Nanoparticle detachment using shock waves

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Abstract: The fundamentals of nanoparticle detachment at the sub-100 nm level using pulsed laser-induced plasma (LIP) shock waves are investigated in the current study. Two detachment mechanisms based on rolling resistance moment and rolling by resonant frequency excitation are identified as possible detachment mechanisms for nanoparticles. The gas molecule–nanoparticle interactions are studied using the direct simulation Monte Carlo method to gain knowledge about the nature of the detachment forces and moments acting on a nanoparticle in the LIP shock wave field. The discrete nature of the gas molecules colliding with the particle on the sub-100 nm length scale is linked to the stochastic transient moment experienced by the particle. Both experimental and computational findings of the current study indicate that nanoparticle detachment at the sub-100 nm level is possible by LIP shock waves.

Keywords: nanoparticle adhesion, nanoparticle removal, rolling moment resistance, laser-induced plasma shock waves, nanoscale contamination

1 INTRODUCTION

The persistent demand for faster and more reliable integrated circuits has led to a shrinkage in the feature size and, as a result, reduction in the allowable particle and defect sizes on substrates to the sub-100 nm level. Damage-free nanoparticle detachment at the sub-100 nm level is a challenge that has to be overcome to maintain rapid progress in nanotechnology as well as the semiconductor and microelectronics industries. According to the 2005 edition of the International Technology Roadmap for Semiconductors (ITRS) [1], the substrate defects sizes or the minimum diameter spherical defects (in polystyrene latex sphere equivalent dimensions) on the extreme ultraviolet lithography (EUVL) substrate beneath the multilayers that cause an unacceptable linewidth change in the printed image are 38 nm by 2008, 35 nm by 2010 and 30 nm by 2013. Complications on the nanometre scale can best be explained by a simple length-scale argument. As the size of the particle with a characteristic length scale (e.g. diameter) $L$ to be removed decreases,

body forces (e.g. gravity) acting on the particle reduces by $O(L^3)$, fluid and electrostatic forces acting on the particle decreases by $O(L^2)$, whereas the force of adhesion is reduced by only $O(L)$. The intermolecular (adhesive) force dominates body and area proportional forces as the particle size decreases. In dry particle removal, the reduction in the length scale (particle size) requires the inclusion of the mean speed of individual gas molecules in predicting forces and moments exerted on the particle since the timescale of the gas molecule–nanoparticle interactions as opposed to that of the speed of the gas flow field in the locality of the nanoparticle needs to be taken into consideration.

As the feature size on an integrated circuit decreases to the sub-100 nm level, new lithography techniques are required to fabricate the fine features [2]. EUVL, a reflective technique, is being explored to meet the upcoming stringent size requirements [3]. Unlike conventional optical lithography masks, the EUVL photomasks are pellicle free since a pellicle would absorb a considerable portion of the extreme ultraviolet (EUV) light [4]. As a result, one of the major requirements for the EUVL process is that the photomask used to print the features should be free of particles and defects. Particles or defects on the photomask will result in defects with magnified sizes in the manufactured integrated circuits. The

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substrate defect size on an EUVL photomask and the maximum front surface particle size for starting materials that can be tolerated are 36 nm and 65 nm respectively by the year 2009 according to the 2005 edition of the ITRS [1]. Also, the cost of manufacturing the photomasks demands a no-damage cleaning process. However, efficient removal of sub-100 nm particles has remained a challenge [5].

The current techniques most commonly applied for silicon substrate cleaning and investigated for sub-100 nanoparticle detachment and removal include brush scrubbing, megasonic cleaning, and CO₂ snow cleaning. The brush cleaning technique relies on the contact of the brush tips on the particle for detachment. Typically, full contact of the brush with the particle is required for efficient particle detachment [6]. The pressure generated by the brush is 4 kPa at a compressed distance of 2 mm, which is considered to be the optimized distance for cleaning [7, 8]. The brush cleaning technique relies on the drag force exerted by the fluid on the particle for particle detachment [8] which decreases by O(L²). Therefore a substantially higher pressure and brush velocity are required for removing smaller particles. As a result, particle redeposition after cleaning and damage are reported as major problems in brush cleaning [7].

Megasonic cleaning, ultrasonic waves above 1 MHz, has been utilized for particle removal in the sub-100 nm range. It is a cost-effective wet method. One of the possible mechanisms of particle detachment in megasonic cleaning is the acoustic streaming-induced pressure gradients acting on particles [9]. According to reference [9] the megasonic cleaning force acting on the particle decays as O(L²) and therefore may not be effective for the detachment of particles smaller than 100 nm [9]. Gas cavitation created by acoustic waves has been considered as a potential localized damage mechanism in megasonic cleaning [10]. In general, damage on the silicon substrate due to cavitation increases linearly with increasing particle removal efficiency [5, 11]. Additionally, drying processes without leaving any water marks on the substrate is often noted as a major potential source of post-cleaning complications [10].

Another nanoparticle removal technique is based on the use of accelerated CO₂ ‘snowflakes’ [12]. In this type of dry cleaning, small dry ice particles formed by the rapid expansion of liquid CO₂ through a small aperture nozzle collide with the particles on the substrate at high velocity. The momentum imparted by the cryogenic particles to the contaminant particles on the substrate, together with the drag force of gaseous CO₂, acts as the major particle detachment mechanism [13]. One limitation of the cryogenic cleaning is reported as possible structural damage to the substrate and redeposition of particles [12]. The purity of CO₂ gas has also been an issue and it appears that the source of hydrocarbon impurities is not well understood.

Owing to particle redeposition [7, 12] and efficiency of cleaning [11], commonly used techniques leave a relatively small number of particles (vis-à-vis the number of particles before cleaning process) after each cleaning cycle. As a result, the need for a novel precision cleaning approach has risen especially when removal of a small number of sub-100 nm size particles at selected locations is required.

In recent years, shock waves generated by a laser-induced plasma (LIP) has experimentally been demonstrated to be an effective non-etching dry method in the detachment of micron-sized and nano-sized particles as low as 60 nm [14–16]. In the current study, fundamental forces in nanoparticle detachment at the sub-100 nm level using pulsed LIP shock waves are investigated. Two detachment mechanisms based on the rolling resistance moment and rolling by resonant frequency excitation are identified as possible nanoparticle detachment mechanisms.

2 DETACHMENT OF NANOPARTICLES USING LIP SHOCK WAVES

The laser shock cleaning tool consists of a high-energy laser and a convex lens to converge the laser beam. The laser beam from the pulsed laser is focused on to a point above the position of the particles using the convex lens. The focusing of the beam results in the dielectric breakdown of air, causing the formation of a rapidly expanding plasma at this location. A schematic diagram of the LIP detachment system used for removal of sub-100 nm particles is depicted in Figs. 1(a) and (b). The dielectric breakdown of air is characterized by four successive stages. The first stage is the initial release of electrons due to the collision of photons with the gas molecules. The subsequent process is the ionization of the gas. With a 7 ns neodymium-doped yttrium aluminum garnet Nd:YAG pulsed laser, these actions occur approximately in the first 100–150 ns of the LIP process. The third phase is the formation of plasma which is in turn followed by strong shock waves created by the propagation high-pressure plasma core propagating at supersonic velocities [17]. At the end of the plasma formation phase, the plasma core reaches a limit diameter and stops its expansion as a plasma core. The separation of the shock wavefront from the plasma boundary follows (in the first few microseconds of the LIP process). While the expansion of the plasma core is a mass
transfer phenomenon, the motion of a shock front is a travelling pressure wave without mass transfer. As a result, in the LIP cleaning, no direct plasma–surface interaction is allowed and, consequently, no electrical charging of particles and/or substrates is expected. The shock wave generated (Fig. 2) plays the critical role in breaking the bond between the particles and the substrate by exerting a moment on the particle due to the collisions of the gas molecules with the particle. Unlike fluid flows over a flat substrate, the interactions of the shock wavefront with the substrate and associated momentum transfer to the particles are not weakened by the formation of a boundary layer. The exerted moment results in the rolling and rocking motions of the particle and its subsequent detachment from the substrate, when the moment exceeds the critical resistance moment of the particle. The shock front colliding with the particle can be considered as individual gas molecules colliding with the particle. The rolling moment exerted on a particle by the shock wave is stochastic owing to the discrete nature of gas molecules. The moment exerted by the shock wave on the particle and the stochastic transient rolling moment act as the particle detachment mechanisms in the LIP.

3 GAS MOLECULE–NANOPARTICLE INTERACTIONS: NUMERICAL SIMULATIONS

Numerical simulations were performed to study the transient forces exerted by the shock wave on the particle and hence to evaluate the rolling moments acting on the particle. The calculated moments provide insight into the particle detachment
mechanisms that play an important role in the nanoparticle detachment observed in experiments and the minimum size ranges of the particles that can be removed by applying these mechanisms.

The characteristic length in the current problem, i.e. the diameter of the particle, is comparable with the mean free path of the gas molecules in the shock wave. Any numerical approach based on the continuum assumption is inappropriate for solving the gas molecule–particle interactions problem [18, 19]. Numerical simulations based on the continuum assumption of the medium valid for micron-sized particles have already been attempted [20]. However, for the current problem the particulate nature of the gas molecules has to be taken into consideration for minimizing errors associated with the continuum approximation. This condition is expressed in terms of the Knudsen number \( \text{Kn} = \frac{\lambda}{L} \), where \( \lambda \) is the mean free path of the molecules and \( L \) is the characteristic length (diameter) of the system. For the pressure \( P = 0.156 \text{ MPa} \), the temperature \( T = 450 \text{ K} \), and the mean diameter \( \Delta = 0.4149 \text{ nm} \) of the gas molecules [air consisting of \( \text{O}_2 \) (20 per cent) and \( \text{N}_2 \) (80 per cent) molecules] in the shock front, the mean free path of the molecules can be calculated from \( \lambda = k_b T / \pi \sqrt{2 P \Delta^2} \) as \( \lambda = 52.07 \text{ nm} \), where \( k_b = 1.380658 \times 10^{-23} \text{ J/K} \) is the Boltzmann constant and \( \Delta \) is the mean molecular diameter. The diameter of the particle, \( L = 60 \text{ nm} \), is of the same order as the mean free path of the gas molecules. The mean speed of the gas molecules in the shock front is approximated by \( \bar{v} = \sqrt{8RT / \pi M} \), where \( R = 8.3144 \text{ J/mol K} \) is the universal gas constant and \( M = 0.0285761 \text{ kg/mol} \) is the molecular mass, and the value of \( v \) is 577.4 m/s for the shock wave. This mean velocity of molecules results in a mean time between molecular collisions of 0.09 ns. For a mean free path of 52.05 nm, the Knudsen number for a particle of 60 nm diameter is 0.867. A Knudsen number \( \text{Kn} \) of 0.1 is considered to be the lower bound between continuum and molecular models. The Knudsen number for the current problem indicates that a numerical scheme that takes into account the particulate nature of the gas is appropriate for the simulations.

The direct simulation Monte Carlo (DSMC) method is a particle-based numerical simulation technique for the modelling of gas flows, based on the kinetic theory of gases [21, 22]. This technique treats the gas flow at the molecular or microscopic level, rather than at the macroscopic level which require the solution of the Navier–Stokes equations. The DSMC method was employed for performing the simulations of shock wave–nanoparticle interactions.
and tracks a number of simulated molecules that statistically represent the real molecules. Each simulated molecule represents a number of actual molecules. The velocity components and position coordinates of these representative molecules are modified with time as the molecules are followed through representative collisions and boundary interactions in simulated physical space. The DSMC scheme employs probabilistic methods to set the initial configuration of the simulated molecules, whereas deterministic techniques are used for the calculation of subsequent molecular collisions and boundary interactions. The time step used for moving the molecules should be less than the mean molecular collision time.

The properties of the incident shock wave such as the pressure, temperature, and number density are used as initial conditions for numerical simulations by the DSMC method. The pressure exerted by the shock wave is obtained from experiments conducted using a 450 mJ pulsed Nd:YAG laser and a pressure transducer (Kistler 603B1) of resonant frequency 500 kHz and surface diameter of 5.54 mm. The high-sensitivity pressure transducer with a frequency bandwidth of 0–150 kHz and a rise time of 1 μs is ideal for dynamic pressure measurements of the shock wave. The selection of the transducer frequency bandwidth was based on our previous experiments with super-broadband (polyvinylidene fluoride) film transducers. For the pressure measurements the pressure transducer was placed below the focal point of the convex lens at a distance \(d\) [Fig 1(a)]. The average pressure of the incident shock wave is converted into a charge output by the transducer which is passed on to a charge amplifier. The output from the charge amplifier is transferred to an oscilloscope from which the transient pressure response is obtained. The distance \(d\) of the location of the pressure transducer is varied from 2 to 15 mm to obtain the pressure exerted by the shock wave on the particle at various distances \(d\).

The transient pressures experienced for various distances \(d\) are plotted in Fig. 3(a). The peak pressures obtained at each \(d\) is used as the pressure input for the simulation by the DSMC method for the corresponding distance of the particle from the plasma core centre \(r\). The fitted curve for the peak pressures used in the simulations is also plotted in Fig. 3(a). The velocity of the shock wave is obtained by taking the time derivative of the distance travelled [Fig. 3(c)]. The maximum propagation velocity of the shock wave in this range is at the minimum distance, \(d = 2\) mm, and the velocity is obtained as 804.05 m/s [Fig. 3(c)]. The decay in the shock wave properties is ignored as the simulation domain is on a nanometre scale and the simulation is performed for only around 15 ns. The temperature of the shock wave at \(d = 2\) mm when it collides with the substrate at \(t = 1.74\,\mu\)s is set to 450 K as reported in reference [23]. The corresponding pressure \((P = 0.156\,\text{MPa})\) is obtained from the measured pressure data [Fig. 3(a)]. The temperatures at further times are approximated with the aid of the Rankine–Hugoniot equation for an ideal gas. The number density of the shock wave is obtained from the ideal gas law. Based on the properties of the shock wave during the period for which the simulations are performed, for a particle with a diameter of 60 nm, the Knudsen number is in the range 0.867–30.56 and, for a 30 nm particle, the Knudsen number is in the range 1.73–61.62. The values of the Knudsen number indicate that numerical schemes based on the Navie–Stokes equation is not valid for simulating the shock wave–sub-100 nm particle interactions.

Three-dimensional simulations for a spherical particle [Fig. 4(a)] and two-dimentional simulations for a cylindrical particle with the length equal to the diameter [Fig. 4(b)] were performed in the current study. The diameters of the particle in both cases were 60 nm. The simulation domain in comparison with the shock wave is depicted as a trapezoid in Fig. 1(b). The dimensions of the simulation domain were 600 nm × 600 nm × 600 nm in the \(x\), \(y\), and \(z\) directions respectively. The centre of the plasma core is located at a distance \(d\) above the film substrate and the particle to be removed is assumed to be located at a distance \(r\) from the center \(O\) [Fig. 1(b)]. Owing to the difference between the magnitudes of the length scales of the shock wave and the simulation domain, the shock front can be assumed to be planar, rather than spherical, and approaching at an angle to the particle. The angle of approach depends on the distance \(r\) of the particle from \(O\) and is given by \(\alpha = \tan^{-1}(r/d)\). In all cases the particle is considered to be at a distance of \(r + 350\) nm away from the centre-line and, since \(r\) is in millimetres, 350 nm is ignored. For the spherical particle simulations, the surfaces representing the particle, substrate, and flow entry boundary were meshed using triangular elements.

The boundary conditions used for the simulations were the flow entry boundary on the left-hand side plane, the diffused surface boundary on the particle surface, and the substrate which is the bottom plane (Fig. 4). All other boundaries were assumed to be stream boundaries. In the case of spherical particle simulations, owing to symmetry of the domain in the \(z\) direction, only half the domain was simulated and the minimum \(z\) plane was assigned symmetry boundary conditions. Flow cells were automatically generated in the case of cylindrical particle whereas, for the simulation of spherical particle, \(1.69 \times 10^6\)
Fig. 3  (a) Transient pressure $P$ of the shock wave measured at the various LIP gap distances $d$ ranging from 2 to 15 mm at an incremental distance of 1 mm, and the numerical fit for the peak pressures (solid curve). (b) Shock wavefront velocities $V$ for increasing distance $r$ along the substrate at an LIP gap distance $d = 2$ mm. (c) Arrival times $\Delta t$ for the shock wave at O’ for the various LIP gap distances $d$.
cells were assigned. The medium inside the domain was assumed to consist of O₂ (20 per cent) and N₂ (80 per cent) molecules, the diameters of which were 0.407 nm and 0.417 nm respectively.

4 NANOPARTICLE DETACHMENT MECHANISMS IN LASER SHOCK WAVE CLEANING

If the pressure field $P$ acting on the surface of a nanoparticle is known, the forces and rolling moments acting on the particle can be calculated. A schematic diagram of the shock wave front acting on the nanoparticle is depicted in Fig. 2. The shock front could initiate rolling and/or sliding of particles if associated critical pressure magnitudes are achieved. Applying a simple moment balance at the point A provides an approximate relation for critical pressure required for detachment of particle in rolling mode according to

$$P_c = \frac{2a(F_A + mg)}{A_s (D \cos \theta - 2a \sin \theta)}$$

(1)

where $A_s$ is the effective area normal to the applied LIP pressure, $m$ is the mass of the particle, $g$ is the acceleration due to gravity (negligible on a submicron length scale), $\theta$ is the angle between the applied force and the plane parallel to the substrate surface, and $a = 3.547 \text{ nm}$ is the radius of contact between the spherical particle and the substrate surface. The bond force of adhesion, $F_A$, between a spherical particle and a flat substrate according to the Johnson–Kendall–Roberts model is given by

$$F_A = \frac{1}{2} \pi W_A D$$

where $W_A$ is the work of adhesion between a spherical particle with diameter $D$ and substrate [24]. From equation (1), the critical pressure required to detach a 60 nm spherical particle can be estimated to be 69.5 kPa for $\theta = 0^\circ$, and the corresponding critical moment is 11.86 nN nm.

Another way of determining the critical pressure under transient loading conditions is to take the rolling resistance and vibrational motion of the particle into consideration. According to the rolling resistance moment theory, rocking motion could be excited by a transient pressure field and, consequently, is a possible potential mechanism for nanoparticle detachment. If an external pressure field is exerted on the substrate, the moment associated with rocking motion of the spherical particle causes a shift in the contact area and the pressure distribution is not symmetric any longer. The resulting moment when the contact area is no longer symmetric is given by [25]

$$M_y = 4F_A a^{3/2} \xi$$

(2)

If the normal forces stay within the range $-F_A < F < F_A$, the factor $a^{3/2}$ varies in the range 0.5–1.2 and, assuming that $\xi = 1$, the rolling
resistance moment for a particle on a flat substrate in static equilibrium is approximated by

\[ M_r = 6\pi W_\lambda r \xi \]  

(3)

Using the equation of motion of a spherical particle in free rotational oscillation on a flat surface, \( I \dot{\theta} + 6\pi W_\lambda \xi \theta = 0 \) where \( \xi \approx 2\theta \) is the shift in contact area due to the asymmetric pressure. Here \( \theta \) is the critical angle to which the particle has to be rotated before it can be detached. Determining the critical angle \( \theta \) is a difficult task and it is often taken as rolling required to make a tangent displacement on the surface of the order of molecular size or the lattice distance of the particle and/or the substrate materials. In the present study, it is approximated in the range 1–5 nm. The corresponding critical angle can be determined as \( \theta_{\text{crit}} = (1-5) \times 10^{-9}/r \). Then the rolling resistance moment required for a 60 nm polystyrene latex (PSL) particle on a silicon substrate is given by \( M_{\text{crit}} = 13.14-66.54 \text{nN nm} \) for \( W_\lambda = 23.5 \times 10^{-3} \text{J/m}^2 \). The critical moment required by this criterion in this case is higher than the moment obtained from the approximate pressure calculation using equation (1).

If the moment exerted on the particle by the gas molecules is less than the critical rolling moment required to detach the particle, the particle will roll to an angle less than the critical angle. Then the particle will stay at its location oscillating back and forth owing to the fluctuations exerted in the moment. If the frequency of fluctuations happens to be close to the resonance frequency of the particle, the amplitude of the rocking motion will increase continuously until the angle exceeds the critical angle. Subsequently, the particle will be detached and removed. Considering the relentless gas molecule impacts with the particle surface, it can be deduced that the moment exerted on the particle surface is never constant, but constantly fluctuating. It is these fluctuations in the moment that form the crux of the particle detachment mechanism based on the rocking motion of a particle, namely rolling by resonant frequency excitation [26] given by

\[ \omega_n = \frac{1}{\rho^3/2} \sqrt{\frac{45 W_\lambda}{14 \rho}} \]  

(4)

where \( \rho \) is the mass density of the particle material. For a PSL particle (\( \rho = 1040 \text{kg/m}^3 \), \( W_\lambda = 23.5 \times 10^{-3} \text{J/m}^2 \)) of diameter 60 nm adhering to a silicon substrate the resonant frequency of rocking motion is 261.2 MHz.

The experimental evidence for the existence of the rolling resistance moment and rocking motion of 21.4 \( \mu \)m PSL particles on an aluminium film substrate has been demonstrated and reported [26]. The resonance frequencies of a 100 nm PSL particle on a silicon substrate for axial [equation (4)] and rocking motions are determined as 1.517 GHz and 227 MHz respectively. Note that the rocking resonance frequency is much lower than the axial resonance frequency. This implies that it is easier to remove particles by exciting the particle’s rocking motion than by its axial motion.

The rolling moment resistance removal mechanisms are essentially the same for both microparticles and nanoparticles. However, the molecular impact mechanism requiring the gas molecule–particle interaction on a nanoscale is inapplicable to microparticles for which such interactions create an averaged pressure field. For nanoparticles, the analysis of removal forces requires a kinetic scheme owing to the high Knudsen number. In particle removal the dominant effect(s) depend(s) on the length scales and timescales of the interactions between the particle, the medium, and the substrate during detachment and, eventually, removal. It is also important to note that the significance of dominant forces and moments differ owing to the length scales and timescales dictated by the mean free path of the air molecules, which lead to a high Knudsen number, and their mean speeds, which result in short-timescale interactions due to high-speed discrete impacts. As a result of the length scale and timescale, in addition to the nature of the dominant forces and moments in detachment and removal, the methods of analysis adopted for the accurate prediction of these forces and moments substantially differ.

5 MOLECULAR DYNAMICS SIMULATIONS

Molecular dynamics simulations were performed to study the moments acting on the sub-100 nm particles due to the resultant shock waves from the LIP and to understand and evaluate the possible detachment mechanisms for such particles. Cylindrical (two-dimensional) and spherical (three-dimensional) particles with a diameter of 60 nm located at various distances \( r \) from the center \( O \) of the substrate were simulated [Fig. 1(b)]. The distance between the centre of the plasma and the substrate was \( d = 2 \text{mm} \). As the shock wave passes over the particle, the moment exerted on the particle first increases to a peak value. The moment then reduces to an average value below the peak value and keeps oscillating around this value with a small amplitude for the rest of the simulation time [Fig. 5(a)]. The average value of the moment during the fluctuations is calculated as around 65 per cent of the peak moment exerted on the particle at each \( r \). The transient moment exerted on a 60 nm cylindrical PSL particle located at \( r = 4 \text{mm} \) for \( t = 0-10 \text{ns} \) is shown in
Fig. 5(a). As the shock wave collides with the particle and passes around it, the moment first increases to a maximum value of 60.5 nN nm and then decreases to a lower value around 41.7 nN nm. The maximum moment exerted in this case is below the upper bound of the critical moment which is 66.4 nN nm. This indicates that the particle might not be rolled away by the shock wave. However, this is the ideal region where the other nanoparticle detachment mechanism introduced, namely rolling by resonance frequency excitation, might play a role in particle detachment. As already discussed, the moment acting on the particle is stochastic because of the discrete nature of molecules colliding with the particle surface. This phenomenon is indicated by the fluctuating part of the moment (Fig. 5(a)). However, the particle experiences a net moment as the shock wave exerts a force on the particle in the direction of its motion when it moves over the particle. From the frequency spectrum of rocking excitation [inset of Fig. 5(b)], the maximum moments and average moments exerted by the shock wave on the cylindrical and spherical particles as a function of the particle position \( r \). The full squares and open squares show the peak moments and average moments respectively for the cylindrical particle; the full circles and open circles show the projected peak moments and average moments respectively for spherical particles. The projected peak moment for the spherical particle is shown since the peak moment output is not obtained from the DSMC method.
of Fig. 5(a)), it can be seen that it covers the resonant frequency of a 60 nm PSL particle, which is 261.2 MHz. Even though the amplitude of the excitation is low, the timescale of the excitation, which is of the order of microseconds, is long enough compared with the nanosecond timescale of the problem. This means that the particle located at \( r = 4 \) mm might be excited to its natural frequency owing to the fluctuations in the moment exerted, thus reaching the critical angle \( \theta_{\text{crit}} \) which causes the particle to be detached from the substrate.

The peak moments and the average moments exerted on the particles by the shock wave at various particle locations \( r \) are summarized in Fig. 5(b). The upper and lower bounds of the critical moments, indicated by dotted lines in Fig. 5(b), are 66.4 nN nm and 13.3 nN nm respectively. With increasing distance from \( O \) the moment exerted by the shock wave first increases and then decreases with increasing distance \( r \). The maximum peak moment exerted on the 60 nm cylindrical particle is 127 nN nm, which occurs at the particle position \( r = 1 \) mm. The maximum peak moment exerted on the 60 nm spherical particle is calculated from simulations as 70 nN nm, at \( r = 1 \) mm. The peak moments exerted on the spherical particle are seen to be approximately 55 per cent of the moments exerted on the cylindrical particle for the corresponding particle position \( r \).

From the maximum moment data [Fig. 5(b)] it can be observed that cylindrical particles located in the range \( 0.5 \text{ mm} < r < 4 \text{ mm} \) can be easily detached since the maximum moments exerted are greater than the upper bound of \( M_{\text{crit}} \). In the range \( 4 \text{ mm} < r < 15 \text{ mm} \) the maximum moments are in between the upper and lower bounds of the critical moment. This result indicates that it is possible to remove these particles. The closer the maximum moment to the upper limit of the critical moment, the greater is the probability of removing the particle.

For 60 nm spherical particles, only at \( r = 1 \) mm, does the peak moment experienced by the particle exceed the maximum critical moment. Therefore, the particle is easily removable only at around \( r = 1 \) mm. However, for the range \( 1 \text{ mm} < r < 8 \text{ mm} \), the peak moments experienced by the particle lies between the upper and lower bounds of the critical moments, indicating that the particle might be removed.

6 EXPERIMENTAL SETUP AND PROCEDURE FOR LIP DETACHMENT OF SUB-100 nm PARTICLES

In order to demonstrate sub-100 nm particle detachment in selected target areas of the substrate, experiments were conducted using the LIP set-up [Fig. 1(a)]. The laser employed for the experiment was a Q-switched Nd:YAG laser of beam diameter 5 mm with a fundamental wavelength of 1064 nm, pulse energy of 370 mJ, pulse width of 5 ns, and pulse repetition rate of 10 Hz. The alignment of the test sample to the Nd: YAG laser beam was performed using a diode laser. The high-energy laser beam was converged on to a focal point using a convex lens with a focal length of 100 mm and with an anti-reflective coating for the laser beam of 1064 nm wavelength. The substrate used was a 6 in, n-type [111]-oriented silicon wafer with approximately 1 \( \mu \)m thermal oxide layers. The particles used for deposition were PSL nanosphere suspensions (Duke Scientific Corporation) of mean diameter 30 nm in the range 10–40 nm. In order to deposit the particles on to the substrate a drop containing PSL particles in a surfactant solution was dispersed in 100 ml of methanol. It is assumed that the effect of a small amount of surfactant in the final diluted solution on the adhesion properties of a nanoparticle to a substrate is minimal.

A sample piece of wafer of dimensions 15 mm \( \times \) 15 mm was cleaved from the 6 in wafer, owing to scanning election microscopy (SEM) constraints, for analysing the sample. The sample was washed with deionized water and methyl alcohol to remove the initial contamination. A diamond shaped reference pattern of area 2 mm\(^2\) was marked on the sample wafer piece in order to locate the cleaning area for SEM imaging. The sample was attached to an aluminium stub using an adhesive tape and aligned to the laser beam using a translation stage whose resolution was 20 \( \pm \) 10 \( \mu \)m. The distance \( d \) from the formation of the centre of the plasma to the surface of the substrate was set to 1.4 mm. In order to remove the contaminants due to marking, the sample was subjected to five laser pulses at \( d = 1.4 \text{ mm} \).

A droplet of the prepared solution was deposited in the test area of the sample, which is inscribed by the marked pattern, and set to dry to remove the methanol. To avoid the agglomeration of PSL particles while drying, the drop of solution was vibrated with an immersible transducer at 20 MHz. This agitation ensured good distribution of the PSL particles in the test area of the sample. The solution evaporated over time, resulting in the adhesion of PSL particles to the sample in the test area. The SEM image of the test area was obtained [Fig. 6(a)]. The pretreatment and deposition were carried out in a class-10 clean-room environment. Once the solution evaporated, the sample was adjusted such that the formation of plasma takes place 1.4 mm above the test area. The test area inscribed in the reference marking is approximately 2 mm\(^2\) and
a single pulse of the LIP is enough to clean this area. However, to ensure good cleaning, around 12 pulses were shot at the same location. The test area images were captured using SEM. The SEM images of the test area before and after LIP cleaning were analysed for particle detachment. Figures 6(a) and (b) show the images of the test area of the sample at 30,000× magnification before and after LIP cleaning respectively. The dashed lines show the marking pattern. It can be seen from the image before LIP cleaning that 10–40 nm particles are distributed uniformly using the deposition technique, and the size of the particles can be confirmed from that SEM image. The particles of 10–40 nm range are successfully detached without any substrate damage using the LIP detachment technique as seen from the SEM image obtained after LIP cleaning.

7 CONCLUSIONS AND REMARKS

In this study, it is demonstrated that laser shock cleaning of nanoparticles using LIP can be used to remove particles of sub-100 nm size efficiently. Both experiments and simulations were performed to show particle detachment on a nanoscale. A new particle detachment mechanism for particles of sub-100 nm size is introduced and explained utilizing the concepts of rolling moment resistance and rocking resonance by natural frequency excitation. The Knudsen number for the gas flow indicates that the continuum approach is invalid and requires an analysis of the problem as discrete gas molecules that collide with the particles. Therefore, simulations based on molecular gas dynamics were performed using the DSMC method to study the moments and forces acting on the particles due to the resultant shock waves from LIP. The gas molecule–particle interactions are revealed by the molecular dynamics simulations. The detachment of particles below a critical particle location is attributed to the mechanism of rolling moment resistance. Beyond this critical distance, simulations indicate that particles could still be detached by the rocking mechanism owing to the collision of the gas molecules on the particle. Particle detachment experiments were performed using PSL nanospheres of 10–40 nm size adhering to a silicon substrate. SEM images of the substrate before and after LIP cleaning demonstrate that LIP can be used to remove 30 nm particles from silicon substrates without causing any substrate damage.

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