{2}-DIW solutions and clusters of bubbles formed. In the next section, we propose a hypothesis to explain how SDS addition to DIW solution or DIW solution with dissolved H\textsubscript{2} gas affects the growth, coalescence, and clustering of bubbles. From recent experimental studies [7,48,49], near-wall bubbles under resonance will come into play, producing cleaning effect. To be specific, bubble oscillation (including re-entrant jet formation) produces strong wall shear stress, leading to particle removal [50,51]. In our visualization of bubbles, we considered the case without cleaning samples (as rigid boundaries). Rigorously speaking, the dynamics of individual bubbles can differ in the resonant frequency [7] and shape instability (such as re-entrant jet formation [50]) between cases with and without rigid boundaries. Yet, our visualization experiments allowed for extracting the general feature of cavitation activity such as the population dynamics through fission (as a result of violent bubble collapse [52]) and coalescence (as a result of the secondary Bjerknes force [6]).

4. Comparative cleaning performance of DIW, H\textsubscript{2}-DIW, DIW + SDS, & H\textsubscript{2}-DIW + SDS solutions

The cleaning performances (both PRE and PD) of DIW and H\textsubscript{2}-DIW with and without SDS added are illustrated in Fig. 11. The highest PRE performance was obtained for H\textsubscript{2}-DIW solutions. Megasonic cleaning using DIW resulted in a PRE of 43 ± 6.25% and PD of 51 ± 1.9%. Addition of 0.8 ppm H\textsubscript{2} gas to DIW resulted in an increase in PRE to 71% and PD to 65%. The presence of dissolved gas increases the number of nuclei, which could be responsible for transient cavitation [53,54]. The higher PD and PRE values obtained are likely related to the number of stable bubbles and transient (coalescence) bubbles. A higher number of transient bubbles results in higher local energies, damaging pattern structures [48,49]. Minimizing pattern damage while maintaining PRE in advanced semiconductor megasonic cleaning applications is therefore challenging. Reducing transient cavitation during megasonic cleaning is essential to minimize pattern damage. Our results indicate that SDS can be used to reduce PD while maintaining the PRE. As shown in Fig. 11, an SDS surfactant concentration of 100 ppm in DIW decreased both PRE and PD. We attributed this to the formation of small bubbles. At a high concentration of surfactant (100 ppm), more adsorption of surfactant at the air–liquid interface would occur. This would reduce the size and population density of bubbles. Thus, 100 ppm SDS completely prevented the coalescence and clustering of bubbles. As shown in Fig. 11, a significant increase in PRE was observed when H\textsubscript{2}-DIW solution with 20 ppm SDS was used as the cleaning solution. We attributed this to the greater number of microbubbles in 20 ppm SDS H\textsubscript{2}-DIW solution than 20 ppm SDS DIW solution. This demonstrates the importance of surfactant and H\textsubscript{2} dissolved gas concentration on PRE and PD. Both PRE
and PD were lower after cleaning with 100 ppm SDS H₂-DIW solution than 20 ppm SDS H₂-DIW solution. However, a significant increase in PRE with a lower PD were observed after cleaning with 100 ppm SDS H₂-DIW solution than 100 ppm SDS DIW solution. The role of SDS addition to DIW and H₂-DIW solution on the growth, coalescence, and clustering of bubbles is explained below.

4.1. Hypothetical model of cavitation in DIW and H₂–DIW solutions containing SDS

In general, an acoustic field affects air bubbles present in liquid in several ways. The schematic in Fig. 12 illustrates how surfactant and dissolved gases influence the characteristics of bubbles generated under a megasonic field. Bubble generation is affected by different chemical environments viz. the presence and concentration of dissolved gases and surfactant type and concentration. The schematic in Fig. 12 illustrates two cases, namely DIW and H₂-DIW. These cases are subdivided into three categories viz no surfactant, low surfactant (20 ppm), and high surfactant (100 ppm) concentrations. As megasonic wave waves pass through a liquid, nuclei form. The growth of these nuclei occurs at the antinode due to a rectified diffusion process or coalescence to form large bubbles. Both coalescence and rectified diffusion occur in DIW. However, the bubbles generated are separated by a short distance. We observed that when the bubbles formed by coalescence were larger than the resonance size, they moved towards the node by primary Bjerknes forces [47]. Addition of 20 ppm SDS resulted in the formation of more bubbles than DIW only. Very few bubbles participated in the coalescence process to become large bubbles; most bubbles formed clusters. The coalescence process was not completely inhibited by the addition of 20 ppm of surfactant. Upon adsorption of surfactant at the air–liquid interface, bubbles became charged [45], preventing coalescence. This resulted in bubble separation due to electrostatic repulsion. At a high concentration of SDS (100 ppm), more adsorption of surfactant occurred at the bubble–liquid interface. This enhanced repulsion and hindrance forces. However, very small bubbles favored rectified diffusion at the antinode, resulting in the formation of a single larger bubble. By contrast, when the electrostatic repulsion force due to adsorption of surfactant was greater than the Bjerknes force, microbubbles did not coalesce. Therefore, DIW with 20 ppm SDS favored stable agglomeration of bubbles [20] whereas 100 ppm SDS inhibited coalescence completely. Very few bubbles formed at 100 ppm SDS, and those that did form were stable, small, and favored clustering. The strength of repulsion was therefore higher compared to that in DIW and DIW with 20 ppm SDS. Thus, PRE and PD were lower for the 100 ppm SDS DIW solution than the 20 ppm and 0 ppm SDS DIW solutions.

The effect of acoustic bubbles formed in H₂-DIW (case-2) is also

Fig. 9. Selected images showing coalescence and clustering of bubbles at different concentrations of SDS surfactant in DIW (scale bar: 1 mm); (a) 0 ppm, (b) 5 ppm, (c) 20 ppm, (d) 50 ppm, and (e) 100 ppm SDS.
schematically illustrated in Fig. 12. Bubbles in H$_2$-DIW grow both by rectified diffusion and coalescence. H$_2$ gas facilitates the growth of bubbles by rectified diffusion due to its high diffusivity and low thermal conductivity. Bubbles formation is accelerated by primary Bjerknes forces and secondary Bjerknes forces bringing the bubbles into contact with one another, resulting in the formation of a single large bubble [15]. More bubbles were obtained when H$_2$-DIW solution was used than DIW solution due to the formation of more nuclei in the former solution. Thus, PRE and PD were higher for H$_2$-DIW than DIW. Addition of 20 ppm SDS to H$_2$-DIW further increased PRE as shown in Fig. 11. More adsorption of surfactant occurred at the bubble–liquid interface in 100 ppm SDS H$_2$-DIW solution. This resulted in a slight reduction in PRE and a moderate PD value compared to 20 ppm SDS H$_2$-DIW solution. A large number of small bubbles resulted in a high PRE and low PD. We attributed the improvement in PRE to the oscillation of individual bubbles or clustering of bubbles that formed during cavitation.

5. Conclusions

Solutions with a high PRE and low PD are required for megasonic cleaning of wafers with pattern structures. We found that dissolved H$_2$ gas in DIW not only enhanced PRE, but also PD. To minimize PD, we added the anionic surfactant SDS to DIW and found that PRE increased at very low concentrations of SDS and then drastically decreased to zero at a higher SDS concentration (100 ppm). In contrast, PD decreased continuously as the SDS concentration increased. High-speed camera results confirmed a larger bubble population at a lower SDS concentration (20 ppm) while the bubble population became negligible at 100 ppm SDS. At 100 ppm SDS, bubble nuclei are covered with surfactant and behave like solid particles. A high PRE and PD were observed after
megasonic cleaning in H$_2$-DIW due to the high growth rate of bubbles and their agglomeration in this cleaning solution. Pattern damage to polysilicon patterns decreased remarkably upon the addition of SDS. Both PRE and PD were found to be maximal for 20 ppm SDS H$_2$-DIW solution. PRE and PD decreased by 4% and 20%, respectively, when 100 ppm SDS H$_2$-DIW solution was used compared to 20 ppm SDS H$_2$-DIW solution. This indicates that microstreaming, the population of bubbles, and clustering of bubbles play critical roles in determining the PRE and PD effects of megasonic cleaning solutions on wafers.

**CRedit authorship contribution statement**

Bichitra Nanda Sahoo: Writing – original draft, Validation, Formal analysis, Investigation. So Young Han: Methodology, Validation, Formal analysis, Investigation. Hyun-Tae Kim: Conceptualization, Methodology. Keita Ando: Supervision, Visualization. Tae-Gon Kim: . Bong-Kyun Kang: Supervision, Resources, Visualization. Andreas Klipp: Supervision, Resources, Visualization. Nagendra Prasad Yerriboina: Supervision, Methodology, Validation, Supervision, Writing – review & editing. Jin-Goo Park: Supervision, Resources, Visualization, Writing –
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2021.105859.

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