Nanoscale Particle Removal using Conventional and Hybrid Laser Shockwave Cleaning

A Thesis Presented

by

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Abstract

As surface contamination by submicron particulates becomes a critical issue in semiconductor industry, efforts have been made to develop noncontact effective laser-based cleaning techniques. The laser shockwave cleaning (LSC) process is one of the promising techniques that has been demonstrated to be effective for inorganic particle dry removal. In the cleaning process, the surface is not directly exposed to irradiation of laser beam, which eliminate the possibility of potential surface damage. In addition, a relatively large area can be cleaned by a single laser pulse. However, even though this technology has those distinct advantages, LSC technique has a difficulty in removing organic particles, which removal mechanism hasn’t been found yet. Recently, the laser shockwave cleaning technique has been combined with ultraviolet (UV) laser for organic particle removal. But, when UV laser cleaning is used in this hybrid approach with LSC, optimization is required to ensure damage free cleaning. This is required whenever a new surface is used.

The reason for ineffectiveness in organic particle removal using LSC has been investigated. The shock wave pressure is sufficiently strong to deform soft particles such as organic particles increasing the contact radius between the particle and the substrate, which leads to higher adhesion force. The deformation of organic particle occurs during LSC process has been verified with high angle SEM images of 300nm PSL particles exposed to laser shockwaves. For theoretical calculation of the contact radius between
300nm PSL particles and Si substrate, the shockwave speed has been measured using newly designed two-probe beam deflection method and The Maugis-Pollock theory is applied. The predicted contact radius agrees with the experimental measurements. Removal moment ratio of PSL particle and silica particle has been also analyzed when applying LSC. It shows that silica particles can be easily removed by LSC, while soft (PSL) particles smaller than 1μm in diameter will be harder to remove. It has been also verified experimentally with three different sized PSL particles such as 300nm, 600nm and 2μm. The removal efficiency of 2μm PSL particles is more than 90%, while in the case of 300nm and 600nm PSL particles, they are 30% and 60% respectively.

In order to remove organic particles, a wet laser shockwave cleaning (WLSC) technique has been refined successfully for wafer scale cleaning as well as for more efficient particle removal. This technique utilizes the advantage of using water to reduce the adhesion force by an order of magnitude, utilize the double layer repulsive force, eliminate the capillary force encountered in dry LSC and increase the drag force by increasing the medium density (by three orders of magnitude). In order to evaluate cleaning performance of the wet laser shockwave cleaning technique, removal of either organic particles or inorganic particles using different size particles have been investigated and compared to original LSC. Complete WLSC removal of 300nm PSL particles as well as 280nm silica particles was achieved. In addition, 28nm PSL particles were successfully removed by WLSC. The removal mechanism for wet laser shockwave cleaning has been investigated using computational fluid dynamics as well as shadow-graphic photography. Removal moment ratio for PSL and silica particle removal using
WLSC has been also analyzed and compared to experimental results, but it shows the disagreement between them in the case of PSL particles. Based on the assumption that the water could be compressed due to the shockwave pressure perpendicular to the substrate leading to a decrease in the water film thickness, the removal moment ratio has been reanalyzed. As a result, it has been shown that when the thickness of the water film decreases to less than 1μm, 28nm PSL particles can be successfully removed.
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Chapter 1 Introduction

The ultraclean surface preparation is of great significance in semiconductor industry, which consists of many complicated and sensitive processes. For example, 500–800 process steps are required for manufacturing of an integrated circuit (IC), depending on the specific type of device. Thus the presence of contaminants and defects in any process influences critically the device performance, reliability, and product yield. These contaminants and defects are usually originated from equipments, processing chemicals, factory operators, wafer handling, gas piping, and film deposition systems.

In addition, as feature size continues to shrink and the device structure is made of more complex form by incorporation of multilevel metallization layers with copper (Cu) and special dielectric materials, particle removal becomes much more important in IC manufacturing processes. The FEOL (Front End Of Line or FEP, Front End Process) critical particle size is expected to decrease from 25nm to 5.6nm in the year 2022 as listed in Table 1.1. The need for cleaning process in the fabrication of microelectronic devices has been well recognized since the dawn of solid-state device technology. For instance, approximately 17% (95 steps) of all process steps in 45 nm technology, which requires 556 total process steps including 11 metal layers and Cu dual damascene technology, are independent cleaning steps [1]. Particles larger than a quarter of the minimum line-width may cause fatal device defects. Current technology node is 50 nm and it will shrink to 11 nm by the year 2022. The smaller the particles, the harder it is to
overcome the adhesion force between the particle and the surface. Therefore, more effective cleaning techniques are required to specifically target removal of nanoscale particles.

Table 1.1 Surface preparation technology requirements, (ITRS, 2007)

<table>
<thead>
<tr>
<th>Year of Production</th>
<th>2009</th>
<th>2010</th>
<th>2012</th>
<th>2015</th>
<th>2018</th>
<th>2022</th>
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<tr>
<td>Technology node* (nm)</td>
<td>50</td>
<td>45</td>
<td>36</td>
<td>25</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td>Critical particle diameter (nm)</td>
<td>25</td>
<td>22.5</td>
<td>17.9</td>
<td>12.6</td>
<td>8.9</td>
<td>5.6</td>
</tr>
<tr>
<td>Killer defect density (#/cm²)</td>
<td>0.17</td>
<td>0.11</td>
<td>0.17</td>
<td>0.17</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>Surface roughness (Å)</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Critical surface metals (10¹⁰ atoms/cm²)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>2012</th>
<th>2015</th>
<th>2018</th>
<th>2022</th>
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<tr>
<td>Interconnect</td>
<td>Critical particle diameter (nm)</td>
<td>25</td>
<td>22.5</td>
<td>17.5</td>
<td>12.5</td>
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<tr>
<td>Killer defect density (#/cm²)</td>
<td>0.02</td>
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<td>0.02</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Critical surface metals (10⁹ atoms/cm²)</td>
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<td>10</td>
<td>10</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Organic contamination (10¹⁰ C atoms/cm²)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Note: "Technology node" is defined as the smallest half-pitch of contacted metal lines on DRAM [2]

The development of effective surface cleaning methods has been a subject of intensive research [3,4,5,6]. Conventional cleaning techniques, including wet cleaning, brush scrubbing, ultrasonic and megasonic cleaning and CO₂ snow cleaning might be effective for removing nanoscale particles. However these techniques still have disadvantages to overcome. Wet cleaning process has a possibility to leave undesirable chemicals on the surfaces [7]. Brush scrubbing has to achieve a good contact with particles on surface to be removed effectively, which could cause surface damages [8,9]. In ultrasonic and
megasonic cleaning technique, there still exists substrate damage concern due to cavitations [10]. CO$_2$ snow cleaning technique is powerful to remove particles from the flat surface, while it easily damages patterns in circuit device [11].

Recently, various laser-based cleaning techniques have been proposed and tried to apply them for real semiconductor process, owing to the advantages of dry cleaning process. In traditional laser cleaning, the direct irradiation of laser beam onto the surface has not been shown to be effective for removing particles without surface damages [12,13]. A novel laser-based cleaning technique, the laser shockwave cleaning (LSC) has been demonstrated to address this shortcoming by adopting a shockwave generated above the surface [14,15,16]. However, LSC technique still has a difficulty to remove organic particles as well as particles deposited from a solution (wet particles), meanwhile it is very effective for inorganic particle removal [17]. Accordingly hybrid laser shockwave cleaning assisted with ultraviolet (UV) laser has been proposed by J. M. Lee et al (2003), which is effective for removing both organic particles and wet particles [18]. But when UV laser cleaning is used, optimization is required to ensure damage free cleaning [19]. There are other types of hybrid laser shockwave cleaning have been introduced since LSC combined with UV laser, such as steam laser shockwave cleaning (SLSC), underwater laser shockwave cleaning(ULSC) and wet laser shockwave cleaning(WLSC) [20,21,22]. SLC is assisted with explosive vaporization of liquid. In the case of ULSC, a laser-induced shockwave is generated in liquid not in air then liquid flow is guided to the substrate to remove particles with a specially designed nozzle.
A wet laser-induced shockwave cleaning (WLSC) technique was proposed first by researchers in Clarkson University. In this thesis, this technique has been presented and studied. It utilizes a shockwave generated from laser-induced plasma and a liquid film as the medium, wherein waves propagate against contaminants through the liquid. The advantage of using water in this cleaning process is to reduce the adhesion force by an order of magnitude, utilize the double layer repulsive force, eliminate the capillary force encountered in dry LSC and increase the drag force by increasing the medium density.
1.1 Research Objectives

The overall goal of this research is to verify the removal mechanism of organic particle in laser shockwave cleaning (LSC) process as well as to develop and investigate a wet laser shockwave cleaning (WLSC) technique that can be effective for the removal of nanoscale particles from the surface, regardless of either organic or inorganic particles. Specific objectives are as follows:

1. To understand the removal mechanism of organic particle during laser shockwave cleaning process by setting up a hypothesis and proving it through both theoretical and experimental approaches.

2. To develop two-probe beam deflection method for the measurement of the velocity of a laser-induced shockwave, which is more precise and reliable compared to conventional one probe beam deflection method.

3. To develop the wet laser-induced shockwave cleaning process in which wafer-scale cleaning is possible.

4. To investigate the particle removal using conventional laser-induced shockwave cleaning technique and compare it to using wet laser shockwave cleaning technique

5. To evaluate the cleaning performance of the wet laser shockwave cleaning technique even for below 30nm particle

6. To understand the removal mechanism in wet laser shockwave cleaning process through analytical approach and numerical modeling. Computational fluid
dynamics (CFD) model was developed to predict the phenomena occurring during WLSC and in addition, the surface velocity of the water flow driven by a laser-induced shockwave was measured experimentally.
1.2 Outline of Dissertation

Following introduction, Chapter 2 reviews the background for particle adhesion and removal with theoretical calculation of adhesion forces and removal models. In addition, laser cleaning technologies including laser shockwave cleaning (LSC) as well as hybrid shockwave cleaning techniques will be introduced. The background for the simulation on wet laser shockwave cleaning will be also briefly reviewed.

Chapter 3 gives the detail explanation of the experimental materials and procedures. The two-probe beam deflection method will be explained for the measurement of the shockwave propagation speed. The high speed imaging system used for investigating the phenomena occur during new hybrid laser shockwave cleaning process will be also described.

Chapter 4 discusses the organic particle removal mechanism in LSC process with analytical and experimental results. Refined wet laser shockwave cleaning process will be presented and evaluated with cleaning experiments. Simple numerical results using computational fluid dynamics will be also displayed. Furthermore, the removal mechanism of WLSC process will be discussed and verified with analytical results from the calculation of the removal moment ratio.

Finally, Chapter 5 summarizes the key results of this work and provides the suggestions for the future studies.
Chapter 2 Background and Literature Review

This chapter provides the background necessary for investigation of particle removal mechanism for conventional laser shockwave cleaning as well as new wet laser shockwave cleaning. The brief review on the particle adhesion will be given first, since particle adhesion phenomena has to be considered in order to clean contaminants from the surface. Following that, the background of particle removal will be given, introducing laser shockwave cleaning, several types of hybrid laser shockwave cleaning. The hydrodynamic cleaning theory with boundary layer theory will be also addressed. Finally, water currents driven by wind will be briefly discussed to establish the numerical model for the investigation of phenomena appear during wet laser shockwave cleaning process based on the similarity with wind-driven currents.

2.1 Particle Adhesion

Since the particle adhesion is closely related to the interaction between a particle and a substrate, it is important to understand how the particle adhesion affects the interaction between particle and substrate.

The particle adhesion is strongly dependent on the type of forces acting on particles. There are many forces related to particle adhesion. The first major force is the omnipresent van der Waals force, which exits when a particle is contacted with a surface. In
the gaseous environment, a liquid can be trapped between the particle and the substrate, due to high humidity or because the substrate is immersed and then withdrawn from a liquid. This causes capillary force. In the aqueous environment like wet chemical cleaning process, the capillary force will be absent. Instead of that, electrostatic double layer force is involved, which is caused by the surface charge of a particle and a substrate.

2.1.1 van der Waals Force

Without any external load applied on the particle, its adhesion onto the surface is caused by the omni-present van der Waals force in first instance. For all atoms and molecules, even for non-polar ones, there exist instantaneous dipoles. And the interaction between these dipoles and the induced dipoles in neighboring atom results in the dispersion forces atoms/molecules, which is the dominant portion of the van der Waals force. The dispersion force together with the induction force and the orientation force form the van der Waals force between polar molecules [23]. Each of these forces has an interaction free energy that varies with the inverse sixth power of the distance.

\[ w_{VDW} = -\frac{C_{VDW}}{r^6} = -(C_{ind} + C_{orient} + C_{disp}) / r^6 \]  

(2.1)

Hamaker [24] calculated the interaction between macroscopic bodies, simply by using the principle of additivity of interactions between all molecules in each body. As a result, the attractive force between a sphere of radius \( R \) and a flat plate at a separation distance \( z_0 \) is given by
\[ F_{\text{vdw}} = \frac{AR}{6z_0^2} \quad (2.2) \]

where \( A \) is the conventional Hamaker constant. The separation distance \( z_0 \) is approximately 4Å for van der Waals-bonded crystals [25,26].

Another useful example is the deformed sphere particle with flat surface, as illustrated in Figure 2.1.

![Figure 2.1 Schematic diagram of van der Waals force between a deformed particle and a flat surface](image)

As shown in Figure 2.1, the original sphere is deformed with a contact radius of \( a \). The separation distance between deformed sphere and flat surface is still \( z_0 \). After deformation,
the length deduction in z direction, \( \delta = R - \sqrt{R^2 - a^2} \). In this case the van der Waals interaction is given by,

\[
W(z_0) = -\frac{A_{12}}{6} z_0^{z=2R-\delta} \int_{z_0}^{(2R-\delta-z)(z+\delta)dz} \frac{2}{(z_0)^2}
\]

\[
= -\frac{A_{12}}{6} \left[ \frac{(2R-\delta)\delta}{2z_0^2} + \frac{R-\delta}{z_0} + \frac{R}{2R-\delta+z_0} + \ln \frac{z_0}{2R-\delta+z_0} \right]
\]

(2.3)

The corresponding van der Waals force is given by

\[
F_{\text{vdW}} = \frac{A_{12}}{6} \left[ \frac{(2R-\delta)\delta}{z_0^3} + \frac{R-\delta}{z_0^2} + \frac{R}{(2R-\delta+z_0)^2} - \frac{2R-\delta}{(2R-\delta+z_0)z_0} \right]
\]

\[
= \frac{A_{12}}{6} \left[ \frac{a^2}{z_0^2} + \frac{\sqrt{R^2-a^2}}{z_0^2} - \frac{(R+\sqrt{R^2-a^2})^2}{z_0^2} \right]
\]

(2.4)

Only when \( R \gg z_0 \) and \( R \gg a \), the above equation becomes,

\[
F_{\text{vdW}} = \frac{A_{12}}{6} \left[ \frac{a^2}{z_0^2} + \frac{R}{z_0^2} \right] = \frac{A_{12}R}{6z_0^2} \left( 1 + \frac{a^2}{Rz_0} \right)
\]

(2.5)

that is commonly used to calculate the van der Waals force for the deformed spherical particle [27,28].
The assumptions of simple pair wise additivity ignore the influence of neighboring atoms on the interaction between any pair of atoms. And further, the additivity approach cannot be readily extended to bodies interacting in a medium. Lifshitz [29] developed the “macroscopic theory” and calculated the van der Waals interaction between macroscopic bodies avoiding Hamaker’s assumption of the additivity of molecular interaction. The resulting Hamaker constant expression for two bodies “1” and “2”, separated by a medium “3” [30] is

\[ A_{132} = \frac{3h}{4\pi} \int_{0}^{\infty} \frac{\varepsilon_1(i\xi) - \varepsilon_3(i\xi)}{\varepsilon_1(i\xi) + \varepsilon_3(i\xi)} \cdot \frac{\varepsilon_2(i\xi) - \varepsilon_3(i\xi)}{\varepsilon_2(i\xi) + \varepsilon_3(i\xi)} d\xi \]  

(2.6)

where \( h \) is Planck’s constant, \( \varepsilon(i\xi) \) is the dielectric constant of the material along the imaginary frequency axis, \( i\xi \).

From the above equation we can see that

\[ A_{132} \approx \sqrt{A_{131}A_{232}} \]  

(2.7)

From this we obtain

\[ A_{12} \approx \sqrt{A_{11}A_{22}} \]  

(2.8)

The other useful relations are [31]
Combining with Eq. 2.9, we get

\[ A_{132} \approx (\sqrt{A_{11} - A_{33}})(\sqrt{A_{22} - A_{33}}) \]  

(2.10)

From the above equation, we can see that it is possible to choose a medium “3” such that the value of \( A_{132} \) is negative, resulting in repulsion[32]. (If the condition \( A_{11} > A_{33} > A_{22} \) or \( A_{11} < A_{33} < A_{22} \) is satisfied) Examples of such combinations of the materials and media are rare and ambiguous. We can also see that the van der Waals force between materials “1” and “2” in the medium “3” such as water is much smaller than that in air, normally one order of magnitude less, depending on how \( A_{11} \) and \( A_{22} \) are close to \( A_{33} \).

2.1.2 Capillary Force

When a small amount of water is trapped between a particle and a surface to form a meniscus, a strong capillary force will have a big effect on the particle adhesion. There are two components of attractive force. One is the force \( F_p \), caused by the negative Laplace pressure inside the meniscus and the other is the force caused by surface tension \( F_{S.T} \), which is given by,

\[ F_{S.T} = 2\pi R_y \sin \phi \sin (\phi + \theta_i) \]  

(2.11)
where $R$ is radius of the sphere and $\gamma_L$ is the surface tension of the liquid.

When the filling angle $\phi$ is small, this surface tension force can be neglected.

As shown in Figure 2.2, considering the simple case of small filling angle $\phi$ and equal contact angle $\theta_1=\theta_2$, the Laplace pressure inside the meniscus will be,

$$P = \gamma_L \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \approx \frac{\gamma_L}{r_1} (\text{since } r_2 \gg r_1) \quad (2.12)$$

where $r_1$ and $r_2$ are the principal radii of the liquid surface curvature.

For small filling angle, $r_1 = \frac{d}{2\cos \theta}$ and the Laplace pressure acts on the area $\pi x^2 \approx 2\pi Rd$.

Therefore, the capillary force is given by,
Theoretically the resulting capillary force given by the above equation is not dependent on the water volume inside the meniscus when the filling angle $\phi$ is small enough.

### 2.1.3 Adhesion Induced Deformation

When a particle and a substrate come into contact with each other, the deformation happens within the contact area, which will change the radius of contact area between a particle and a surface. In addition, larger contact radius will result in increasing the adhesion force. The changed contact radius can be predicted by adopting appropriate theory model depending on the material property and size of particle.

Hertz established in 1882 his famous theory on the contact of two spheres having radii $R_1$ and $R_2$ pressed by an external load $P$ [33]. (A flat surface can be considered as a sphere having an infinite radius) The circular contact radius is given by

$$a_0^3 = \frac{PR}{K}$$  \hspace{1cm} (2.14)
where \( R = \frac{R_1 R_2}{R_1 + R_2} \) and \( \frac{1}{K} = \frac{3}{4} \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right) \), \( E \) and \( \nu \) is Young’s modulus and Poisson ratio respectively.

Johnson et al. [34] observed that the contact radius between two contact rubber spheres is considerably larger than that given by Hertz theory under conditions of light loading, which led them derive the famous JKR theory, in which the effect of attractive surface force is included.

Compared to the Hertzian case, the introduction of surface energy increases the area of contact and modifies the penetration and the stored elastic energy. JKR theory gives the contact area as bellow,

\[
\frac{a_0^3}{R_w A} = \frac{R}{K} \left\{ P + 3w_A \pi R + \left[ 6w_A \pi R P + (3w_A \pi R)^2 \right]^{3/2} \right\} \tag{2.15}
\]

where \( w_A \) is the work of adhesion.

When there is no external load, Eq. 2.15 simplifies to

\[
a_0^3 = \frac{6\pi w_A R^2}{K} \tag{2.16}
\]

An alternative approach to calculate the contact radius between two spheres was
proposed by Derjaguin et al [35] (referred to as the DMT theory). DMT theory assumes that the attractive surface forces act in a ring-shaped non-contact zone and would not be able to change the profile outside the contact area from the Hertzian profile. The compressive pressure within the contact area is still Hertzian pressure distribution. The attractive van der Waals force \(2\pi R w_A\) acting outside the contact area can be simply regarded as an additional load added into the Hertz equation. The relation of the contact radius with the external load under DMT theory is given by,

\[
a^3 = \frac{R}{K} (P + 2w_A\pi R)
\]

At zero applied load, DMT theory gives the contact radius,

\[
a_0^3 = \frac{2\pi w_A R^2}{K}
\]

Tabor is the first to compare JKR and DMT theories [36]. Tabor pointed out the drawback in the DMT theory is neglecting the deformation due to attractive surface close to the edge of the contact. On the other hand, JKR theory assumes that the attractive forces exist at the contact area only and neglects the attractive force acting outside the contact area. As shown in Figure 2.3, Tabor pointed out that when the height \(h\) of the “neck” around the contact area, which is of the order of \((w_A^2 R / E^2)^{1/3}\), becomes comparable to the equilibrium separation distance \(z_0\), the JKR theory must be corrected to take into account the forces outside the contact area, which means that when the
A dimensionless parameter $\mu = h/z_0 = (R_w A^2 / E^2 z_0^3)^{1/3}$ is comparable and less than one, the JKR theory has to be corrected.

![Diagram showing difference between DMT and JKR interactions](image)

Figure 2.3 Difference between (a) DMT and (b) JKR interactions

Muller et al. [37] performed a self-consistent numerical solution using a Lennard-Jones potential and abandoned the hypothesis that adhesion forces do not change the Hertzian profile. Muller et al.’s results show that the continuous transition from the DMT to the JKR theory is governed by a single parameter $\mu_{MYD}$ which is proportional to that introduced by Tabor [36].

$$\mu_{MYD} = \frac{32}{3\pi} \left[ \frac{2 R_w^2}{\pi E^2 z_0^3} \right]^{1/3} \approx 2.92\mu$$

(2.19)
where \( \frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \)

For \( \mu_{\text{MYD}} >> 1 \), corresponding to soft materials with higher surface energy and larger radius, JKR theory should properly describe the system. Conversely, when \( \mu_{\text{MYD}} << 1 \), corresponding to harder, lower surface energy materials and smaller particle, DMT theory has to be used.

The theory on the adhesion-induced non-elastic deformation is far behind that of elastic deformation. The adhesion force-induced stresses between a sphere and a substrate can be sufficiently high, so as to exceed one of the yield strength of the contacting materials. Plastic deformation may occur even in the absence of any external loads.

When the deformation is fully plastic, the compressive pressure within the contact area becomes constant and is equal to

\[
p_m = H = 3Y
\]

(2.20)

where \( H \) is the hardness and \( Y \) is the yield strength.

Considering the effect of adhesion force between a sphere and a flat surface, the total attractive force between the sphere and the flat surface is \( P + 2\pi\nu_A R \), where \( P \) is the
external applied load and $2\pi w_a R$ is the surface adhesion force. Maugis and Pollock [38] gave the following equation,

$$P + 2\pi w_a R = \pi a^2 H = 3\pi a^2 Y$$

(2.21)

where $a$ is the contact radius.

When the applied load is zero, the contact radius (full plasticity) is given by,

$$a_0 = \left(\frac{2w_a R}{3Y}\right)^{1/2}$$

(2.22)

**2.1.4 Electrostatic Double-Layer Force**

A surface immersed in the liquid will be charged through absorption of ions or disassociation of surface groups. For the balance of final surface charge, two equal but oppositely charged regions of counter-ions are formed around surface. One is the so-called Stern layer, which is bound to the surface. Another layer is the diffuse layer, which is formed in the outer region of Stern layer. These two layers together are called the electric double layer. The zeta potential is defined as the electric potential at the boundary between them. Zeta potential has been shown to be a key parameter in controlling particle removal and particle re-deposition. Figure 2.4 shows a schematic of zeta potential and double layer.
Figure 2.4 Schematic of zeta potential and double layer

Figure 2.5 illustrates the zeta potential for various particles as a function of pH. It is shown that at the pH of water, silica, PSL, PVA, and tungsten particles are all negatively charged. Thus, repulsion is expected between particles and the substrate, which are of these materials. In contrast, alumina and silicon nitride (Si$_3$N$_4$) particles typically carry a positive charge at the pH of water and thereby they will be attracted to the silicon wafer surface and hard to remove due to increase in total adhesion force between particles and substrate. However using a high pH cleaning solution such as SC1, we can expect that even for these three different kinds of particles (tantalum pentoxide, alumina and Si$_3$N$_4$), electrical double layer force occurs as a strong repulsion even between the particle and the substrate.
Figure 2.5 Zeta potential for various particles as a function of pH

DLVO theory have been celebrated by Derjaguin and Landau [39], Verwey and Overbeek[40]. It describes the total net interaction between two surfaces, including van der Waals interaction and electrical double layer interaction when two charged surfaces approach to each other. The electrical double layer force, either attractive or repulsive depending on the sign of the charge on the surface, forms between them. Several approximate expression of electrical double layer forces have been introduced such as Hogg, Healy, and Fuerstenau (HHF) under constant potential [41] or surface charge [42, 43], compression approximation under constant charge [44, 45], and linear superposition approximation (LSA) [40].
Hogg, Healy, and Fuerstenau amongst others extended the DLVO theory to the interaction of nonidentical particles and calculated the force of repulsion when two particles of different radii approach each other under the conditions that either the potential $\Psi$ or the charge $\sigma$ remains constant. Under the condition of small potential ($< 25$ mV), constant surface potential, smaller separation distance than sphere radius, and large $\kappa R (> 5)$, the interaction force between a sphere and a flat surface is given by

$$F_{el}^{\Psi}(z_0) = 2\pi \varepsilon_r \varepsilon_0 R \left( \Psi_{01}^2 + \Psi_{02}^2 \right) \frac{\kappa e^{-\kappa z_0}}{1 - e^{-2\kappa z_0}} \left[ \frac{2\Psi_{01} \Psi_{02}}{\Psi_{01}^2 + \Psi_{02}^2} - e^{-\kappa z_0} \right]$$

(2.23)

where $R$ is the radius of particle, $\Psi_{01}$ and $\Psi_{02}$ are the zeta potential of particle and surface, respectively, $\varepsilon_r$ is the dielectric constant of the medium, and $\varepsilon_0$ is the dielectric constant of a vacuum. The Debye-Hückel parameter $\kappa$ of the electrolyte solution is given by

$$\kappa^2 = \left( e^2 / \varepsilon \varepsilon_0 k_B T \right) \sum_i z_i^2 n_{iy}$$

(2.24)

where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $z_i$ is the valency of ion $i$, and $n_{iy}$ is the bulk concentration (molecules/cm$^3$), and $e$ is the electronic charge.

Gregory [44,45] derived the interaction energy per unit area between flat plates at constant surface charge condition. Since the charge on the approaching surfaces remains constant, the total charge in the solution between the surfaces does not change. When two surfaces approach to each other, the charge density in solution will increase by the
introduction of the diffuse layer charge of the second surface and the “compression” of the entire diffuse charge into the space between the surfaces. Based on this, Gregory derived an approximate expression of the potential at the mid-plane and then the force per unit area between two parallel flat surfaces was obtained. The interaction force between a sphere and a flat surface referred as compression approximation is given by,

$$F_{el}^{\psi}(z_0) = \frac{4\pi R n_e k_B T}{\kappa} \left[ 2Y \ln \left( \frac{B + Y \coth(\kappa z_0/2)}{1 + Y} \right) - \ln(Y^2 + \cosh(\kappa z_0) + B \sinh(\kappa z_0) + \kappa z_0) \right]$$

(2.25)

where, $T$ is the temperature, $Y = (y_1 + y_2)/2$ and $y = ze\psi/kT$

and $B = [1 + Y^2 \csc h^2(\kappa z_0/2)]^{1/2}$.

Direct measurement results have proved that constant surface charge boundary condition describes the electrical double layer interaction much better than the constant surface potential boundary condition at small separation between the two surfaces.

Another simple and widely used equation is linear superposition approximation [40]. The basic idea is to assume the potential at the mid-plane of the two flat surfaces is small and is simply the sum of the contribution from each surface when they are isolated. The interaction force between spheres is given by

$$F_{el}^{\psi}(z_0) = \frac{128\pi R n_e k_B T \gamma_1 \gamma_2}{\kappa} \exp(-\kappa z_0)$$

(2.26)
where \( \gamma = \tanh\left(\frac{ze\Psi}{4k_BT}\right) = \frac{\exp\left(\frac{ze\Psi}{2kT}\right) - 1}{\exp\left(\frac{ze\Psi}{2kT}\right) + 1} \)

The linear superposition approximation is based on neither constant surface potential nor constant surface charge condition.
2.2 Particle Removal

Laser shockwave cleaning which has entirely different concepts from conventional laser cleaning is not a particle removal technique commonly used in semiconductor industry. It was proposed first by J. L. Vaught in KLA-Tencor in 1990[46]. 10 years later, J. M. Lee et al. demonstrated its effectiveness for small particle removal in 19th International Congress on Applications of Lasers and Electro-Optic[77]. Since then, this cleaning method has been investigated by researchers. However it still has some shortcoming to overcome and the exact removal mechanism hasn’t been found yet.

In this section, following the brief review on conventional laser cleaning, laser shockwave cleaning will be discussed with its particle removal mechanism and introduction of its hybrid-type methods. Finally the theory of hydrodynamic cleaning necessary for investigating the removal mechanism of wet laser shockwave cleaning will be addressed.

2.2.1 Conventional Laser Cleaning

The origin of laser cleaning can be traced back to the 1960s when Arthur Schawlow, one of the pioneers of the laser, proposed a tool called the laser eraser which would be able to selectively vaporize strongly absorbing black pigment from strongly reflecting white paper. Then, Asmus and co-workers found the first practical application in 1973 in which a pulsed ruby laser could be used to remove black encrustations from a decaying marble
sculpture without apparent alteration to the marble surface [47, 48]. They suggested the idea that the strongly absorbing black encrustation was removed by several pulses of laser radiation while the strongly reflecting white marble surface was left intact as the energy in the laser beam was simply reflected away (more detailed description could be found in the following section). Asmus believed that if this was indeed the case in practice then the use of laser radiation would lead to a major advancement in cleaning techniques i.e. a tool that could effectively detect a difference between layers of dirt and an object surface and respond accordingly. This was different method from other techniques available at the time. Since then, many efforts have been carried out in order to investigate the cleaning mechanisms [49, 50, 51, 52] and to find the practical applications in various fields [53, 54, 55, 56, 57].

One of the basic principles of laser cleaning is the photo-thermal effect as suggested by Asmus, which means heating and vaporization of surface particles by direct laser beam absorption on target material. In many cases, the contamination layer has a large absorptance to the laser beam (although it depends on material properties, laser wavelength, etc). Assuming that material constants such as thermal diffusivity and thermal conductivity are the same for both the contaminant and the substrate, and only difference is surface absorptivity, then the principle of the removal of contaminant from the surface can be easily described as shown in Figure 2.6.

The temperature of the contaminant having relatively larger laser absorption is raised to high temperature very quickly, resulting in vaporization. Once all of the contaminant has
been removed, further laser pulses are simply reflected away from the substrate normally having a smaller laser absorptance. Since very little heat is induced by the poor absorptance in the substrate an intact surface is retained by the limited temperature rise. This is called selective vaporization processor “self-limiting process,” which is one of the most beneficial characteristics for laser cleaning since ablation of material from the surface of an object stops as soon as the contamination layer has been removed. The self-limiting cleaning can be observed in many cases, e.g. removal of strongly absorbing encrustation or paint from weakly absorbing white marble or metal substrate respectively.

Figure 2.6 Schematic illustration of basic principle of laser cleaning
Figure 2.7 Self-limiting nature: laser ablation thresholds for clean and contaminated surface

Figure 2.7 shows the self-limiting nature graphically. If cleaning is carried out at an energy density below $E_d$ but above $E_c$ then the process will be self-limiting. The slope of the plots is a result of the inhomogeneous nature of the surface i.e. some areas of a surface are more easily cleaned than others. It is most important to realize that the cleaning threshold depends to some extent on the condition of the surface and cleaning is much more likely to be self-limiting if carried out at low energy density so that the most selective cleaning operates.

However it should be noted that laser cleaning is conducted not only by the photothermal effects but also by other effects such as photo-chemical effects [58,59,60] and mechanical effects [61,62,63,64,65] which are mainly dependent on laser parameters (laser wavelength, pulse length etc) and material properties. In particular, laser wavelength is believed to be one of the critical parameters for laser cleaning since the
absorptivity of a material is strongly dependent on the wavelength of the incident radiation, ranging from ultraviolet to infrared [66]. Normally shorter wavelengths give higher energy coupling producing more efficient removal of a material while this provides more possibility of substrate damage due to its high laser absorption even on the substrate material (e.g. metals, semiconductors) as well as mechanical pressure induced by rapid evaporation and rapid expansion of the plasma plume. The proper selection of a laser beam with a particular wavelength (by considering the materials treated, such as contaminant and substrate) is therefore important for successful laser cleaning.

2.2.1.1 Applications of Conventional Laser Cleaning

*Cleaning of Stone for Art Conservation*

The formation of unsightly and damaging black encrustation on stone monuments due to interaction with atmospheric pollution has become a familiar problem. Traditional cleaning techniques such as particle abrasion and liquid jets have often proved successful in restoring the outer appearance of a sculpture. However, by their very nature these techniques damage the underlying stone and often result in the loss of fine details from a sculpture. Recently, it has been found that laser process has given promising results in which polluted layers are removed selectively from the sculpture without damage to the underlying stone [48,60,67,68] with the added advantage of sterilizing the surface during the high temperature process.
Figure 2.8 shows one of the examples of laser applications in the cleaning of a marble sculpture [69]. A Q-switched Nd:YAG laser with a fundamental wavelength of 1064nm has been used in this work. Contaminants such as soil and whitewash on the surface have successfully been removed by the laser treatment without damaging the substrate marble. However, this has to be done in a very controlled manner since laser induced under-lying substrate damage is a fatal fault in art conservation. In addition, the growing number of uses of laser in art conservation include the removal of corrosion products from bronze, encrustation from stained glass, fungi from leather and vellum, and recovering original paintings and so on [70,71].

Figure 2.8 Laser cleaning of a Greco-Roman marble head which was excavated in Shropshire, England: (a) initial appearance covered in soil and whitewash, (b) appearance in the middle of laser cleaning process and (c) restored appearance after completion of laser cleaning [69]


**Cleaning of Molds in Tire-Manufacturing**

The method for cleaning tire molds traditionally involves scouring the moulds with glass beads applied at high pressure. Molds for high-end tires with details on the side-walls have to be cleaned every two or three weeks. This technique is expensive, messy and can erode the mold surface, which eventually results in low quality outputs and requires replacement of the expensive moulds.

Figure 2.9 shows a well-cleaned area in the right side of the mold by excimer laser irradiation, which removes the surface contaminants successfully and causes no damage to the underlying mold surface [72]. In this case, the pulsed laser lifts off contaminants from a mold and a pure inert gas then sweeps the contaminants from a trap. As a result, the laser cleaning technique for tire-manufacturing can dramatically cut production costs, reduce environmental impacts and perform cleaning without degrading the tire molds.

Figure 2.9 Surface morphology of tire mold before laser cleaning (left side) and after laser cleaning (right side) [72]
Semiconductor Wafer Cleaning

The conventional cleaning techniques used in the semiconductor fabrication lines such as ultrasonic or megasonic cleaning and high pressure gas jet cleaning are inefficient in removing the micron or sub-micron particles as well as avoiding mechanical pressure-induced damage to delicate parts. These lead to significant yield loss and provide a limitation of further development of the chip technology. The laser cleaning a promising new approach for effective removal of the very small particles on the surface, in which conventional cleaning techniques are inadequate for the removal [73,74,75].

Figure 2.10 shows the SEM (Scanning Electron Microscopy) images of the Si wafer surface before and after laser cleaning. The particles on the surface are copper in the size of around 1μm. The XeF excimer laser having the wavelength of 350nm and pulse length of 8nsec has been used. It is shown in Figure 2.10 (b) that a well-cleaned surface without any damage is obtained by 10 pulses of the laser with laser beam density of 0.34J/cm² [76].

Figure 2.10 SEM images of the Si wafer surface (a) before and (b) after laser cleaning of 1μm Cu particles [76]
2.2.2 Laser Shockwave Cleaning

This technique uses a plasma shock wave produced by a breakdown of gas due to an intense laser pulse to remove the encrustations from the underlying material substrate [77]. The beam is directed parallel to the surface in order to avoid direct laser interaction with the target material and is tightly focused a few mm's above the area to be cleaned. When the power density of the beam at the focal point is higher than threshold which is around $10^{12}$W/cm$^2$, the gaseous ambient constituents begin to break down and ionize. As a result, a shockwave is produced which has an audible snapping sound. In air, the typical peak pressure of the shockwave front for spherically expanding plasma is estimated to be the order of hundreds of MPa. However, the precise value depends on the laser beam power density and the distance from the shockwave center [78]. This method has unique characteristics compared to conventional laser cleaning techniques, since it includes neither direct laser-particle interactions nor the use of ultraviolet radiation for the removal of particles from surfaces. The schematic diagram of the experimental set-up is shown in Figure 2.11. A Q-switched Nd:YAG laser beam with a fundamental wavelength of 1064nm is used since a high laser beam power density is required for this process. The area cleaned by the shock waves is over ten times larger than that achieved by conventional laser cleaning techniques. This is a significant advantage in speed of cleaning of large areas. This shock process also utilizes the fundamental wavelength of a Q-switched Nd:YAG laser for the generation of the shockwaves while conventional laser cleaning techniques mostly employs ultraviolet radiation for the removal of particles from surfaces. This is another advantage in cost for cleaning systems. These unique
characteristics of this shock cleaning process may allow laser techniques to become a real alternative to conventional cleaning methods based on mechanical and chemical reactions in semiconductor and microelectronic industries.

Figure 2.11 Experimental set-up (on left hand side) and for the removal of particles from silicon wafers using airborne plasma shock waves induced by gas breakdown in air and real laser-induced plasma (on right hand side)

**Damage Issue in Laser Shockwave Cleaning**

Due to these advantages of laser-induced shockwave cleaning (LSC) technique, it has been intensively studied with the demonstration of effectiveness in removal of particle down to 200nm from silicon wafer [77,79]. However, recently it has been reported that damages on the surface could occur due to thermal radiation from laser-induced plasma [80]. The damage on structures of a wafer has been treated as a crucial issue in cleaning process, which is mostly related to the cleaning force. The stronger cleaning force, the higher probability damages can happen on the structure. For example, ultrasonic cleaning
is very powerful due to the effect of cavitations, but these cavitations are the main reason for causing damages. Therefore it is very important to secure effective cleaning process without damages. Figure 2.12 shows damages on surface of a patterned wafer occur during LSC process. In order to avoid these damages, it is necessary to bring the surface down from the plasma, while cleaning force is exponentially decreasing with increasing gap distance between the laser focus and the surface. LSC cleaning process must be conducted at the gap distance of more than 10mm to prevent damages occurred on the patterned surface, in which particle removal efficiency becomes relatively low.

Figure 2.12 Patterned wafer’s map taken by KLA-Tencor’s SURFSCAN 7600 (on the right hand side) and optical photographs (on the left hand side) showing damages on patterned surface

**Damage-Free Laser Shockwave Cleaning**

Recently, a damage-free laser shockwave cleaning system has been developed by IMT. Co. Ltd. through system modification. They demonstrated that there wasn’t any damage
occurred with their own system modification during cleaning process even at small gap distance, such as 5.5mm. Figure 2.13 shows SEM images of 60nm gate pattern before and after LSC cleaning with and without system modification.

Figure 2.13 SEM images of 60nm gate patterns before and after LSC cleaning either with or without system modification by IMT. Co. Ltd.

Figure 2.14 shows microscopic images before and after damage-free laser shockwave cleaning of particles on the IMD (Inter Metal Dielectric) structures. In this case, any damage on whole patterned wafer isn’t observed. In addition, due to high power of laser shockwave at gap distance 5mm, particle removal efficiency is close to 100%, which is comparable to wet scrubber (80%).
Figure 2.14 Damage-free laser shockwave cleaning of various types of particle on the IMD (Inter Metal Dielectric) structures

2.2.2.1 Particle Removal Mechanism

The laser shockwave cleaning (LSC) technology is still under development, aiming at removal of nanoscale particles. However, from a theoretical standpoint, it is difficult to obtain the net force acting on a very small particle on a solid surface when an impinging shockwave sweeps the surface, forming a turbulent boundary layer (the particle is mostly in the laminar sublayer). If the particle size is smaller than the value that corresponds to a critical Knudsen number, e.g., $Kn>0.1$, the flow around the particle is no longer in the continuum regime and evaluating the drag and lift force becomes a challenging task. In
order to avoid this complexity of analysis and clearly observe the aerodynamic effect on particle removal, appropriate size of particle which gives $Kn$ less than 0.1 in given LSC system has to be chosen.

Figure 2.15 shows the force diagram representing the removal force acting on a partially deformed spherical particle sitting on a solid surface. The removal moment, $M_R$ and the adhesion resisting moment, $M_A$ with respect to the contact point, $p$ can be calculated by

$$M_R = F_x h_y$$ \hspace{1cm} (2.27)

$$M_A = F_y (h_a + a) + F_A a$$ \hspace{1cm} (2.28)

where $F_x$ and $F_y$ are the parallel component and vertical component of LSC cleaning force, $F_S$, respectively, $F_A$ is the total adhesion force, and $a$ is the radius of contact area between the particle and the substrate. Other symbols are defined in Figure 2.15.

It is noted that a similar approach has been utilized to model particle removal by a megasonic cleaning process [81]. The removal force, $F_S$ acts on a particle first by the net pressure difference when the shock passes through the particle and then by the dynamic pressure associated with the high-speed gas stream behind the shock front. Since the magnitude of the dynamic pressure is smaller than the shock pressure, the magnitude of the cleaning force is thus estimated by integrating the pressure force.
\[ F_S = \int_{A_P} (P_2 - P_1)n \cdot dA \]  

(2.29)

where \( P_1 \) and \( P_2 \) are pressures of the unperturbed gas and the shockwave front, respectively, \( n \) is a unit vector normal vector, \( A \) is the area, and \( A_P \) is the particle surface area that contacts the shockwave. The resisting moment is due to particle adhesion forces by van der Waals, electrostatic and capillary interactions.

Figure 2.15 Force diagram for modeling the particle removal mechanism by the LSC process

If \( M_R > M_A \), rolling of a particle is initiated and the particle is swept away by a shockwave. The removal moment ratio given by

\[ \text{Moment Ratio}(MR) = \frac{M_R}{M_A} \]  

(2.30)
where $M_R$ is the removal moment and $M_A$ is the adhesion resisting moment.

Moment ratio (MR) is very useful to predict the possibility of contaminant removal in any circumstance (such as different size and different material of a particle and different kinds of substrate) that cleaning process is strongly required in semiconductor manufacturing process before applying it directly to real manufacturing process.

### 2.2.2.2 Hybrid Laser Shockwave Cleaning Methods

Conventional laser shockwave cleaning has unique characteristics such as dry cleaning, high throughput and high physical cleaning power. However it has been reported that this technique has damage issue, ineffectiveness in removal of organic particles as well as particles deposited from liquid solution and difficulty for protecting re-deposition of detached particles. Accordingly, in order to overcome these shortcomings and improve the cleaning performance, many efforts has been made to develop hybrid type of laser shockwave cleaning which is combined with UV laser or water.

**UV Laser assisted Laser Shockwave Cleaning**

In aiming effective removal of organic particles, the UV laser assisted LSC technique was proposed by J. M. Lee et al in 2003. As shown in Figure 2.16, a Q-switched
Nd:YAG laser with a fundamental wavelength of 1064nm is used for the generation of laser shockwaves and a UV laser is generated at a wavelength of 266nm from the same source using a harmonic generator.

As shown in Figure 2.17, when UV laser is exposed onto deposited particles on the substrate, organic particles absorb UV laser due to high absorptivity and immediately are expended with loosening up the bonding with other adjacent particles. Another role of UV laser in this hybrid technique is explosive evaporation of liquid trapped between particles and the substrate resulting in decreasing the capillary force. Therefore, following the exposure of UV laser, shockwaves can remove effectively organic particles as well as ones deposited from liquid solution, which is comparable to conventional laser shockwave cleaning.
This hybrid LSC technique still has a distinct advantage as a dry cleaning process. In addition, it gives high removal efficiency close to 100% even for 63nm PSL particles, as shown in Figure 2.18. However, the UV laser cleaning process has to be optimized to determine the damage-free cleaning condition of the used substrate, whenever new substrate is used. Because the interaction between UV laser beam and surface is highly dependent on the optical property of the surface for absorbing UV laser. Therefore, the damage-free condition has to be found by varying the energy density of UV laser beam. Figure 2.19 shows AFM images of EUV Si capping layers after UV laser as a function of the laser energy density. It is shown that as the UV laser beam density decreases, the damages appear in AFM images becomes less and less and finally at laser beam density of 8mJ/cm², no more damages occur.
Figure 2.18 Removal efficiency of 63nm PSL particles after UV irradiation and combined UV and LSC [19]

Figure 2.19 AFM images of EUV Si capping layer after UV irradiation [19]
Steam Laser Shockwave Cleaning

The steam laser shockwave cleaning (SLSC) was developed by a research team in POSTECH, Korea [82]. It is one of hybrid laser shockwave cleaning combined with conventional steam laser cleaning, which uses explosive vaporization of thin liquid film on the substrate occurs due to the direct laser beam exposure onto the liquid. As shown in Figure 2.20, eximer laser is employed for rapid vaporization of provided vapors through nozzle. In order to obtain high removal efficiency using SLSC, it is important to synchronize the shockwave generation with the vaporization of liquid. This hybrid technique was reported to be more powerful than conventional LSC due to increase in the density of medium in which a shockwave propagates, however its cost becomes too much higher by employing eximer laser (mostly very expensive). In addition, it is not only uncontrollable, but can also cause damages on vulnerable structures of a wafer, since the uniform vaporization induced by eximer laser is tough to be obtained and the failure in uniform vaporization induced by eximer laser can give a rise to damages on patterned surface, when it is combined with shockwave can lead to excessive increase in the cleaning power. The phenomena appears in SLSC process is very unpredictable, which is similar to high speed jet spray cleaning method.
**Underwater Laser Shockwave Cleaning**

When a shockwave is generated and propagates through water by converging intense laser beam underwater, the phenomena appears has been one of interesting topics to researchers particularly in bio industry, since medical treatments using laser is conducted over human body in which more than 70% of it consists of water. Therefore the underwater laser-induced shockwave can often occur in medical treatment. On the other hand, recently attempts to apply it for semiconductor industry have been made in order to remove particles from the wafer surface. In 2004, W. D. Song et al. demonstrated that shockwaves generated underwater could remove 1μm silica particles as well as 51nm and 110nm PSL particles [83]. The removal mechanism corresponding to these cleaning
results was explained as the effect of cavitations produced during the process. It is well known that when cavitations are released, it produces too strong physical force to cause damages on the patterned surface of a wafer. This damage due to cavitations in ultrasonic cleaning as well as megasonic cleaning has been already reported [10]. Figure 2.21 shows the schematic diagram of underwater laser shockwave cleaning system which is the patent application filed by A. Rastegar in SEMATECH [84]. He designed a special nozzle head containing water, where laser beam converges into water creating laser-induced plasma and consequently the underwater shockwave is generated. Finally high speed water jet can be formed and guided to the substrate in such a way that the jet flow impacts on particles and removes them from the surface.

This technique is very powerful for nano-scale particle removal due to high speed water jet and cavitations’ effect. However, these formed cavitations can cause damages on patterned surface easily, since when they are released near the pattern surface, generated shocks is too strong (its speed is up to 100m/s). In addition, theses are uncontrollable, so
it is very difficult to find the optimum condition for securing damage-free cleaning.

**Wet Laser Shockwave Cleaning**

The wet laser-induced shockwave cleaning (WLSC) technique was originally proposed by V. K. Devarapalli et al. in 2006 [85]. As shown in Figure 2.22, they formed thin liquid film which thickness was fixed to 100 μm with imposing laser-induced plasma above the liquid surface. Consequently laser shockwaves impinges against the liquid and generates the liquid flow, which is responsible for particle removal. They also demonstrated that the 710 nm glass particles and 404 nm polystyrene latex (PSL) particles on a 2 cm x 2 cm piece of a wafer could be removed mostly by using the technique. The removal mechanism hasn’t been found yet due to the complexity of the phenomena appear during the process although it is very effective in particle removal.

![Figure 2.22 Schematic diagram of wet laser-induced shockwave cleaning system [85]](image-url)
2.2.3 Hydrodynamic Cleaning

Hydrodynamic method is one of the practical ways to remove particles from surface. The fluid velocity distribution, wall shear stress, drag and lift forces applied on a sphere and some other important parameters are well established for fluid flow over a surface. Obviously, the removal of small particles from surfaces needs higher velocity, as a result, the flow normally is turbulent. The particles on the surface are subject to the stresses in the laminar sub-layer of the turbulent boundary layer. The quasi-static approach assumes that when the hydrodynamic forces applied on the particle overcome the adhesion forces, the particle will leave from its initial position either by lifting, sliding or rolling, causing instant re-suspension. The direct observations of particles near a wall in turbulent flow show that the motion of an individual particle is quite random and unsteady and that particle often rolls along the surface and then suddenly moves, almost at right angles, away from the surface into the mean flow [86,87].

2.2.3.1 Boundary Layer

When the fluid flows along a no-slip palate, the friction of the surface retards the motion of the fluid in a thin layer near the wall. In this layer, the velocity of the fluid increases from zero at wall (no slip) to its full value that corresponds to external frictionless flow (free stream). The layer under consideration is called the velocity boundary layer. The velocity boundary layer thickness is defined as the value of $y$ where $u = 0.99U$. 
L. Prandtl investigated the essential influence of viscosity in flows and clarified that a shear layer must be very thin if the Reynolds number \( \text{Re} = \frac{U \cdot L}{\nu} \), where \( \nu \) is the kinematic viscosity, is large. Thus the following approximations apply to a boundary layer [88]:

i. \( \delta \ll L \), where \( L \) is the characteristic length of the plate

ii. \( \nu \ll u \)

iii. \( \frac{\partial u}{\partial x} \ll \frac{\partial u}{\partial y}, \frac{\partial v}{\partial x} \ll \frac{\partial v}{\partial y} \)

Applying these approximations to continuity and momentum equation results in Prandtl’s boundary layer equations

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad (2.31)
\]
Momentum along wall:
\[
\frac{u}{\partial x} + v \frac{\partial u}{\partial y} = U_\infty \frac{dU_\infty}{dx} + \frac{1}{\rho} \frac{\partial \tau}{\partial y} \quad (2.32)
\]

where
\[
\tau = \begin{cases} 
\frac{\mu}{\partial y} & \text{laminar flow} \\
\frac{\mu}{\partial y} - \frac{\rho u v}{\partial y} & \text{turbulent flow}
\end{cases} \quad (2.33)
\]

**Laminar Boundary Layer**

For laminar flow past the flat plate, it is assumed that the free-stream velocity \( U_\infty \) is a constant \( \frac{\partial U_\infty}{\partial x} = 0 \). The boundary layer equations were solved by Blasius and later on by Howarth with an increased accuracy [89]. The laminar velocity boundary layer thickness is given by

\[
\delta_{La, min} = 5.0 \left( \frac{v}{U_\infty x} \right)^{\frac{1}{2}} \cdot x = 5.0 \left( \frac{1}{Re_x} \right)^{\frac{1}{2}} \cdot x \quad (2.34)
\]

where \( Re_x \) is the local Reynolds number of the flow along the plate surface and it is given by

\[
Re_x = \frac{U_\infty x}{v} \quad (2.35)
\]

The kinematic viscosity \( v \) is given by
\[ \nu = \frac{\mu}{\rho} \quad (2.36) \]

where \( \mu \) is the viscosity of fluid and \( \rho \) is the density of fluid. Table 2.1 shows the viscosity, density and kinematic viscosity of air and water at 1 atm and 20°C.

Table 2.1 Summary of viscosity, density and kinematic viscosity of air and water at 1 atm and 20°C

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( \mu ) (kg/m·s)</th>
<th>( \rho ) (kg/m³)</th>
<th>( \nu ) (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>( 1.8 \times 10^{-5} )</td>
<td>1.20</td>
<td>( 1.50 \times 10^{-5} )</td>
</tr>
<tr>
<td>Water</td>
<td>( 1.0 \times 10^{-3} )</td>
<td>998</td>
<td>( 1.01 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

Karman assumed that the velocity profiles had an approximation parabolic shape [90]. The velocity inside a boundary layer is given by

\[
u(x, y) = U_e \left( \frac{2y}{\delta} - \frac{y^2}{\delta^2} \right) \quad 0 \leq y \leq \delta(x) \quad (2.37)\]

**Turbulent Boundary Layer**

In the turbulent boundary layer, three different regions may be delineated as shown in Figure 2.24. Near the wall there is a laminar sub-layer in which transport is dominated by diffusion and the velocity profile is nearly linear. There is an adjoining buffer layer in
which diffusion and turbulent mixing are comparable. Finally, in turbulent region, transport is dominated by turbulent mixing [91].

According to Prandtl’s theory, turbulent boundary layer thickness is given by

\[
\delta_{\text{Turbulent}} = 0.16 \left( \frac{v}{U_\infty x} \right)^{\frac{1}{7}} \cdot x = 0.16 \left( \frac{1}{\text{Re}_x} \right)^{\frac{1}{7}} \cdot x
\]  

(2.38)

We define dimensionless velocity and length

\[
u^+ = \frac{u}{U^*} \\
y^+ = \frac{y U^*}{v}
\]

(2.39)
Here, $U^*$ is the shear velocity (or friction velocity), which is defined as

$$U^* = \frac{\tau_0}{\sqrt{\rho}} \quad (2.40)$$

where $\tau_0$ denotes the shearing stress at the wall. In the case of the flow on the smooth flat plate, $\tau_0$ can be calculated using following equation [91].

$$\tau_0 = 0.0225 \rho U_*^2 \left( \frac{V}{U_* \delta} \right)^2 \quad (2.41)$$

The average velocity distribution can be expressed as

Laminar sub-layer ($y^+ < 5$): \hspace{1cm} $u^+ = y^+$ \hspace{1cm} (2.42)

Buffer layer ($5 < y^+ < 30$): \hspace{1cm} $u^+ = 10 \arctan(0.1 y^+) + 1.2$ \hspace{1cm} (2.43)

Turbulent region ($y^+ > 30$): \hspace{1cm} $\left( \frac{u}{U_*} \right)_{\text{Turb}} = \left( \frac{y}{\delta} \right)^{1/7}$ \hspace{1cm} (2.44)

2.2.3.2 Drag and Lift forces

The flow past a particle leads to drag and lift forces acting on the particle. The drag force
on a spherical particle in a Newtonian fluid without the no-slip assumption can be expressed by the following equation

\[ F_D = C_D \frac{\pi}{8} \rho D^3 u^2 \]  \hspace{1cm} (2.45)

where \( C_D \) is the drag coefficient, \( \rho \) is the density of fluid, \( D \) is the diameter of the particle, \( u \) is the streaming velocity and \( C_C \) is Stokes-Cunningham slip correction.

An important assumption in deriving Stokes’ relation and in determining the correlations from experiments (with \( Kn < 0.1 \)) is the no-slip boundary condition at the particle-fluid interface. As the diameter of a particle becomes of the order of the mean free path of the fluid (\( Kn > 0.1 \)), the no-slip boundary condition no longer holds. In 1910, Cunningham derived a correction factor for Stokes’ law to account for this effect [92]. The expression for \( C_C \) is

\[ C_C = 1 + 2Kn \left( 1.257 + 0.400e^{-0.550Kn} \right) \]  \hspace{1cm} (2.46)

The Kundsen number, \( Kn \), is used to describe the interaction between the particle and fluid. \( Kn \) is defined as

\[ Kn = \frac{\eta}{D} \]  \hspace{1cm} (2.47)
where $\eta$ is the fluid’s mean free path, which is the average distance traveled by a molecule between successive collisions.

It has been shown that for particles larger than 10nm, Kn is very small and therefore Stokes-Cunningham slip correction is almost one [93]. That means if we are dealing with particles larger than 10nm, the no slip assumption is still valid.

In the case of nanoscale particle removal using wet cleaning, the particle is embedded either in a laminar boundary layer or the laminar sub-layer in a turbulent boundary layer. For both cases, the velocity profile applied on the particle is assumed to be linear, as shown in Figure 2.25.

![Figure 2.25 Spherical particle in contact with a flat surface in a linear shear flow](image)

O’Neil [94] derived an exact solution of the linearized Navier-Stokes equations for a viscous flow past a fixed sphere in contact with a fixed surface when Reynolds number is sufficiently small and the drag force is given by,
\[ F_D = 1.7 \cdot 6\pi \mu U_R \approx 32R^2 \tau_0 \]  

(2.48)

where \( U_R \) is the fluid velocity at the center of the spherical particle.

Accordingly, the resulting moment applied on the particle at its center is given by

\[ M_D = 0.944 \cdot 8\pi \mu R^2 U_R \approx 23.7R^3 \tau_0 \]  

(2.49)

Therefore, the total moment at the contact point is given by,

\[ M_D + F_D R = 55.7R^3 \tau_0 = 1.74F_D R \]  

(2.50)

The resultant equation in Eq. 2.50 shows that the drag force \( F_D \) acts at the point which is 1.74\( R \) above the surface as illustrated in Figure 2.25.

In O’Neil’s analysis, the lift force is negligible. Later on, Leighton and Acrivos [95] determined the lift on a stationary sphere in contact with a surface in a linear shear flow under condition of small Reynolds number,

\[ F_L = 9.22 \rho \frac{\tau_0^2 R^4}{\mu^2} \]  

(2.51)

Because lift force \( F_L \) is proportional to \( R^4 \) and drag force \( F_D \) is proportional to \( R^2 \), lift force is much smaller than drag force for small particle.
2.2.3.3 Moment Ratio Analysis for Particle Removal

There are three different mechanisms for particle removal: sliding, rolling or lifting. In hydrodynamic cleaning, the lifting force is negligible, since it is much lower than the drag force. Therefore rolling mechanism can be responsible for the particle removal mechanism in hydrodynamic cleaning method.

\[
MR = \frac{F_d(1.74R - \delta') + F_d.a}{F_d.a}
\]  

(2.52)
where MR is the removal moment ratio, $\delta'$ is the deformation height of the particle, $a$ is the contact radius between the deformed particle and the surface, $F_D$ is the drag force, $F_{el}$ is the electrostatic double layer force and $F_A$ is the adhesion force.

When the removal moment overcomes the adhesion moment, theoretically, the particle is removed by rolling. The drag moment acting on the particle will lead the particle to roll over and detach from the surface [96].
2.3 Wind-Driven Water Currents

Wind action over water generates both waves and surface drift. Waves contribute to the surface drift through Stokes mass transport. A portion of the total rate of momentum transfer to the water is through the normal stress acting on the disturbed surface and the other portion is due to the tangential stress which contributes, at least in part, to the surface drift [97].

Previous investigations of surface drift were obtained by Van Dorn (1953) [98] in a pond and by Keulegan (1951) [99], Wu (1968) [100], Pate and Trawle (1970) [101] and Wright and Keller (1971) [102] in the laboratory. The first two observers found the surface drift to be about 3% of the wind speed under turbulent conditions. The surface drift was found to be independent of surface waves which they were able to show by suppressing the waves by spreading detergent over the water surfaces. The other investigators recorded surface drifts in the range 2.5~5.0% of the wind speed. An interesting computation of surface drift based on Stokes mass transport was carried out by Kenyon (1969) for a fully developed sea [103]. The computation suggests that the entire wind stress is supported by waves in a fully developed sea.

2.3.1 Governing Equations

Due to the complexity of the phenomena occur in wind-driven currents, it has been numerically studied by many researchers, because numerical modeling approach is less
costly as well as being easily controlled and executed. Recently, Huang built up the numerical model which incorporates wave-induced mean Reynolds stress on the wind-driven current in shallow water [104]. The wind was assumed steady and uniform over the fetch and the stratification and the earth rotation were not considered. The numerical example was presented for the idealized long, shallow channel.

As shown in Figure 2.27, surface waves riding on a wind-driven current in a water of finite, constant depth $h$ is considered. The fluid is incompressible with constant density $\rho$. The horizontal extent is assumed to be infinite so that the flow is two dimensional. The $x$-coordinate lays on the plane of the still water level (SWL) and $z$-coordinate is pointing upward with its origin at the SWL. The surface displacement from the SWL is denoted by $\eta(x,t)$. The rigid and smooth bottom is located at $z = -h$.

Figure 2.27 Velocity profiles of the wind and the water driven by wind along $z$-axis
The fluid motion in water is governed by the equation of continuity and the equations of momentum

\[
\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0 \quad (2.53)
\]

\[
\rho \left( \frac{\partial u}{\partial t} + \frac{\partial uu}{\partial x} + \frac{\partial uw}{\partial z} \right) = -\frac{\partial p}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{xz}}{\partial z} \quad (2.54)
\]

\[
\rho \left( \frac{\partial w}{\partial t} + \frac{\partial uw}{\partial x} + \frac{\partial ww}{\partial z} \right) = -\frac{\partial p}{\partial x} + \frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{zz}}{\partial z} \quad (2.55)
\]

which implies that waves and turbulence have distinct time and length scales. In Eq. 2.53, 2.54 and 2.55, \( u \) and \( w \) are the velocity components in the \( x \)- and \( z \)-directions, respectively. The dynamic pressure is \( p \), which is related to the total pressure \( P \) by

\[
P = p - \rho g z. \quad \tau_{ij} \text{ are the stress components including the viscous stress and the Reynolds stress. The stress components are related to the viscosity } \nu \text{ by}
\]

\[
\tau_{xx} = 2 \rho \nu \frac{\partial u}{\partial x}, \quad \tau_{zz} = 2 \rho \nu \frac{\partial w}{\partial z} \quad (2.56)
\]

\[
\tau_{xz} = \tau_{zx} = \rho \nu \left( \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \quad (2.57)
\]

where \( \nu \) is the kinematic viscosity.
2.3.2 Boundary Conditions

On the air-water interface, free surface, there is no mass flux through the interface, which leads to the surface boundary conditions.

\[
\frac{\partial \eta}{\partial t} + u \frac{\partial \eta}{\partial x} = w, \quad z = \eta \tag{2.58}
\]

The continuity of the normal and tangential stresses across the air-water interface leads to the following dynamic surface boundary conditions.

• Normal stress condition

\[
-(p - \rho g \eta) + \tau_{zz} - \tau_{\eta \eta} \frac{\partial \eta}{\partial x} = 0, \quad z = \eta \tag{2.59}
\]

• Tangential stress condition

\[
-[\left(- (p - \rho g \eta) + \tau_{\eta \eta}\right) \frac{\partial \eta}{\partial x} + \tau_{\eta \eta} = \tau_s, \quad z = \eta \tag{2.60}
\]

where \(\tau_s\) is the wind stress exerting on the water surface, which is given by

\[
\tau_s = \rho u^2_s = \nu \frac{\partial u}{\partial z} \tag{2.61}
\]

where \(u_s\) is the surface shear velocity.
At the bottom, the no-flux condition requires

\[ w = 0, \text{ at } z = -h \]

And the no-slope condition requires that

\[ u = 0, \text{ at } z = -h \]

In addition, the initial condition gives \( \eta(x,0) = 0 \). And due to open boundary condition, it is assumed that there are no counterflow.
Chapter 3 Experimental Materials and Procedure

3.1 Particle Removal

3.1.1 Materials and Wafer Pre-cleaning

The substrate used in experiments was a 4-inch silicon wafer. In order to investigate the cleaning performance for particles with diameter of less than 50nm, it was necessary to compare images of the same location before and after cleaning by using scanning electron microscopy (SEM). Therefore, some of wafers were marked through the simple fabrication process. All wafers were cleaned first by Piranha (H\textsubscript{2}SO\textsubscript{4}(96\%) : H\textsubscript{2}O\textsubscript{2}(30\%) = 2 : 1) at 105-115°C for 10 minutes and following that, cleaned in a quartz megasonic batch tank (PCT) using dilute SC1 (H\textsubscript{2}O : H\textsubscript{2}O\textsubscript{2}(30\%) : NH\textsubscript{4}OH(29\%) = 40 : 2 : 1) at 45°C for 40 minutes prior to particle deposition.

Particles used were polystyrene latex (PSL) spheres with mean diameters of 2\textmu m, 600nm, 300nm and 28nm (Duke Scientific Corp.) and silica spheres with mean diameters of 280nm. PSL particles were originally in an aqueous solution with some surfactants, while silica particles were in powers. These surfactants affect the adhesion force between particles and substrate, because when particles are deposited onto the surface of wafers, aqueous solution containing surfactants can be trapped between particles and surface and
as a consequence, due to increase in repulsive double layer force, the adhesion force will become lower especially when applying wet cleaning process to remove particles.

In order to decrease the effect of the surfactants, particles were washed in a dialysis tube with excessive amount of DI water for more than a week and water was changed twice each day. Figure 3.1 shows the comparison between washed and unwashed 300nm PSL particles on Si wafer. The removal efficiency of unwashed 300nm particles on wafer by spinning it in 7500rpm is much higher than one of washed 300nm particles.

Figure 3.1 Comparison of removal efficiencies between washed and unwashed 300nm PSL suspended in the liquid, when particles are cleaned from the surface of a wafer by rotating it in 7500rpm with water
3.1.2 Experimental Procedure

3.1.2.1 Particle Deposition

300nm PSL particles and 280nm silica particles were suspended in two different solutions, deionized (DI) water and isopropyl alcohol (IPA) solution. 600nm and 2μm PSL particles were suspended in only IPA solution to decrease the effect of capillary force leading to higher adhesion force, since these two different sized particles were used only for the verification of the removal mechanism of organic particles in LSC.

A few drop of such suspension were applied on the wafer while it was rotated on the spin dryer at a low rotation speed (200rpm) and then spun dry at a relatively high speed (2000rpm). Approximately 1000 to 1500 particles were deposited on each wafer. For 28nm PSL particles, a nebulizer was used to spray and deposit them onto the wafer from IPA solution, because particle deposition by a spin dryer resulted in huge particle agglomeration.

3.1.2.2 Cleaning Methods

Laser Shockwave Cleaning

A Q-switched Nd:YAG laser with a fundamental wavelength of 1064nm, a pulse energy
of 1.8 J, a pulse width of 10ns and a pulse repetition rate of 10Hz (YG980, Quantel) was utilized in experiments. The laser beam was converged into a laser focus by lens with the focal length of 150mm to generate the laser-induced plasma shockwaves. The gap distance between the focal point and the wafer surface was 5mm, which was optimized for preventing damages from laser-induced plasma and maximizing the cleaning performance, since the closer to the laser-induced plasma the substrate surface is, the stronger the power of a shockwave is. For wafer scale cleaning, a rotational and linear translation stage was used to give the uniform exposure of shockwaves over whole area of a wafer. The distance among generated shockwaves (from center to center) was fixed to 5mm, which is the minimum in the LSC system. Nitrogen gas with high purity was also utilized to blow out detached particles from a wafer for protecting re-deposition during LSC process.

**Wet Laser Shockwave Cleaning**

In the application of wet laser-induced shockwave cleaning technique, clean DI water was used as a liquid film on the top of a wafer. For the formation of thin water film, small amount water of approximately 200μl from 1000μl micro-pipette was applied onto the wafer and then it was spun gently until the dropped water covered whole area of the wafer, which gave approximately 25μm-thick film layer on the surface of 4-inch wafer. After cleaning process with thin water film, the wafer was dried by spinning it at 1000rpm.
3.1.2.3 Particle Removal Measurement

All experiments were carried out in Class 10 cleanroom environments except imaging 28nm PSL particles before and after cleaning on the wafer surface with the field emission scanning electron microscopy (FESEM, Carl Zeiss). The number of 28nm particles was quantified from FESEM images. For 300nm, 600nm and 2μm PSL particles and 280nm silica particles, the number of particles before and after cleaning was counted by surface particle scanner (SurfScan 5500, KLA-Tencor), which is capable of inspecting the particle size down to 200nm on 4, 6 and 8” wafer.

To evaluate the cleaning performance for particle removal, it is necessary to calculate the particle removal efficiency (PRE), which is given by

$$PRE(\%) = \frac{n_d - n_i - n_c}{n_d - n_i} \times 100$$

(3.1)

where $n_i$ is the initial number of particles before particle deposition, $n_d$ is the number of particles after particle deposition, and $n_c$ is the number of particles after cleaning.
3.2 Measurement of Deformation of Particles in LSC

The Si wafer was first diced into small pieces of 1.5cm by 1.5cm, and then those chips were cleaned by Piranha (H₂SO₄(96%) : H₂O₂(30%) = 2 : 1) at 105-115°C for 10 minutes. Following that, they were cleaned in a megasonic tank using dilute SC1 (H₂O : H₂O₂(30%) : NH₄OH(29%) = 40 : 2 : 1) at 45°C for 30 minutes prior to particle deposition. A few drop of diluted 300nm PSL particles suspension (Duke Scientific Corp.) were applied on the chip. The chip with particle solution was then rotated on spin dryer at a relatively low speed (200rpm) and gently dried out by Nitrogeon gas. This procedure was repeated several times to deposit as many particles as could be found on the edge of a chip, because the sample substrate would be tilted at an angle of 86°-87° from the beam for imaging of it. Unless there are particles on the edge, it will be much harder to find particles in SEM.

After deposition of 300nm PSL particles on the chip, it was placed right underneath laser-induced plasma and then exposed by 1 pulse or 5 pulses of the shockwave at different gap distancees of 5mm and 10mm between the focal point of laser beam and the Si wafer surface. Following that, high angle SEM images were taken to measure the radius of the contact area between the particle and the surface.
3.3 Two-Probe Beam Deflection Method

The shadow-graphic photography or the phase measurement such as interferometry has been used to investigate the behavior of laser-induced gas breakdown [105,106,107]. These methods are so powerful that tremendous valuable information can be obtained. However it usually costs too much to build those systems and in addition, it’s difficult for set-up. In this study, only velocity of laser shockwave propagation was necessary to be measured. Therefore, as an alternative method, the probe beam deflection method was applied, which is effective, inexpensive and easy to set up with such advantages as a relatively wide bandwidth, dynamic range, and negligible influence on the probe wave field [108,109].

To measure the velocity of the laser-induced shockwave, two-probe beam deflection method was designed. A continuous He:Ne laser beam emitting at 632.8 nm with an output power of 2mW (HRR020, Thorlabs) was used as a probe beam. As shown in Figure 3.2 (b) and (c), this laser probe beam was split into two by beam splitter (CM1-PBS1, Thorlabs) and then they were focused at the positions underneath laser-induced plasma by two plano-convex lenses (focal length=50 mm, Thorlab). Following that, these two laser beams were collimated by other two convex lenses after focal points respectively. Finally, after passing through band pass filters, each laser beam was detected by two photodiodes (Thorlab, DET10A), P1 and P2 respectively, which was connected to a 1GHz digital oscilloscope (Tektronix, TDS5104) to monitor the deflection signals of the probe beam. These all optical components were set up on an optical rail with an x-y-z
translation stage as shown in Figure 3.2 (a).
Figure 3.2 (a) Image of experimental setup, (b) schematic diagram of two-probe beam deflection method and (c) simple diagram showing the positions of two He:Ne laser beams.

Figure 3.3 illustrates the geometry of two probe beams deflected by a shockwave. As a shockwave propagates, when it reaches the first He:Ne laser beam which is closer to laser-induced plasma, it makes a change in the density of the medium and accordingly the reflective index of the medium becomes different. The probe beam originally in straight path gets bent and it causes a parallel shift ($\phi L$ in Figure 3.3) of the probe beam after its passage through the knife edge which is placed at a distance $L$ from the interaction region between a shockwave and probe beam. As a consequence, the shift of the probe beam leads to the change of the absorbed energy of laser beam in the photodiode (P1). The shockwave propagates further after passing through 1st He:Ne laser beam and then deflect 2nd He:Ne laser beam resulting in the detection of signal in another photodiode (P2). The deflection angle $\phi$ can be also calculated using following equation [110].
\[
\phi = \frac{1}{n_0} \int \nabla, n ds = \frac{1}{n_0} \int \frac{dn}{dr_L} \frac{dr_L}{dz} ds
\]

(3.2)

Where \(n_0\) indicates the normal refractive index and \(r_L\) is the radius of a probe beam at a distance \(L\) from interaction region.

Figure 3.3 Geometry of two deflected probe beams with Gaussian intensity profile

Shockwave speed can be obtained from the measured time delay between detected shockwave signals in two photodiodes (\(\Delta t\)), and gap between 1st HeNe laser beam and 2nd HeNe laser beam (\(d_{1st&2nd}\)), which is fixed to 0.6mm. The shockwave speed is given by

\[
\text{Shockwave Speed} = \frac{d_{1st&2nd}}{\Delta t}
\]

(3.3)

The gap distance between two focal points of Nd:YAG laser beam and the first He:Ne laser beam was varied to measure the shockwave speed at different locations by moving
the two-probe beam optical system up and down.
3.4 Measurement of Surface Velocity of Water Flow driven by a Laser-induced Shockwave

3.4.1 Shadowgraph Technique

Shadowgraph technique is a basic and valuable tool in various scientific and engineering disciplines, which has been widely used in industries such as aeronautical engineering, combustion research, ballistics, explosions and the testing of glass. It is an optical method which allows us to see the invisible such as the inhomogeneities in transparent media like air, water, and glass by using index-of-refraction differences in the media. The method relies on the fact that rays of light bend toward regions of higher refractive index while passing through transparent media. A shockwave propagating through air, for example, can disturb the homogeneity in air changing the density of media and as a result, light rays get refracted with casting shadows [111].

The father of the optics of inhomogeneous media, Robert Hooke (1635-1703), first discussed these natural visualizations in Observation LVIII of his famous Micrographia [112]. Having covered light refraction due to density variations in the atmosphere and in liquids, Hooke proceeded to explain the twinkling of stars, “heat haze,” mirages, and the distortion of the setting sun seen through a chimney plume. He understood these optical phenomena thoroughly, and was able to generalize laboratory instruments from such outdoor observations. Two centuries later, Ernst Mach mentioned several shadowgraph visualizations in his popular scientific lectures [113]. These included background
distortion due to convection from objects heated by the sun and sunlight shadowgraphy of the blast wave from a dynamite explosion. In 1887, he took the world’s first photos of shock waves from bullets in flight [114]. Cooper and Rathert first studied the use of sunlight shadowgraphy to reveal shock wave locations on high-speed aircraft wings in 1948 [115]. A modern account of shadowgraphy is given by G.S. Settles [111].

3.4.2 Experimental Setup for Shadow-Graphic Photography

A charge-coupled-device (CCD) camera (PCI 800S, Redlake Masd, Inc.) mounted with a zoom lens was used to record images at a frame rate of 60 to 8000 frames per second. These images would be digitized and stored in a computer with frame grabber (MotionScope PCI 9400, Redlake Masd, Inc.). Using an optical fiber, Halogen lamp was connected to the backlight (QVABL, Dolan-Jenner Industries, Inc.), which gives the uniform distribution of the light propagating toward to the CCD camera. As illustrated in Figure 3.4 (b), the backlight was placed underneath glass plate. In order to start recording images when the shockwave-induced water flow is generated, CCD camera should be synchronized with laser beam firing. The delay time between laser beam firing and shockwave generation is too short to be negligible. Therefore the Nd:YAG laser system was connected with oscilloscope (Tektronix, TDS5104), which was used as the pulse generator. When the firing order corresponding to the rising edge of a positive TTL signal (5V, 20mA, 25ps duration) is detected by pulse generator, the pulse generator triggers CCD camera by sending a 5V signal. Finally the captured images are stored in a
Prior to taking images, a glass plate used in experiments was cleaned by Piranha (H$_2$SO$_4$(96%) : H$_2$O$_2$(30%) = 2 : 1) at 105-115°C for 10 minutes to remove airborne particles from the surface, which can cause the hydrophobic surface. If the surface isn’t hydrophilic, it is difficult to form thin water film with uniformity over whole area. Images of the water flow driven by a shockwave were taken at different frame rates such as 1000, 2000, 4000 and 8000 frames per second in order to measure the surface velocity of the water flow more precisely. Figure 3.4 (a) and (b) show real experimental setup and schematic diagram of shadow-graphic photography respectively.
Figure 3.4 (a) Image of experimental setup and (b) schematic diagram of shadow-graphic photography system with high speed camera
As a matter of fact, the water layer on the top of a glass plate is too thin to recognize the exact boundary of the water flow which consists of the surface fluctuation formed by hydraulic jump as shown in Figure 3.5 (a). Therefore to take more clear images, a transparency film with scale bars printed on it was put on the backside of the glass plate. The gap distance among scale bars was 2mm. Consequently, clear boundary of the water flow could be observed as indicated in Figure 3.5 (b).

![Figure 3.5](image)

Figure 3.5 Photographs of the water flow driven by a laser-induced shockwave on the glass plate (a) without and (b) with the transparency film in which scale bars are printed.

The system software provided with high speed camera enabled to easily measure the surface velocity of the water flow from images. After marking two points on the image, if the distance between markers is setup as real physical distance, the software calculates it by number of pixels put between markers. Once the system is calibrated, it can measure
all distances. If a set point is placed on another frame, the system can calculate the time and distance between the data points and show the velocity.

Figure 3.6 User interface of the software showing an example of the measurement of the surface velocity of the water flow driven by a laser-induced shockwave
Chapter 4 Experimental Results and Discussion

4.1 Removal Mechanism of Organic Particles in Laser Shockwave Cleaning Process

Laser-induced shockwave cleaning (LSC) has proven effective in the dry removal of particles from surfaces. The process is also fast due to the large cleaned area per pulse. Moreover, it is also well known that LSC technique is effective for inorganic particle removal. However, it is not as effective for organic particle removal, such as polystyrene latex (PSL)\cite{116,117}. This phenomenon has not been fully explained since the adhesion forces are comparable as well the adhesion induced deformation is not an issue since the removal is ineffective even when conducted a short time after particle deposition. In this section, the reason for the ineffectiveness of the LSC organic particle removal will be discussed.

4.1.1 Removal of Organic and Inorganic Particle using Laser Shockwave Cleaning

Removal of both of organic and inorganic particles was conducted to verify ineffectiveness in LSC process, which has been reported in several papers. 300nm PSL particle and 280nm silica particles were suspended in isopropyl alcohol (IPA) and
deposited on 4-inch Si bare wafers in such way that capillary force doesn’t affect on the total adhesion force of particles as much as when particles are suspended in DI water. Following that, those particles were cleaned by LSC process and then we measured the removal efficiencies of 300nm PSL and silica particles. As shown in Figure 4.1, the removal efficiency of 300nm PSL particles is relatively low (30%) compared to the removal efficiency of 280nm Silica particles (90%). According to this result, ineffectiveness in removing organic particle could be confirmed again.

![Figure 4.1 Removal Efficiencies of 300nm PSL and 280nm Silica particles](image)

**4.1.2 Hypothesis of Organic Particle Removal Mechanism in LSC**

As shown in Fig. 4.3, shockwaves generated by laser-induced plasma can be easily measured and visualized by the laser shadow photography method (Schlieren photography). The figure shows the airborne plasma generated by intense laser beam and
the resulting shockwave propagation. The first frame shows the intense laser beam focused above the wafer, which is at the bottom of the photo. The rapid expansion of the plasma produces the intense shockwave (shown as a dark ring in the center image) outside the plasma.

![Image of shockwave propagation](image)

Figure 4.2 Laser shadow-graphic microphotographs of a laser-induced shockwave generated in air [118]

This shockwave propagates and impacts the surface to be cleaned. Due to the high velocity of the shockwave, faster than 1000m/s, it is sufficiently high to remove particles. However, spherical propagation of the shockwave will give two flow (velocity) components, one normal to the surface and one parallel flow which is responsible for particle removal. The flow normal to the surface makes little contribution to particle removal. The effect of the normal flow to the surface has been reported by Lim et al [131]. They showed that particles located underneath laser-induced plasma couldn’t be removed.
Based on the fact that shockwave has two flow components and particles are hardly removed by the flow normal to the surface, we made a hypothesis for organic particle removal in LSC process. As shown in Figure 4.3, the pressure waves propagated by shockwave are sufficiently strong to deform soft particles such as organic particles. These pressure waves cause the deformation of the soft particles and that increase contact radius between the particle and the surface which leads to increasing the particle adhesion force. The shockwave induced deformation is plastic and therefore irreversible. The increase in the adhesion force as a result of the LSC induced deformation is sufficiently large that these soft particles, such as PSL particles, are not removed even at high powers.

Figure 4.3 Schematic diagram showing the hypothesis in which particle is deformed by vertical components of shockwave pressure

4.1.3 Deformation of Organic Particles Due to Laser Shockwaves

To assess the effect of the shockwave induced deformation, 300nm PSL particles on Si
wafer were exposed to shockwaves. High angle FESEM images were then taken to measure the radius of the contact area between the particle and the surface.

Figure 4.4 and 4.5 show that particles are easily deformed due to the pressure of the laser-induced shockwave. In the case of a particle exposed to 5 laser induced shockwaves at a gap distance of 5mm, the contact radius increased from 40nm to 70nm as compared to the contact radius of unexposed particle. Even at a larger gap distance, 10mm, Figure 4.4 shows that a particle is deformed, regardless of the number of pulses applied. Figure 4.5 shows the FESEM images of unexposed 300nm PSL particle and 300nm PSL particles exposed to 1 shockwave and 5 laser shockwaves at gap distance (between the focal point and the substrate) of 5mm

![Diagram](image)

**Figure 4.4** Radius of contact area of 300nm PSL particle exposed to 1 shockwave and 5 shockwaves at gap distance of 5mm and 10mm
Figure 4.5 FESEM images of 300nm PSL particle on Si wafer at different conditions: (a) unexposed, (b) exposed to 1 shockwave and (c) exposed to 5 shockwaves at gap distance (between the focal point and the substrate) of 5mm

To see how much adhesion force is increased by the deformation of particles, total adhesion force between PSL particles and Si wafer was calculated only by van der Waals force. In the present study, capillary force wasn’t included in total adhesion force, because IPA was used as a particle suspension to minimize the effect of capillary force.

When the spherical particle adheres to the flat solid substrate and is deformed by the adhesion force or the external load, the van der Waals force for the deformed particle includes the component of the deformation. It is written as [119,120]

\[
F_{vdW-deform} = F_{vdw} + F_{deformation} = \frac{AR}{6z_0} \left( 1 + \frac{a^2}{Rz_0} \right)
\]  

(4.1)

where \(A\) is the Hamaker constant, \(R\) is the radius of the spherical particle, \(a\) is the contact radius of the deformed particle and \(z_0\) is the separation distance between particle and the
substrate (4 Å). The effective Hamaker constant for silica/Si in air was $12.9 \times 10^{-20}$ J \cite{121}.

Figure 4.6 shows the adhesion force calculated using Eq. 4.1 with the measured contact radii of 300nm PSL particles, which are unexposed, exposed to 1 shockwave and exposed to 5 shockwaves at gap distance of 5mm. Once 300nm PSL particle is exposed to just one shockwave, the adhesion force ($2.81 \times 10^2$ nN) becomes almost two times stronger than unexposed ($5.22 \times 10^2$ nN). Increase in the adhesion force of PSL particles due to shockwave induced particle deformation can give a good explanation for the reason why organic particle is more difficult to be removed by LSC.

![Figure 4.6 Adhesion force between 300nm PSL particle on Si wafer at different conditions: (a) unexposed, (b) exposed to 1 shockwave and (c) exposed to 5 shockwaves at gap distance (between the focal point and the substrate) of 5mm](image-url)
4.1.4 Theoretical Verification of Organic Particle Removal Mechanism in LSC

As shown in previous section, deformation of PSL particle in LSC process causing increase in adhesion force can be a good proof supporting our hypothesis. However, it is still necessary to verify it by comparing the removal moment ratio of both organic and inorganic particles with cleaning experimental results.

In this section, the calculated contact radius using the shockwave pressure and the measured contact radius will be shown and compared. Based on our hypothesis for removal mechanism of organic particle, the calculation results of the removal moment ratio for organic particle and inorganic particle will be displayed and discussed with cleaning experimental results.

4.1.4.1 Shockwave Velocity and Pressure

In order to calculate the removal moment ratio, first thing must be made is to obtain the velocity of laser-induced shockwave as well as its pressure, because the pressure is a key parameter which cause the deformation of particles.

There are two ways to obtain the shockwave speed. One is the calculation using explosion theory, and another is the measurement using probe beam deflection method.
Point Explosion Theory

If the laser-induced breakdown of air is approximated as instantaneous energy release at the focal point in an ideal and generated shockwave is assumed spherical, according to the self-similar solution of the point strong explosion theory, the time $t$ at the radius $R_S$ of a shockwave and the Mach number $M_S$ are related by following equations [122,123,124].

$$R_S = \left( \frac{E}{\alpha \rho} \right)^{1/5} t^{2/5} \quad (4.2)$$

$$t = \left( \frac{2}{5c} \right)^{5/3} \left( \frac{E}{\alpha \rho} \right)^{1/3} M_S^{-5/3} \quad (4.3)$$

where $c$, $E$, $\alpha$ and $\rho$ are the sound speed at room temperature, the absorbed energy and the gas constant and the density of the gas, respectively. Since in our case the absorbed energy is sufficiently high ($E \gg 0.25\text{J}$), the counter pressure of the shockwave isn’t considered [123]. It has been demonstrated that about 65% of the laser energy is converted to the kinetic energy of the shockwave in a typical LSC process [125]. Based on this energy conversion, $M_S$ can be derived from Eq. 4.2 and 4.3 and given by

$$M_S = \left( \frac{2}{5c} \right) \left( 0.65E/\alpha \rho \right)^{1/2} R_S^{3/2} \quad (4.4)$$

We calculated the shockwave propagation speed from $M_S$ obtained using Eq.4.4. As shown in Figure 4.7, the shockwave propagation speed at gap distance of 5mm, where LSC is conducted in the experiments is around 1200m/s.
**Probe Beam Deflection Method**

As explained in Chapter 3, newly designed two-probe beam deflection method was used to measure the velocity of laser-induced shockwave propagation. This technique is much more accurate and easier to use than one probe beam deflection method, because once x-y-z translation stage with two probe beams is set up and fixed at desired gap distance such as 5mm, it doesn’t have to be moved up and down to find another shockwave signals for the calculation of the shockwave speed.

As shown in Figure 4.7, when the laser is focused in air, the breakdown of air generates the plasma plume with a high-intensity of the light emission and the emission from the plasma corresponds to the first high intensity peak monitored in the photodetector as a function of time. The propagation of shock waves changes the refraction index of air [126,127,128]. This change of the refractive index causes deflection of a probe beam and generates the second peak in the photo detector signal. Figure 4.7 shows the two-probe laser beam deflection signals at gap distance of 5mm with laser beam energy of 1.8 J, where two second peaks are detected in oscilloscope by one measurement. Therefore the shockwave speed can be easily calculated dividing the distance \(d_{1st\&2nd}\) by delay time \(\Delta t\) between 1\(^{st}\) and 2\(^{nd}\) He:Ne laser beams. In this case (gap distance = 5mm), it is around 1100m/s. We also mapped the shockwave speed at different gap distances by moving the x-y-z stage along z-axis as shown in Figure 4.8.
Figure 4.7 Shockwave signals from an oscilloscope at gap distance of 5mm ($\lambda=1064\text{nm}$, $E=1.8\text{J}$)

Figure 4.8 shows shockwave propagation speeds as a function of the distance from the focal point which are calculated on the basis of the point strong explosion and measured by two-probe beam deflection method. These two velocities are becoming almost same in further distance from the focal point. Even at smaller distance, they are not making big differences.
Figure 4.8 Shockwave propagation speed as a function of the distance from the focal point of laser beam ($\lambda=1064$nm, $E=1.8$J)

**Shockwave Pressure Calculation**

The symbol $\gamma$ in Eq. 4.5 is the adiabatic coefficient of the gas and the subscripts 1 and 2 indicate the unperturbed gas and the shockwave front, respectively. The density $\rho$, pressure $P$ and temperature $T$ at the shock front can be expressed by

$$\frac{\rho_2}{\rho_1} = \left(\frac{\gamma + 1}{\gamma - 1 + 2M_s^2}\right)$$

$$P_2 = \frac{P_1}{\gamma + 1} \frac{2\gamma - (\gamma - 1)M_s^2}{M_s^2}$$

$$= \frac{2}{\gamma + 1} \rho_1 U^2 \left[ 1 - \frac{\gamma - 1}{2\gamma} M_s^2 \right]$$

$$T_2 = P_2 / \rho_2 R_G$$
where $U$ and $R_g$ denote the shockwave propagation speed and the specific gas constant, respectively. Once the shockwave speed is obtained, the pressure, density and temperature can be easily calculated using above-described equations. In the present study, we used the measured shockwave speeds instead of theoretically calculated ones to get more confident data in the calculation of contact radius, removal moment, resisting moment and so on. In Figure 4.9, the pressure in the air is displayed as a function of the distance from the focal point for Nd:YAG laser with the pulse energy of 1.8J.

![Figure 4.9 Shockwave pressure at the shock front in the air as a function of the distance from the focal point ($\lambda=1064\text{nm}$, $E=1.8\text{J}$)](image-url)
4.1.4.2 Verification of Knudsen Number

It is important to verify the Knudsen number, because if the size of particle used in experiments is smaller than the value that corresponds to a critical Kn=0.1, the flow around the particle is no longer in the continuum regime and then it becomes hard to evaluate the drag force. From the measured shockwave speed, the calculated temperature and pressure values, the Knudsen number

\[ Kn = \frac{\eta}{D} = \frac{k_B T}{\pi \sqrt{2 P d_s^2} D} \]  

(4.8)

can be estimated as a function of the distance from the focal point and the particle size ($\eta$: mean free path, $D$: particle diameter, $k_B$: Boltzmann constant, $d_s$: hard-sphere diameter for binary collisions $3.66 \times 10^{-10}$m for air). The results displayed in Figure 4.10 confirm that the assumption of continuum flow is still valid in the entire range of the experiment with 280nm and 300nm particles. Otherwise the cleaning force of laser-induced shockwave should be adjusted by Stokes-Cunningham slip correction [129].
Figure 4.10 Knudsen number as a function of distance from the focal point in LSC for different particle diameters ($E=1.8J$)

4.1.4.3 Verification of Contact Radius calculated by Particle Adhesion Theory

To theoretically investigate the change of the contact radius of 300nm PSL particles, we adopt Maugis-Pollock (MP) theory, because the adhesion-induced stress between a small soft particles and a flat surface can be sufficiently great, even in the absence of any additional applied load, so as to exceed the yield strength, $Y$ of at least one of the contacting materials. Therefore in the case of 300nm PSL particles, the deformation can be fully plastic.

For particles unexposed to shockwaves, we also compared the experimentally measured
contact radius with the theoretically calculated ones applying different particle adhesion theory model such as MP, DMT and JKR models as listed in Table 4.1. As a result, when MP model is applied, the theoretical radius of contact area between a 300nm PSL particle and a Si surface without external load, 39.7nm agrees with experimentally measured value, 40nm, most.

Table 4.1 Contact radii of 300nm PSL and 280nm silica particles calculated by different particle adhesion theory model and measured experimentally

<table>
<thead>
<tr>
<th>Contact Radius (m)</th>
<th>300nm PSL</th>
<th>280nm Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP model</td>
<td>3.97E-08</td>
<td>8.78E-09</td>
</tr>
<tr>
<td>DMT model</td>
<td>1.78E-08</td>
<td>8.09E-09</td>
</tr>
<tr>
<td>JKR model</td>
<td>2.56E-08</td>
<td>1.17E-08</td>
</tr>
<tr>
<td>Measurement</td>
<td>4.00E-08</td>
<td>-</td>
</tr>
</tbody>
</table>

According to the hypothesis we formed, the normal component of shockwave cleaning force would affect the particle deformation. The total cleaning force can be easily calculated using Eq. 2.27 in Chapter 2 as a function of distance ‘s’ from the center of cleaned area (underneath the center of laser-induced plasma). The normal cleaning force $F_y$ can be also calculated by using the angle of shockwave and particle surface, $\theta = \cos(s/R_S)$ (shown in Fig.2.7, Chapter 2), where $s$ is the distance from the center of cleaned area and $R_S$ is the radius of shockwave when it reaches to the particle surface. Therefore, by replacing the external load $P$ in Eq. 2.21 (Chapter 2) with $F_y$, the changed contact radius $a$ is given by
where \( w_A \) is the work of adhesion, \( R \) is the particle radius, \( H \) is the hardness and \( Y \) is the yield strength. From Eq. 4.9, we calculated the contact radius of both 300nm PSL and 280nm Silica particles as a function of distance from the center of cleaned area when they are deformed by shockwave pressure. In addition, in order to verify the theoretical calculation of the contact radius, we measured the contact radius of deformed 300nm PSL particles after 1 pulse of shockwave in different positions, such as the center of cleaned area, 5mm and 10mm far from the center of cleaned area at gap distance of 5mm. The result displayed in Figure 4.11 shows the theoretically calculated contact radii of the laser shock induced deformation of 300nm PSL and 280nm Silica particles. PSL particle located even 5mm far from the center is deformed increasing the contact radius from 40nm to 45nm, which means that 300nm PSL is hard to be removed over large area. The figure also shows that the theoretical calculations are in good agreement with the experimental measurements.
Mapping Adhesion force of PSL and silica Particles over Cleaned Area

To evaluate the effect of shockwave-induced particle deformation on adhesion force at different positions in Si substrate, we calculated the adhesion force as a function of the distance from the center of cleaned area using all contact radius values in Figure 4.11. According to Figure 4.12, in the case of 300nm PSL particles located underneath the laser induced plasma, its adhesion force is almost two times stronger than at distance of 10mm.
far from the center, while silica particle’s adhesion force doesn’t change much wherever it’s located. It can be also seen that the adhesion force of PSL particle even at distance of 5mm is still 50nN higher than barely affected by shockwave pressure (10mm far from the center).

Figure 4.12 Adhesion force of 300nm PSL and 280nm Silica particles after exposure of 1 laser-induced shockwave as a function of the distance from the center of the cleaned area at a gap distance of 5mm

*Removal Moment vs. Adhesion Resisting Moment*

Using the cleaning force of laser-induced shockwave and the contact radii and adhesion forces for 300nm PSL and 280nm silica particles obtained from above results, we calculated the removal moment and adhesion resisting moment as a function of the
distance from the center of cleaned area at gap distance of 5mm. As shown in Figure 4.13, there are two interesting phenomena. One obvious phenomenon is that in the case of 300nm PSL particles, adhesion resisting moment is much higher than removal moment, while it is reversed in 280nm silica particle. Another phenomenon appears in common for both of these two particles. Removal moment in both of cases is zero underneath laser-induced plasma and then it is getting larger as further from the center. This is because the shockwave flow has two velocity components (parallel and normal to the substrate), so the flow normal to the substrate is more dominant near the center of cleaned area leading to lower particle removal efficiency.
Figure 4.13 The calculated LSC removal moment and adhesion resisting moment of (a) 300nm PSL and (b) 280nm silica particles as a function of the distance from the center of cleaned area at a gap distance of 5mm
Finally we have calculated the removal moment ratio of the LSC removal moment to the
resisting adhesion moment for both 300nm PSL and 280nm silica particles. Consequently,
as shown in Figure 4.14, the removal moment ratio for 280nm silica particle is
significantly higher than for 300nm PSL particle. When the removal moment ration is
greater than 1, the rolling is initiated and the particle is swept away for the surface
[130,131]. Therefore it is obvious that 280nm can be removed over much larger area by
one pulse of laser-induced shockwave, whereas 300nm PSL particle is hard to be
removed due to its removal moment ratio much lower than 1 at any positions. In Figure
4.14, it is shown that 280nm silica particles sitting near the center of the cleaned area
can’t be removed even though the force of the laser-induced shockwave was the highest
compared to those with other positions. This is because the velocity of a shockwave flow
parallel to the surface is zero at the center and also the normal flow of a shockwave is still
faster than the parallel flow. However silica particles located around the center will be
removed if another shockwave is exposed nearby, because silica particles are hardly
deformed by a shockwave and the expected cleaned area is large enough to be easily
overlapped (The minimum distance among shockwaves impacting the surface is 5mm in
LSC system used in the present study).
Figure 4.14 Removal moment ratio of LSC removal moment to adhesion resisting moment for 300nm PSL and 280nm silica particles as a function of distance from the center of cleaned area at a gap distance of 5mm

Removal moment ratio for various sized PSL particles and its verification with cleaning experimental results

Following the comparison of removal moment ratios between PSL and silica, we have calculated the removal moment ratios for various sized PSL particles to find the critical size of PSL particles, which is possibly removed by laser shockwave cleaning. As illustrated in Figure 4.15, the removal moment ratio becomes larger with increasing particle size, however it seems to be hard to remove particles with diameter of less than
1μm due to the deformation of PSL particles induced by laser shockwaves.

Figure 4.15 Removal moment ratio of LSC removal moment to adhesion resisting moment for various sized PSL particles as a function of distance from the center of cleaned area at a gap distance of 5mm

In order to verify the calculation results shown in Figure 4.15, we carried out cleaning experiments for three different sized PSL particles such as 300nm, 600nm and 2μm. Figure 4.16 indicates that the removal efficiencies of 300nm and 600nm PSL particles are 30% and 60% respectively, while for 2μm PSL particle, it is relatively high more than 90%. This means most 2μm PSL particle on Si wafer could be effectively removed by LSC. In addition, from the comparison between Figure 4.15 and 4.16, the theoretical calculations of removal moment ratio for PSL particle is in good agreement with the
experimental results.

Figure 4.16 Particle removal efficiencies of various sized PSL particles which diameters are 300nm, 600nm and 2μm

### 4.1.5 Summary

LSC has a distinct advantage as a dry cleaning process, however, it has been shown that LSC is not as effective for removing organic compared to inorganic particle. The removal efficiency of 300nm PSL particles is relatively low (30%) compared to the removal efficiency of 280nm Silica particles (90%). The reason for ineffectiveness in organic particle removal is that the shock wave pressure is sufficiently strong to deform soft particles such as organic particles increasing the contact radius between the particle and the substrate leading to a higher particle adhesion force. It has been proven by measuring
the contact radius between 300nm PSL particle and Si substrate with high angle SEM images, which shows the contact radius increases from 40nm to 55nm after a particle is exposed to even 1 shockwave at gap distance of 5mm.

The velocity of the shockwave was directly measured by two-probe beam deflection method. Using the calculated pressure, temperature and density at shockwave front, Knudsen number was calculated. It was verified that the flow around particles used in experiments is in the continuum region, which allows us to easily apply the particle removal model of LSC. The contact area was also calculated applying the Maugis-Pollock theory with the calculated force. The predicted contact radius agreed with the experimental measurements.

Removal moment ratios of PSL particle and silica particle show that silica particles can be easily removed by LSC, while soft (PSL) particles < 1μm in diameter will be harder to remove. To experimentally verify it, three different sized PSL particles was used. Therefore it was shown that the removal efficiency of 2 μm PSL particles is more than 90%, while in the case of 300nm and 600nm PSL particles, they are just 30% and 60% respectively.
4.2 New Wet Laser Shockwave Cleaning

The wet laser-induced shockwave cleaning (WLSC) technique was originally proposed by V. K. Devarapalli et al (2006), which has been shown that the 710nm glass particles and 404nm polystyrene latex (PSL) particles on 2cm x 2cm piece of a wafer could be removed mostly by using the technique [132]. In the present study, this technique is adopted and refined for wafer-scale cleaning of much smaller particles. In addition, numerical modeling results and the removal moment ratio calculated based on the measurement of the surface velocity of water flow will be displayed and discussed to investigate the removal mechanism of the wet laser shockwave cleaning.

4.2.1 Concept of Wet Laser Shockwave Cleaning

A new wet laser shockwave cleaning (WLSC) technique utilizes a shockwave generated from laser-induced plasma and a thin liquid film as the medium, wherein waves propagate against contaminants through the liquid.

As shown in Figure 4.17 (a) and (b), the system for wafer-scale cleaning was developed. When the laser beam converges into a laser focus by a focus lens, it results in generating a laser-induced plasma by the initiation of gas breakdown, which occurs when the energy of the laser beam is greater than or equal to a threshold in the laser focus. The plasma expands very fast and the collision of expanding plasma with the gas around that plasma leads to the generation of a shockwave. As a result, a laser-induced plasma shockwave, a
supersonic wave, propagates to the liquid layer and then a liquid flow with high velocity is formed. The speed of liquid flow is sufficiently high to remove small contaminants more efficiently, compared to using a laser-induced plasma shockwave without the liquid layer. The mechanism of particle removal in WLSC technique hasn’t been identified. In spite of that, there are possible advantages of using liquid, which are the reduction of the adhesion force between particles and the surface of a wafer by an order of magnitude, the utilization of the double layer repulsive force, the elimination of the capillary force encountered in dry-surface cleaning using laser-induced plasma shockwave and a increase in the drag force by three orders of magnitude higher medium density.
Figure 4.17 Schematic view (a) and side view (b) of the wet laser-induced shockwave cleaning (WLSC) system, which shows how a liquid flow with high velocity is generated by a laser-induced shockwave and then a liquid layer is formed on the top of a wafer as well as how the propagation of a liquid flow affects on the contaminants.
4.2.2 Particle Removal Results

In the application of wet laser-induced shockwave cleaning technique, clean DI water was used as a liquid film on the top of a wafer. For the formation of thin water film, small amount water of approximately 200μl from 1000μl micro-pipette was applied onto the wafer and then it was spun gently until the dropped water covered whole area of the wafer, which gave approximately 25μm-thick film layer on the surface of 4-inch wafer. After cleaning process using thin water film, the wafer was dried by spinning it at 1000rpm.

In several preliminary experiments with thick water film of unspecified thickness on the top of a wafer, the removal efficiency of 300nm PSL particles was less than 80%. In addition, huge variation existed in cleaning efficiency. It turned out that in order to increase the cleaning performance, the thickness of water film needed to be as thinner as possible. Thus, the minimum amount of water volume covering whole area of a 4-inch wafer was applied onto wafers in every WLSC cleaning experiments to form thin and uniform film layer with a thickness of 25μm on the wafer surface. As a result, removal efficiencies of both 300nm PSL particles and 280nm silica particles using WLSC were successfully increased up to near 100%, regardless of either DI water or IPA used as the particle solution (shown in Figure 4.18 and 4.19).

However, as shown in both Figure 4.18 and 4.19, it was also observed that when LSC technique was applied on the particle removal, removal efficiencies of 300nm PSL
particles in both DI water and IPA solution were less than 30%, while for 280 silica particles in DI water and IPA solution, they were higher than 70% and 90% respectively. As a matter of fact, it is well known that silica particles deposited by dry deposition method (where particles in IPA solution were sprayed by nebulizer) can be removed completely by conventional LSC as compared to PSL particles [116]. Therefore, lower removal efficiency of 280 silica particles in DI water seemed to be due to the capillary force generated by trapped liquid between particles and the surface after wet particle deposition. As shown in Figure 4.18, this effect of the capillary force was also observed in the removal of 300nm PSL particles with LSC, while the same effects weren’t found in removal of both PSL and silica particles owing to elimination of the capillary force by using DI water as a cleaning medium.

![Figure 4.18 Removal efficiencies of 300nm PSL particles in DI and IPA after LSC and WLSC](image)

Figure 4.18 Removal efficiencies of 300nm PSL particles in DI and IPA after LSC and WLSC
Figure 4.19 Removal efficiencies of 280nm silica particles in DI and IPA after LSC and WLSC

Figure 4.20 shows FESEM images for the laser-induced shockwave removal of 28nm PSL particles without DI water film (a and b) and with DI water film (c and d). From those SEM images, we quantified the number of particles before and after cleaning to estimate the particle removal efficiency, which is displayed in Figure 4.21. It was observed that even 28nm PSL particles were successfully removed by wet laser-induced shockwave cleaning (WLSC), compared to conventional laser shockwave cleaning (LSC).
Figure 4.20 FESEM images of wafer surfaces with 28nm PSL particles at 10000 x magnification: (a) before and (b) after LSC, (c) before and (d) WLSC
The obvious phenomena occurring during removal process is similar to wind-induced water currents, which shows that the velocity of water flow on the water free surface decreases with increasing water layer thickness on the surface of the substrate\[133,134,135,136,137,13819-24\]. This corresponds to results showing higher removal efficiency with decreasing the thickness of water film on the wafer and furthermore explains how WLSC could achieve effective removal of 28nm PSL particles. The detail of removal mechanism in WLSC will be explained later.

**4.2.3 Numerical Modeling for Wet Laser Shockwave Cleaning**

The particle removal mechanism of the wet laser-induced shockwave cleaning (WLSC) has never been identified yet. We expected that the velocity of the water flow formed by
shockwave’s intense impact would be high enough to remove nanoscale particles. However the phenomena during WLSC process are too complicated to be analyzed theoretically, because we need to consider many things, such as interaction between laser-induced shockwave and water, how the force of shockwave can be transferred to water through the interface, how the water flow will be formed.

Therefore prior to theoretical approach, computational fluid dynamics (CFD) model was developed to predict the flow field for the phenomena of WLSC to see how fast the water flow would be. Initially, the parallel air flow above water surface was considered. The interface between air and water was assumed to be free surface. The thickness of water layer used in CFD simulation was 500μm, which is much thicker than one used in experiments, 25μm. CFD simulation was carried out for various velocities of air flow. The simulation results using three different velocities of air flow, 10m/s, 100m/s and 1000m/s, are displayed in Figure 4.22, 4.23 and 4.24, respectively, showing (a) the behavior and (b) the velocity profile of both air and water flows. In (a), red and blue color indicate water and air, respectively. As for (b) the velocity profile, we displayed two kinds of figures to confirm the exact velocity of water flow in the simulation results. 2-dimensional velocity profile is on the left hand side and another one on the right hand side shows 1-dimensional velocity profile along z-axis at fixed x=0.5mm.

These three simulation results support the concept of WLSC in the beginning, where the water flow with high velocity would be formed. It can be seen that as the velocity of air flow increases, the water flow is also moving faster as well as fluctuating much more
significantly, which doesn’t give the water flow speed linearly proportional to the air flow speed. The velocities close to the bottom surface in these three cases are 5.5m/s, 11m/s and 28m/s, which might be high enough to remove nanoscale particles efficiently. According to the simulation results, it can be expected to obtain high velocity of water flow in our real WLSC process such as 30m/s.
Figure 4.22 Simulation results using the air flow with velocity of 10m/s: (a) behavior of both air and water flow, (b) 1-dimensional (on the left hand side) and 2-dimensional (on the right hand side) velocity profiles of both air and water flow
Figure 4.23 Simulation results using the air flow with velocity of 100m/s: (a) behavior of both air and water flow, (b) 1-dimensional (on the left hand side) and 2-dimensional (on the right hand side) velocity profiles of both air and water flow
Figure 4.24 Simulation results using the air flow with velocity of 1000m/s: (a) behavior of both air and water flow, (b) 1-dimensional (on the left hand side) and 2-dimensional (on the right hand side) velocity profiles of both air and water flow.
4.2.4 Theoretical Verification of Particle Removal Mechanism in Wet Laser Shockwave Cleaning

Although the velocity of the water flow near the bottom surface could be predicted from numerical modeling, it is still required to find the more exact particle removal mechanism from experimental and theoretical investigation, because the phenomena occurring during wet laser shockwave cleaning process is much more complicated. For example, when shockwave impact the water surface, the water can be compressed due to the shockwave propagation normal to the surface. It might be more powerful to form the shockwave-induced water flow compared to the usual water flow driven by wind, wherein only parallel flow is considered. In addition to that, shockwave speed is not constant on the top of water surface. It is decreasing as shockwave is propagating further. Consequently, the velocity of water flow can be relatively low far from the center of the formed water flow, while much higher near the center.

For better understanding the mechanism of wet laser shockwave cleaning, first of all, velocity profile in the water side should be obtained, which flow is induced by laser-induced shockwave. Because from velocity profile, drag force can be calculated for various sized particles providing the removal moment and then with comparing adhesion resisting moment, the particle removal moment ratio can be calculated as well. Finally it’s possible to investigate the particle removal mechanism in wet laser shockwave cleaning through the comparison of removal moment ratio with experimental results shown in previous section.
4.2.4.1 Measurement of the Surface Velocity of Shockwave-induced Water Flow

In order to estimate the speed of water flow driven by a laser-induced shockwave, we have adopted shadow-graphic photography with high speed camera which is capable of taking images with frame rate up to 8000. As shown in Figure 4.25, shadow-graphic photographs were taken with frame rate of 1000, 2000, 4000 and 8000 respectively. In Figure 4.25 (a), the diameter of the shockwave-induced water flow is around 20mm in 2nd images, which means the water has moved in 1msec since laser-induced plasma was formed. The water flow was moving too fast to be captured with frame rate of 1000. So it was necessary to increase the frame rate, even though the quality of images became worse. With the frame rate of 4000 and 8000, initiation and propagation of the water flow could be observed.
Figure 4.25 Shadow-graphic photographs of water flow driven by a laser-induced shockwave taken by high speed camera with frame rate (frames per second) of (a) 1000, (b) 2000, (c) 4000 and (d) 8000 respectively.

In order to quantify the velocity of the water flow, the software provided with high speed camera was used, which allowed us to calculate the velocity by calibrating real scale in images (distance between lines shown in above photographs is 2mm) and marking the specific positions (boundaries of water flow) frame by frame. Figure 4.26 shows the measured surface velocity of the water flow exerted by a shockwave as a function of the distance from the center. Its velocity is decreasing dramatically as going further from the center of it. This phenomenon should be due to shockwave propagation in air, which velocity is also decreasing with further propagation, because lower velocity of a
shockwave gives rise to less momentum transfer from the air to the water resulting in lower velocity of the water flow.

Figure 4.26 Measured surface velocity of the water flow driven by a laser shockwave as function of the distance from the center of water flow

4.2.4.2 Removal Moment Ratio Calculation

In order to calculate the removal moment ratio, the most important thing is to obtain the velocity profile. From the measured surface velocity of the shockwave-induced water displayed in previous section, the velocity in the water side can be calculated based on the assumption that it is linearly decreasing with getting close to the surface or the flow is laminar or turbulent.
In this section, for the calculation of removal moment ratio, the surface velocity of the water flow driven by a laser-induced shockwave is fixed to 32m/s, which is the average velocity at distance of 2.5mm from the center of the water flow. Because when we exposed shockwaves onto the water, the distance between shockwaves (from center to center) is 5mm. Therefore the shockwave velocity in air becomes the lowest at the location 2.5mm far from the center of the water flow driven by a shockwave, which results in the lowest momentum transfer from air to water and consequently the lowest surface velocity of the water flow. In outer region (where distance from the center is more than 2.5mm), decrease in the velocity of the water flow can be compensated by exposing another shockwave on the point 5mm far from the center of previous shockwaves.

**Removal Moment Ratio on the basis of Linear Velocity Profile**

Assuming that the velocity of shockwave-induced water flow is decreasing linearly underneath water surface, we have calculated the drag force acting on PSL and silica particles sitting on Si substrate. As shown in Figure 4.27 and 4.29, calculated drag force as well as repulsive double layer force between particles and surface are illustrated. Compression approximation derived by Gregory [139] was applied to calculate the double layer force, which could be attractive or repulsive, also plays a role in the removal of particles. Direct measurement results have proved that constant surface charge boundary condition describes the electrical double layer interaction much better than the constant surface potential boundary condition at small separation between the two
surfaces [140]. Zeta potential of PSL, silica and bare Si in DI water (pH=6) is -50mV, -20mV and -68mV respectively. Based on these zeta potential values and the pH of cleaning solution (DI water), double layer force for PSL and silica particles on Si substrate in DI water was calculated and subsequently presented in Figure 4.27 and 4.29 respectively. Applying different adhesion theories, such as MP, JKR and DMT, the calculated van der Waals forces between particles and Si substrate were also displayed in both Figure 4.27 and 4.29 to compare these forces with drag force.

Figure 4.27 Various forces affecting on PSL particle removal from Si wafer using WLSC as a function of particle size: drag force, double layer force and van der Waals force based on JKR, DMT and MP models.
As shown in Figure 4.27, for small particle less than 100nm, double layer force is in the same order of magnitude with drag force. In addition, the total removal moment is high enough to remove even 60nm PSL particle if DMT model is applied. However, it is well known that MP model is more applicable for small PSL particles. It has been also proven in section 4.1 by showing that 300nm PSL particle was also plastically deformed. Therefore, considering MP model in Figure 4.28, it seems that PSL particle with diameter of less than 400nm is harder to be completely removed by WLSC. But this doesn’t agree with experimental results, which showed 300nm as well as 28nm PSL particles were removed successfully by WLSC.

![Figure 4.28 Removal moment ratio of WLSC removal moment to adhesion resisting moment for a PSL particle sitting on Si wafer with applications of JKR, DMT and MP theories as a function of particle size](image)

Figure 4.28 Removal moment ratio of WLSC removal moment to adhesion resisting moment for a PSL particle sitting on Si wafer with applications of JKR, DMT and MP theories as a function of particle size
Figure 4.29 Various forces affecting on silica particle removal from Si wafer using WLSC as a function of particle size: drag force, double layer force and van der Waals force based on JKR, DMT and MP models.

In the contrary, no matter which adhesion theory is applied, even 30nm silica particle can be expected to be removed effectively, according to analysis of removal moment ratio shown in Figure 4.30. Figure 4.31 indicates $\mu_{MYD}$ as a function of silica particle size, showing which theory is valid between JKR and DMT. When $\mu_{MYD}$ is more than 1, JKR theory should be applied, otherwise DMT theory is valid. Therefore, based on calculated $\mu_{MYD}$ in Figure 4.31, DMT should be applied for silica particles with diameter of less than 160nm when MP theory isn’t applicable. Consequently, 15nm silica might be expected to
be removed, according to removal moment ratio calculated with applying DMT model in Figure 4.30.

Figure 4.30 Removal moment ratio of WLSC removal moment to adhesion resisting moment for a silica particle sitting on Si wafer with applications of JKR, DMT and MP theories as a function of particle size
Removal Moment Ratio for PSL particles based on the Assumption that the Shockwave-induced Water Flow is Laminar or Turbulent

The removal mechanism of WLSC for silica particles can be explained with calculated removal moment ratio from above figures, because it shows that silica particles with diameter of more than 30nm can be expected to be removed by WLSC. It doesn’t disagree with any experimental results. However it is different in the case of PSL particle. PSL particle is usually more difficult to be removed than silica particles, because it has stronger adhesion force due to plastic deformation occurred when it adhered to the surface. Despite all difficulties in removing PSL particles, it was achieved by WLSC. Even 28nm PSL particles could be removed successfully. One possible reason for disagreement between experimental and theoretical results can be the wrong assumption
for velocity profile of the shockwave-induced water flow. The flow can be laminar or turbulent, which gives higher velocity. Its velocity profile might not be linear.

Therefore, the velocity profile based on laminar or turbulent flow has been obtained. When calculating the velocity of the water flow, the thickness of boundary layer, $\delta$, has been assumed to be equivalent to that of the thin water film on the top of Si substrate, which is approximately 25\(\mu\)m. Figure 4.32 shows velocity profiles of the water flow driven by a shockwave based on the assumptions the flow is laminar or turbulent. When the shockwave-induced water flow is turbulent, the velocity is highest at any points. It is also shown that in the case of turbulent flow, the thickness of laminar sub-layer is approximately 2.4\(\mu\)m, wherein the velocity profile is nearly linear.

![Figure 4.32 Velocity profile of the water flow driven by a shockwave underneath the water surface with different assumptions such as linear, laminar and turbulent as a function of the distance from Si surface](image)

Figure 4.32 Velocity profile of the water flow driven by a shockwave underneath the water surface with different assumptions such as linear, laminar and turbulent as a function of the distance from Si surface
Figure 4.33 shows removal moment ratio for PSL particle removal using WLSC, which was calculated based on the assumption the water flow driven by laser-induced shockwave is laminar. According to removal moment ratio calculated on the basis of MP model, the minimum size of PSL particles possibly removed by WLSC decreases from 400nm to 250nm. However, this result can’t still give a good explanation for how WLSC could accomplish the removal of 28nm PSL particles shown in section 4.2.2.

![Graph showing removal moment ratio](image)

Figure 4.33 Removal moment ratio of WLSC removal moment with assumed as laminar flow to adhesion resisting moment for a PSL particle sitting on Si wafer with applying JKR, DMT and MP theories as a function of particle size

As illustrated in Figure 4.34, assuming that the water flow is turbulent, removal moment ratio for WLSC of PSL particles has been calculated by applying JKR, DMT and MP
models applied. If either JKR or DMT theory is applied, it may be able to explain the removal mechanism of WLSC for 28nm PSL particles, because PSL particle bigger than 40nm can be completely removed by WLSC according to results displayed in Figure 4.34. However even though high values in removal moment ratio appear in the case of JKR and DMT models applied, these results are not reliable, because it has already been demonstrated by many researchers that the plastic deformation happens when small PSL particles come into contact with the surface. This theory has been also verified by experimental results in section 4.1. Therefore MP model should be more focused than any other models to investigate the WLSC removal mechanism for PSL particles. According to the removal moment ratio calculated with applying MP model displayed in Figure 4.34, the minimum size of removable PSL particle by WLSC is just 180nm, which is still in disagreement with experimental results. This means that the removal mechanism can’t be fully explained only with assuming the water flow in WLSC is turbulent.
Figure 4.34 Removal moment ratio of removal moment of WLSC turbulent flow to adhesion resisting moment for a PSL particle sitting on Si wafer while applying JKR, DMT and MP theories as a function of particle size

**Removal Moment Ratio for PSL particles based on the Assumption the Shockwave-induced Water Flow is compressed and the subsequent water film layer becomes much thinner than initial layer**

In order to account for the exact WLSC removal mechanism of 28nm PSL particles, another assumption should be made. Because even though the flow in water driven by a laser-induced shockwave was assumed to be turbulent, it doesn’t give a good agreement between experimental results and theoretical calculations. Therefore we have assumed that when a shockwave impacts onto the water surface, the water film layer is
compressed due to the shockwave propagation normal to the substrate and as a consequence, it will become much thinner especially near the center, while the surface velocity doesn’t change. Finally we can expect more powerful drag force acting on particles in thinner water film layer. The schematic diagram for this assumption is described in Figure 4.35. As a matter of fact, this phenomenon could be predicted from shadow-graphic photographs taken with high speed camera, since the boundary of the water flow appears in those photographs is formed from distortion in lines marked as scale bars by fluctuation in water surface. This is caused by mass flow from the center to the outer region as shown in below schematic diagram.

Figure 4.35 Schematic diagram showing the compressed water film layer by laser-induced shockwave propagation normal to the surface resulting in different velocity profile depending on the location of the shockwave
The result in Figure 4.36 indicates the removal moment ratio for PSL particle removal using WLSC based on linear velocity profile with different thicknesses of the water film layer. It can be seen that the thickness of water film layer should be decreased to down to 500nm so that 28nm PSL particle is completely removed. In fact, 500nm is so small in such way that the water dries out easily, so it was hardly observed in WLSC experiments. Therefore the water film layer might become thinner and then be recovered immediately after a shockwave vanished. Otherwise the velocity profile in water might not be linear.

Figure 4.36 Removal moment ratio for PSL particle removal using WLSC based on linear velocity profile in the water with different thicknesses of the water film layer as a function of particle size

As shown in Figure 4.37, the removal moment ratio for PSL particle removal using WLSC was determined based on the assumption of the water flow as laminar flow. The
thickness of boundary layer is also assumed to be the same as one of the water flow. According to Figure 4.37, 28nm PSL particle can be effectively removed with water film thickness of 1μm, whose value is relatively high as compared to when linear velocity profile applied. Although the water film layer thickness increases from 1μm to 5μm, PSL particle bigger than 90nm can be expected to be removed completely.

![Image of Figure 4.37](image1.png)

Figure 4.37 Removal moment ratio for PSL particle removal using WLSC based on laminar velocity profile in the water with different thicknesses of the water film layer as a function of particle size

As a matter of fact, the Reynolds number of the water flow driven by a shockwave in present study can indicate which flow between laminar and turbulent occurs. The Reynolds number, Re, for wind-induced water currents is given by
\[ \text{Re} = \frac{\rho V l}{\mu} = \frac{\rho V_S h}{\mu} \]  

(4.10)

where \( \rho \) is the density, \( \mu \) is the viscosity, \( l \) is the characteristic length, \( h \) is the water depth, \( V \) is the velocity and \( V_S \) is the surface velocity [138]. The flow transition from laminar to turbulent occurs in the range of \( 10^3 < \text{Re} < 10^4 \) and when \( \text{Re} \) is greater than \( 10^4 \), the flow becomes turbulent. Otherwise it is laminar flow. The computed value of \( \text{Re} \) without changing the water film thickness is approximately 792 as listed in Table 4.2, which is below \( 10^3 \). Therefore the shockwave-induced water flow must not be turbulent in present study.

<table>
<thead>
<tr>
<th>Water Depth (( \mu m ))</th>
<th>25</th>
<th>15</th>
<th>5</th>
<th>3</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>792.0792</td>
<td>475.2475</td>
<td>158.4158</td>
<td>95.0495</td>
<td>31.68317</td>
</tr>
</tbody>
</table>

From Table 4.2, the velocity profile should be linear or hyperbolic (laminar flow) even though the water film isn’t compressed by a shockwave at all. Furthermore, in the case of linear and hyperbolic velocity profile with the water film thickness of 0.5\( \mu m \) and 1\( \mu m \) respectively, 28nm PSL particle can be removed completely by WLSC.
4.2.5 Summary

Laser-induced shockwave cleaning (LSC) is still one of good candidates for next generation of cleaning techniques due to the distinct advantage as a dry cleaning. However, LSC technique has a difficulty in removing particles deposited from a solution (wet particles) as well as organic particles such as PSL particles. In order to remove these kinds of particles especially of small dimensions (<100nm), hybrid laser shockwave cleaning (LSC) utilizes laser shockwave with UV laser to remove particles has been developed. However, when UV laser cleaning is used (in hybrid approach with LSC), optimization is required to ensure damage free cleaning. This is required whenever a new surface is used.

A wet laser shockwave cleaning (WLSC) technique utilizes the advantage of using water to reduce the adhesion force by an order of magnitude, utilize the double layer repulsive force, eliminate the capillary force encountered in dry LSC and increase the drag force by increasing the medium density (by three orders of magnitude).

WLSC Technique was successfully refined to remove contaminants from whole wafer surface in this work. In addition, the wet laser shockwave cleaning results shows that 300nm PSL particles were completely removed and demonstrates efficient removal of 28nm PSL nanoparticles.

For better understanding the removal mechanism of WLSC, first of all, computational
fluid dynamics (CFD) model was developed to predict the flow field for the phenomena occurs during WLSC. It was found that the velocity of the water flow near Si substrate is around 30m/s.

Secondly the surface velocity of the water flow driven by a laser-induced shockwave was obtained from shadow-graphic photographs taken by high speed camera. Removal moment ratio for PSL and silica particle removal using WLSC was determined. However in the case of PSL particles, it didn’t agree with experimental results unlike silica particles. Therefore based on the assumption that the water flow could be compressed and consequently its thickness decreased, removal moment ratio was recalculated. As a result, it was seen that when the thickness of the water film decreases down to 0.5μm or 1μm with a linear or hyperbolic velocity profile respectively, the determined removal moment ratio was in good agreement with experimental results.
Chapter 5 Conclusions and Future Work

5.1 Conclusions

Laser shockwave cleaning (LSC) has been considered as a good candidate for new cleaning methodology in next semiconductor generation, since it has distinct advantages such as physical dry cleaning at room temperature and fast process leading to high throughput. However it has been reported by researchers that LSC is not as effective for organic particle removal as for inorganic particle. In addition, the removal mechanism for organic particles using LSC techniques hasn’t been found yet. Accordingly, some of researchers have developed new hybrid types of LSC technique by combining it with either UV laser or water in order to increase removal efficiency of organic particles. The present study focuses on the identification of the organic particle removal in laser shockwave cleaning as well as the development of new hybrid laser shockwave cleaning technique, wet laser shockwave cleaning (WLSC), including the investigation of its removal mechanism.

Removal Mechanism for Organic Particle in Laser Shockwave Cleaning

Ineffectiveness in organic particle removal using laser shockwave cleaning has been verified by comparing particle removal efficiency between 300nm PSL and 180nm silica particles. The removal efficiency of 300nm PSL particles is relatively low (30%)
compared to the removal efficiency of 280nm Silica particles (90%). The reason is that the shock wave pressure is sufficiently strong to deform soft particles such as organic particles increasing the contact area between the particle and the substrate, which leads to a higher adhesion force. The deformation of organic particle occurs during LSC process has been observed with high angle SEM images. After a 300nm particle is exposed to even 1 shockwave at the distance of 5mm from the focal point, the contact radius between a particle and Si substrate increases from 40nm to 55nm. Accordingly the adhesion force becomes approximately two times higher.

Two-probe beam deflection method has been designed to obtain more accurate values of shockwave speeds, which enabled us to calculate the pressure, temperature and density of shockwave as well as its Knudsen number. According to calculated Knudsen number, the flow around particles used in experiments has been shown to be in the continuum region. Therefore the particle removal model of LSC addressed in chapter 2 can be easily applied. Otherwise the cleaning force must be modified by Stokes-Cunningham slip correction. The Maugis-Pollock theory is applied to calculate the contact radius in the case of 300nm PSL particles sitting on a Si substrate. The predicted contact radius agreed with the experimental measurements.

Removal moment ratio of PSL particles and silica particles has been analyzed, when LSC is applied to remove them. It shows that silica particles can be easily removed by LSC, while soft (PSL) particles < 1μm in diameter will be harder to remove. It has been also verified experimentally with three different sized PSL particles such as 300nm, 600nm
and 2μm. It shows that the removal efficiency of 2 μm PSL particles is more than 90%, while in the case of 300nm and 600nm PSL particles, they are just 30% and 60% respectively.

**Wet Laser Shockwave Cleaning and its Removal Mechanism**

One of hybrid type laser shockwave cleaning, UV assisted LSC has been demonstrated to be very effective even in removing small organic particle as small as 65nm. However UV laser cleaning requires optimization to ensure damage free cleaning whenever a new surface is used, since UV laser is directly exposed to the surface and photochemical reaction occurs which can cause damages depending on the surface material. On the contrary, another hybrid type LSC, wet laser shockwave cleaning (WLSC) technique doesn’t have to be optimized regardless of the surface material. This new hybrid technique is advantageous for using water to reduce the adhesion force by an order of magnitude, utilize the double layer repulsive force, eliminate the capillary force encountered in dry LSC and increase the drag force by increasing the medium density.

WLSC Technique has been successfully refined to remove contaminants from whole wafer surface in present study. In addition, the thickness of water film on the top of Si wafer has been well controlled with reducing it down to 25μm in order to increase removal efficiency. The wet laser shockwave cleaning results indicate that 300nm PSL particles as well as 280nm silica particles can be completely removed. It also shows the successful removal of 28nm PSL nanoparticles, with a removal efficiency of more than
90%.

In order to investigate the removal mechanism of WLSC, computational fluid dynamics (CFD) model was developed to predict the flow field for the phenomena occurring during WLSC. It has been found that the velocity of the water flow near Si substrate is around 30m/s. And for a more precise analysis, the shadow-graphic photographs with a high speed camera have been obtained, which enabled us to measure the surface velocity of the water flow driven by a laser-induced shockwave. The measured velocity at a distance of 2.5mm from the center of the water flow is 32m/s, which is in good agreement with the simulation results. Accordingly, velocity profile, drag force, electrostatic double layer force and adhesion force have been determined. Removal moment ratio for PSL and silica particles using WLSC has been also analyzed. However for PSL particle, removal moment ratio doesn’t agree with experimental results unlike silica particles. Therefore based on the assumption that the water flow could be compressed and consequently its thickness decreased, removal moment ratio has been reanalyzed. As a result, it has been shown that when the thickness of the water film decreases down to 0.5\(\mu\)m or 1\(\mu\)m with the linear or hyperbolic velocity profile respectively, the determined removal moment ratio can be in good agreement with experimental results for removal of 28nm PSL particles.
5.2 Future Work

While progresses have been made in understanding the removal mechanism of organic particle in LSC and investigating new wet laser shockwave cleaning, more work is needed to get a better understanding. Listed below are some topics that will be useful in not only expanding the present work but also developing other new hybrid LSC methodology to increase the cleaning efficiency.

1) Further study of the particle removal mechanism for laser shockwave cleaning. Present study used the particle removal model in which the drag force was calculated based on the shockwave pressure, while the drag force was calculated from velocity profile in the traditional way. The speed of laser-induced shockwave decreased as it propagated further through air. Therefore it was not easy to obtain velocity profile near the surface as a function of the distance from the center of cleaned area. However the exact solution can be determined analytically applying the point explosion theory to an example of the stagnation in plane flow. Otherwise, numerical modeling should be used to obtain the velocity profile.

2) Further study of the removal mechanism for wet laser shockwave cleaning. In the present study, the velocity was predicted using the numerical modeling and measured using shadow-graphic photography. However in the developed numerical model, only air flow parallel to the water surface has been considered. Although the simulation results show that the water surface level becomes lower and it also does agree with the
assumption for high removal efficiency of 28nm PSL particles, the phenomena occurs during WLSC still needs to be investigated and verified more precisely using numerical modeling. It is very difficult to develop the exact computational fluid dynamics (CFD) model, since many parameters have to be considered to predict the more realistic flow field. Another way to observe the water surface behavior is shadow-graphic photography. Camera with much higher frame rate and high resolution may be able to capture the moment that water surface is compressed by a shockwave.

3) Investigation of other hybrid type laser shockwave cleaning methods. Present study introduced the improved wet laser shockwave cleaning method including the evaluation of its cleaning performance and the analysis of its removal mechanism. Another hybrid laser shockwave cleaning combined with water is underwater laser shockwave cleaning which utilizes shockwaves generated underwater by converging laser beam into water. Although it has been reported that cavitations occur during shockwave generation, this technique is very attractive due to its powerful cleaning performance. If cavitations are controllable, it can be expected to be alternative method of next cleaning technique.
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