Efficiency studies of particle removal with pulsed-laser induced plasma

THOMAS HOOPER, JR. and CETIN CETINKAYA *
Department of Mechanical and Aeronautical Engineering, Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699-5725, USA

Received in final form 27 January 2003

Abstract—The detachment and removal of micro- and nanoparticles from surfaces is of importance in many industries. The cleaning of silicon wafers is of great interest in the semiconductor, microelectronics, and optics industries. The development and adoption of dry, rapid, non-contact, and non-damaging particle removal technologies is a critical process. The proposed laser-induced plasma (LIP) removal technique is a novel method for detaching and removing fine particles from substrates. The current technique is a dry, non-contact method that takes advantage of the strong shock wavefront from expanding plasma, created by focusing a laser pulse in air above the substrate. The transient pressure field acts on the target particles to produce a rotational moment and a rolling mode of detachment from the substrate. In the current study, the LIP removal technique is employed repeatedly to remove particles over an area of a silicon wafer, and a systematic efficiency study for the removal effectiveness is performed. A Q-switched Nd:YAG pulsed laser operating at 1064 nm with a 370 mJ pulse energy and 5 ns pulse length is used in experiments. 0.99 μm diameter silica spheres and 3.063 μm diameter polystyrene spheres were successfully detached and removed with no substrate damage. The removal efficiency at various gap distances between plasma core and substrate is determined and reported. This work is the first laboratory demonstration of the LIP technique over an extended area. The reported results substantiate the LIP removal technique as a serious option for particle detachment and removal from extended areas.

Keywords: Particle removal; laser ultrasonics; laser cleaning; micro-manufacturing; nano-manufacturing; micro-contamination.

1. INTRODUCTION

Practically in every industrial process, particles with various shapes and sizes are generated and introduced to the environment. The detachment and removal of particles during manufacturing processes is of great importance in many indus-
tries, including semiconductors, nano-manufacturing, optics, photonics, and microelectromechanical systems (MEMS). According to the 2001 International Technology Roadmap for Semiconductors, the maximum critical particle size in semiconductor manufacturing is given as 58 nm, and it is predicted to reach as low as 30 nm by 2007 [1]. As removal of smaller particles is needed, the need for improved cleaning technologies becomes apparent. These novel technologies must remove particles quickly and efficiently while avoiding substrate damage. Likewise, reducing chemical usage is of serious concern for workplace safety and environmental conservation. The development and demonstration of dry, rapid, non-contact, and non-damaging particle removal methods is a critical need in various industries.

2. MODES OF PARTICLE DETACHMENT

In the literature, three main modes of particle detachment from substrates have been identified [2]. These are rolling, sliding, or lifting detachment modes. In pure rolling detachment, a moment acting about a point in the adhesion area must be of critical magnitude to initiate a separation crack in the (van der Waals) adhesion bond between the particle and the substrate. Once the adhesion bond is broken, crack propagation occurs until the particle is free from the surface. In pure sliding detachment, a force parallel to the substrate surface acts on the particle. This force must be greater than the frictional forces between the particle and the surface for the particle to be detached. Finally, in pure lifting detachment, a force perpendicular to the substrate surface acts on the particle. This mode is the dominant removal mechanism in the direct laser method [3]. The lift-off force must be greater than the combined forces of adhesion and gravity in order to lift the particle from the surface. In application, detachment will be some combination of these three effects. It is known that rolling detachment is the dominant mode for spherical particles on flat substrates [2], and so this will be referenced as the principal mechanism in the current technique.

As particle size decreases, removal becomes an increasing challenge. The Johnson, Kendall, and Roberts (JKR) model of particle adhesion gives the force of adhesion, $F_A$, between a spherical particle and a flat substrate as

$$F_A = \frac{3}{4} \pi W_A D,$$  \hspace{1cm} (1)

where $W_A$ is the work of adhesion between the particle and the substrate and $D$ is the diameter of the spherical particle [4]. The radius of the contact circle, $a$, between the substrate and particle at the onset of detachment is determined as

$$a = \left(\frac{3\pi W_A D^2}{8K}\right)^{1/3},$$  \hspace{1cm} (2)
Figure 1. Geometric features of a spherical particle attached to a smooth surface. \( \alpha \) is the compression distance of the particle in the adhesion area.

where

\[
K = \frac{4}{3} \left[ \frac{(1 - \nu_1^2)}{E_1} + \frac{(1 - \nu_2^2)}{E_2} \right],
\]

where \( \nu_1 \) and \( E_1 \) are, respectively, the Poisson’s ratio and the Young’s modulus of the particle material, and \( \nu_2 \) and \( E_2 \) are, respectively, the Poisson’s ratio and the Young’s modulus of the substrate material. The average adhesion stress at the moment of detachment can then be calculated as

\[
\sigma_A = \frac{F_A}{\pi a^2} = \left( \frac{3W_A K^2}{\pi^2 D} \right)^{1/3}.
\] (3)

Therefore \( \sigma_A \) is inversely proportional to the cube root of \( D \).

In the LIP removal technique under investigation, the dominant removal mode is assumed to be rolling under a transient pressure field generated by a shock wavefront. While it is possible that both substrate motion and sliding particle motion increase cleaning efficiency, the pressure field acting on the particle is more likely to generate a rolling motion since the resistance to rolling is very low. In Fig. 1, a spherical particle on a flat surface under an applied pressure field is depicted. Due to the small size of the particle, the pressure field is reasonably approximated to be uniform over the entire particle surface. In analyzing the rolling mode of removal, the moment equilibrium about point \( O \) is applied. From this analysis, it is determined that the critical pressure needed for detachment can be expressed as

\[
p_{\text{rolling}}^* = \frac{2a(F_A + mg)}{A_s(D|\cos \theta| - 2a \sin \theta)},
\] (4)

where \( A_s \) is the effective cross-sectional area perpendicular to the pressure field, \( g \) is the gravitational acceleration, and \( \theta \) is the angle between the force vector and the plane parallel to the substrate surface. Since \( F_A \) is many orders of magnitude larger than \( mg \) when dealing with micrometer and submicrometer particles, \( mg \) can
be neglected in equation (4). Since the cross-sectional area $A_s$ is proportional to $D^2$, the rolling pressure $p_{\text{rolling}}^*$ is proportional to $1/(D^{7/3} - D^2)$, further illustrating the difficulty in removing ever smaller particles. However, compared to the lift-off mode, in which the required removal force is on order of $1/D^3$, the LIP technique promises a several order of magnitude performance benefit for nanoparticles.

Using equations (1) and (3), adhesion forces and required pressures for detachment and removal can be calculated. In the case of a $1 \mu m$ silica particle on a silicon wafer, the force of adhesion is 51 nN and the magnitude of the required pressure field for detachment is approximately 690 Pa when $\theta$ approaches 0 or $\pi$. For a $3 \mu m$ polystyrene particle, the force of adhesion is 146 nN and the required pressure for removal is approximately 521 Pa when $\theta$ approaches 0 or $\pi$. These calculations, coupled with the use of varying particle sizes, could be used to characterize unknown pressure fields based on observed removal. The smallest particles removed would be used to approximate the maximum pressure present.

3. LASER-INDUCED PLASMA

In the LIP technique, a plasma core is generated by focusing a laser beam to a point in air. Near the focal point the energy density is so high that it causes the breakdown of air into plasma. This phenomenon has been known and studied since the early 1960’s [5]. In the plasma burst core, very high temperature elevations are experienced. Strong shock waves are generated as the plasma rapidly expands outward. It is known that in the near field, the pressure, $p$, is related to the radial distance from the blast center, $r$, by $p \sim 1/r^3$ [6–8]. In the far field, $p \sim 1/r$. Shadowgram images of the evolution of LIP by an Nd:YAG with a pulse energy of 300 mJ and a pulse duration of 10 ns are presented in Fig. 2 [9].

The laser-induced plasma technique is a novel method for particle detachment and removal using the pressure field created by LIP [10–12]. The current experimental set-up is depicted in Fig. 3. In the experiments, an incident laser beam is focused through a convex lens. Near the focal point of the lens, the energy density is high enough to cause the breakdown of air into plasma. The pressure field created acts over the surface of the particle as in Fig. 1, creating an equivalent moment about the adhesion area. If the moment due to the pressure field is strong enough, a crack is initiated in the adhesion bond between the particle and the substrate. The crack will propagate as the particle rolls. The removal of the particle will be initiated when it loses contact with the surface. It is observed that the removal effectiveness relies heavily on the distance, $d$, between the center of the plasma and the substrate since this dictates the applied pressure field on the surface of the particle [10]. The closer the particle is to the blast center, the higher the pressure that will act over the surface of the particle. Moving the substrate closer to the blast center increases the magnitude of the moment experienced by the particle, which increases the effectiveness of the removal phenomenon. Damage concern increases as the substrate is moved closer to the plasma core. However, as seen in Fig. 2, the hot
Figure 2. A sequence of shadowgrams for laser-induced plasma (LIP) evolution in air. The laser beam is incident from the left. Each frame has an original dimension of 36 mm by 48 mm. (Reproduced with permission of C. Parigger et al. [9].)

Figure 3. Laser-induced plasma (LIP) removal technique schematic.

$r_0 = \text{incident radius}$

$r(x) = \text{expanded beam radius}$

$f_i = \text{focal length of lens}$

$d = \text{distance from beam center to substrate}$
plasma core is rather stationary compared to the cooler propagating shock waves. Therefore, thermal damage can be eliminated if the surface is fixed at a sufficient distance from the static plasma core.

4. EXPERIMENTAL METHODS AND SETUP

The particles used in the experiments were silica spheres with a diameter of $0.99 \pm 0.05 \mu m$ and polystyrene spheres with a diameter of $3.063 \pm 0.027 \mu m$. The substrates were 125 mm silicon wafers with a $1 \mu m$ thermal oxide layer (Silica-Source Technology, Tempe, AZ). Prior to particle deposition, the wafers were cleaned using an ultrasonic bath to minimize initial contamination. A 132 kHz ultrasonic generation system was used. The bath contained a 2% solution of Chem-Crest 14 (Crest Ultrasonics) in de-ionized water. It was held at $50^\circ C$ with full power from the generator for 25 min. Following ultrasonic cleaning, the wafers were rinsed with de-ionized water. A brush scrubber (Evergreen Solid State Equipment, Horsham, PA) was used to dry the wafers at a spinning cycle of 1800 rpm for 25 s.

Particles were deposited onto the silicon wafers using a drop-agitation technique. The objective of deposition was to achieve a uniform distribution of particles with minimal aggregation and proper density to facilitate analysis in the target areas of the wafer. Methanol was used as the suspending medium owing to its quick evaporation time and lack of residual contaminants left on the substrate. The wafers were attached to a rigid post sitting in a jewelry cleaning machine in order to vibrate the surface. The surface vibration was found to reduce particle aggregation while the suspension was drying on the surface. The suspension was applied to the center area of the wafer. The wafer was allowed to completely dry following deposition. It was sufficient to repeat this process twice per wafer in order to obtain the appropriate particle density. Both initial cleaning and deposition were conducted in a class-10 cleanroom.

The wafers were then taken to the laser setup outside of the cleanroom for application of the LIP removal technique. The laser used was a Q-switched Nd:YAG operating at a fundamental wavelength of 1064 nm with a pulse energy of 370 mJ, a pulse length of 5 ns, a repetition rate of 10 Hz, and a beam diameter of 5 mm. A 25 mm diameter, 100 mm focal length lens with a 1064 nm specific antireflective coating was used to converge the laser beam. A shorter focal length lens would be more ideal due to the high quality of the plasma burst produced [11, 12], but wafer positioning requirements demanded a larger focal length lens.

Prior to laser irradiation, the specimen wafer was placed onto an optical stage and held in place with a light adhesive tape. Horizontal translation was achieved in two dimensions using sliding posts with millimeter markings. More exact translation was required in the vertical dimension to control the critical parameter $d$. A linear translational stage with a $20 \mu m \pm 10 \mu m$ resolution was used for this purpose. A He-Ne laser was used for positioning of the lens and vertical alignment of the sample with the Nd:YAG beam. A diode laser was used to mark the horizontal position of
Figure 4. Firing positions for $8 \times 8$, $s = 1$ mm grid. Each grid intersection marks a firing position. Firing begins in lower left hand corner. Arrows denote sequential firing order path.

the plasma and to align the sample. Previous experimental results showed that a single pulse affected a circular area with a diameter of about $2–3$ mm [12]. In order to completely remove particles from a larger area, these circular areas needed to be overlapped. An $8 \times 8$ square grid was used with a spacing, $s$, of 1 mm (see Fig. 4). The wafer was positioned so that the lower left grid corner was the first to be cleaned. The firing then proceeded in the direction of the arrows shown in Fig. 4. After each alignment, one pulse was delivered to each point on the grid.

In counting the particles on surfaces, a Surface Analysis System (Particle Measuring Systems, Inc.) and an optical microscope were used. The surface analysis system is capable of taking surface analysis scans (SAS) confined to any circle centered on the wafer. These radially-specific measurements are accomplished through varying the edge size parameter. The edge size is the radial distance from the edge of the wafer that is not counted in the Surface Analysis System. This allows for localized measurements to be taken in and between any concentric circles. An SAS with edge size of 59 mm was used for analysis with the grid in Fig. 4, giving data on the 7 mm diameter circular region inscribed in the grid. This approach was sufficient to analyze the ability of the laser technique to clean an extended area. Optical microscopy was used to support the SAS data collection. Both techniques were employed prior to and following all LIP trials reported in this work.

5. EXPERIMENTAL RESULTS AND DISCUSSION

In the experimental trials, 3.063 $\mu$m polystyrene spheres were used at the gap distance between the plasma core and substrate, $d$, set to 3.0 mm, 2.5 mm, 2.0 mm, and 1.5 mm. Due to the range in actual particle size and the variation in the particle counting system, the SAS recorded the 3.063 $\mu$m particles in range from 2–4 $\mu$m. This range was used to calculate the removal efficiency of the process. No removal was observed with $d = 3.0$ mm. At $d = 2.5$ mm and $d = 2.0$ mm, the removal
Figure 5. The surface analysis scan of 3.063 μm polystyrene particles after laser-induced plasma (LIP) removal at \( d = 1.5 \) mm. The oval indicates the boundary of the particle deposition area. The square surrounds the removal zone.

Figure 6. Removal efficiency of 3.063 μm polystyrene particles for laser-induced plasma (LIP) removal trails at four different gap distances, \( d \).

Efficiencies rose to 27% and 73%, respectively. At \( d = 1.5 \) mm, the removal efficiency was 96%. The SAS scan taken after the \( d = 1.5 \) mm trial can be seen in Fig. 5. A summary of the cleaning efficiency results is presented in Fig. 6. The SAS reports particle counts in both a color-coded graph and a spatial representation of the wafer. In Fig. 5, green domains denote 5–10 μm particles, blue denotes 2–4 μm particles, red denotes 0.7–1.5 μm particles, purple denotes 0.4–0.6 μm particles, and light blue denotes 0.1–0.3 μm particles.
In the second part of the experimental work, smaller particles were used. A series of trials was performed with 0.99 μm silica spheres with \( d \) set to 2.5 mm, 2.0 mm, and 1.5 mm. Optical microscope analysis verified that deposition was uniform with minimal clumping (see Fig. 7a). At \( d = 2.5 \) mm, Figs 7b and 7c show a significant reduction in the number of particles present in two separate areas. Note that there remains an aggregation of two particles in Fig. 7b along with an aggregation of three particles in Fig. 7c. It is expected that these clusters of particles will require a much greater applied pressure to induce rolling removal due to increased contact.
Figure 7. (Continued).

area and changed geometry. At \( d = 1.5 \text{ mm} \), no particles were found to remain in the intended removal zone at the center of the silicon wafer. See Fig. 7d for an optical microscope image of the surface after firing at \( d = 1.5 \text{ mm} \). The SAS recorded varying particle sizes with the 0.99 \( \mu \text{m} \) silica particles for an unknown reason. A potential cause of this error is the particle material type. The particle measuring system uses the optical properties of silicon in its process. Therefore, using particles with the same optical properties may make proper detection difficult, if not impossible. Although the SAS images were insufficient in determining particle sizes and exact removal numbers for these trials, they provided a qualitative picture of the particle density in the removal zone. Figure 8 presents these SAS
Figure 8. SAS images of silicon wafer substrates (a) after deposition of 0.99 μm silica spheres, (b) after laser-induced plasma (LIP) removal at $d = 2.5$ mm, (c) after LIP removal technique at $d = 2.0$ mm, and (d) after LIP removal at $d = 1.5$ mm. The shape of the removal grid becomes visible in the center zone of the wafer.
Figure 8. (Continued).
images. The color change in the center of the wafer from image to image indicates the effect of the LIP removal technique.

6. CONCLUSIONS AND REMARKS

Particle detachment and removal for large areas using laser-induced plasma has been evaluated. It is demonstrated that the laser-induced plasma (LIP) technique is effective in detaching and removing particles over an extended area on a full-size silicon wafer. Both 3.063 μm diameter polystyrene spheres and 0.99 μm silica spheres were removed at a gap distance of 1.5 mm. The removal was accomplished with no visible mechanical substrate damage. In a separate study [11], visible mechanical damage was documented to first occur at a gap distance of 0.75 mm. It must be noted that the potential for non-visible lattice damage exists, but as of yet no work has been performed to characterize this threat. Removal of particles with diameters less than 0.99 μm is expected to be possible using gap distances between 1.5 mm and the damage threshold of 0.75 mm. Further study is proposed to determine the minimum particle size removable with the LIP technique. In previous studies, it was reported that 460 nm silica particles were successfully removed without substrate damage [11, 12]. For process optimization, additional research is proposed in order to incorporate potential modifications into the removal process. Further research is underway.

Acknowledgements

The authors would like to thank Dr. Parigger for providing the laser-induced plasma images, Richard Vanderwood (currently with Bechtel Plant Machinery) for his help with the original LIP set-up, and Jiadao Lin for her aid with adhesion calculations. Thanks to Tom Norment of Brumley-South for providing a calibration standard wafer. Thanks must be given to the Clarkson University Honors Program and the Ronald E. McNair Program for their support. The authors also acknowledge the New York State Science and Technology Foundation and the Center for Advanced Materials Processing for their financial support.

REFERENCES


