Conditions for laser-induced plasma to effectively remove nano-particles on silicon surfaces*

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Particles can be removed from a silicon surface by means of irradiation and a laser plasma shock wave. The particles and silicon are heated by the irradiation and they will expand differently due to their different expansion coefficients, making the particles easier to be removed. Laser plasma can ionize and even vaporize particles more significantly than an incident laser and, therefore, it can remove the particles more efficiently. The laser plasma shock wave plays a dominant role in removing particles, which is attributed to its strong burst force. The pressure of the laser plasma shock wave is determined by the laser pulse energy and the gap between the focus of laser and substrate surface. In order to obtain the working conditions for particle removal, the removal mechanism, as well as the temporal and spatial characteristics of velocity, propagation distance and pressure of shock wave have been researched. On the basis of our results, the conditions for nano-particle removal are achieved.

Keywords: laser-induced plasma, shock wave, nano-particles, surface cleaning

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1. Introduction

In semiconductor manufacturing, the micro/nano particulates residing on the surface of most components are detrimental to their performance and operational lifetime. Consequently, they must be eliminated or removed effectively so as to enhance the yield of production.[1,2] The particles are generally cleaned with traditional methods, which cannot meet the ever-increasing demands for super clean surfaces as the feature size of many devices shrinks to the sub-micron scale and nanoscale.[3] Laser cleaning has emerged as a new technique because of its ability to remove nano-particles and because of its non-contact characteristics.[4] The process of laser cleaning is actually complicated and the cleaning results are affected by numerous parameters, such as the characteristics of the laser plasma, the laser energy and so forth.[5–7] After absorbing laser energy, the particles will be heated, they will expand and they will then be removed by the laser plasma shock wave (LPSW). The properties of the laser plasma will undoubtedly influence the effective removal of particles.[8–10] In view of the important role played by laser plasma, we investigate the effects of plasma radiation on the removal of nano-particles and the pressure distribution of the shock wave due to laser plasma. The laser utilized in our research is a nanosecond pulsed Nd:YAG laser with a wavelength of 1064 nm. The optimum parameters to remove particles are pursued.

2. Experiment and result

A Q-switched pulsed laser (Quanta Ray, GCR) of 8 ns (FWHM, the full-width half-maximum) at 1064 nm is employed in our experiments and the fluctuation of energy is $\sim 3\%$. The laser beam is focused through a lens with a focal length of 5 cm onto a position that is a gap away from the silicon surface, and the gap is tunable. The laser plasma due to the breakdown of air by the laser beam is ignited, the spectra was monitored by a fiber grating spectrometer (1300 mm, focal length 25 cm, working wavelength 250–800 nm), as illustrated in Fig. 1.

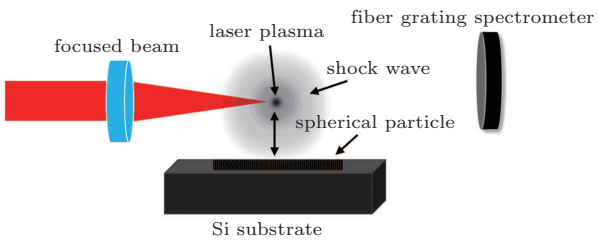


Fig. 1. (color online) Experiment setup.

The influence of the laser pulse energy and the gap on the dry laser cleaning are investigated. The particles on the silicon surface are formed by the deposition of laser ablation, and the morphologies of the test area are captured using SEM. To ensure good cleaning, 12 pulses are shot at the same location and

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the laser pulses frequency is 3 Hz. The test area morphologies before and after LPSW cleaning with different gaps and laser pulse energies are shown in Figs. 2 and 3 respectively.

In Fig. 2(a), the maximum particle size on the silicon before cleaning is about 220 nm, and the sizes of most particles are 10–30 nm. With a laser pulse energy of 0.5 J and a gap of 5 mm, the large particles above 100 nm are removed and most of the particles below 50 nm are left, as shown in Fig. 2(b), which is in sharp contrast with the case when the gap is 3.5 mm. As shown in Fig. 2(c), almost all of the particles, except for the very few particles below 10 nm, are removed from the surface.

The removal of particles from the silicon surface is studied with a gap of 3 mm at different laser pulse energies. The surface of the silicon before cleaning, which is presented in Fig. 3(a), shows that 10–30 nm particles are distributed uniformly on the silicon surface, with a few larger particles about 700 nm. Over half of the particles, especially the particles larger than 50 nm, have been removed from the surface with a laser pulse energy of 0.2 J. A complete removal of all of the particles can be achieved at a higher energy of 0.4 J.

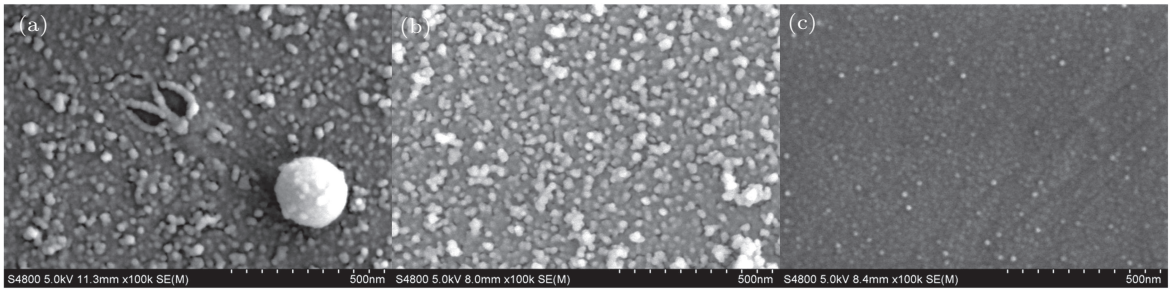


Fig. 2. Morphologies of silicon surface with particles before cleaning (a) and after cleaning with a laser pulse energy of 0.5 J, and a gap of 5 mm (b) and 3.5 mm (c).

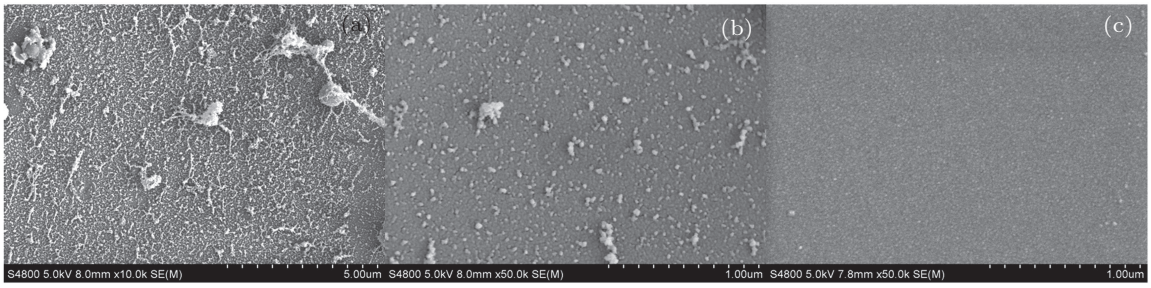


Fig. 3. Morphologies of silicon surface with particles before cleaning (a) and after cleaning with a gap of 3 mm, and a laser pulse energy of 0.2 J (b) and 0.4 J (c).

These results indicate that the cleaning effectiveness may be dependent on the size of the particles to be removed as well as on the laser pulse energy and the gap. Based on these experiment results, the particle removal mechanisms of LPSW and the expansion of a shock wave are discussed theoretically.

3. The effects of laser plasma radiation

3.1. The influence on the particles' adhesion force

The forces responsible for particle adhesion on a dry surface include the Van der Waals force, capillary force, and electrostatic force. For particles smaller than 50 μm, the predominant adhesion force is the Van der Waals force.[6] The adhesion force can be influenced by the absorption of the laser plasma irradiant. The temperature rises of the particles and the silicon substrate will be different because of their different heat absorption and expansion coefficients, which result in different thermal expansions. This allows us to remove the particles from a silicon surface. The absorption depends on the material's properties and the laser plasma, which can be shown by the absorption spectra. The absorption spectrum of silicon that is shown in Fig. 4(a) indicates that the absorptivity of silicon is closely dependent on the laser's wavelength. The light will be almost absorbed for a wavelength of < 900 nm. The spectrum of a laser plasma is generally wider than that of an incident laser, so it is more efficient to remove particles using laser plasma than by using the laser itself. The different expansions due to different absorptions of the silicon substrate and the contaminant particles allow us to more readily remove the particles. A typical laser plasma spectrum is presented in Fig. 4(b).

Figure 4(b) demonstrates two distinct features of the spectra. One is the continuous wide spectra, and the other is the

discontinuous spectra consisting of many spikes. The continuous wide spectra, which is referred to as bremsstrahlung, results from the transition of higher energetic free electrons to lower energy state.[11,12] The spikes are due to the selective transitions between certain levels of energy states, which are characteristic of chemical elements. These two kinds of transition will decrease the energy of a laser plasma. The plasma spectra is rather wide, from infrared (IR) to ultraviolet (UV), and the main part ranges from 350 nm to 650 nm, which is absorbed well by the silicon. This will be instrumental in removing the particles from the silicon substrate.[13,14]

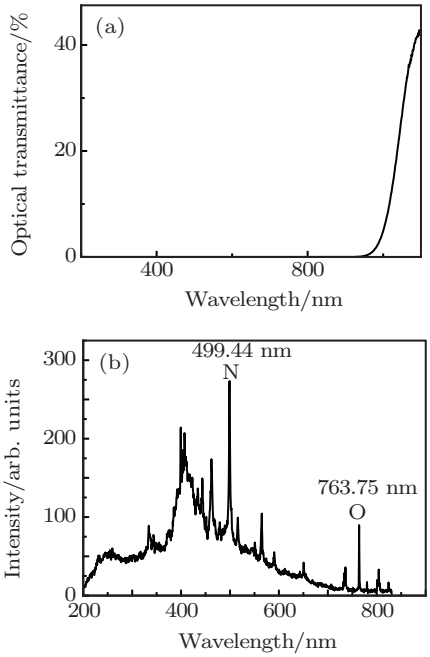


Fig. 4. The spectral characteristic of the silicon and the laser plasma radiation. (a) The transmittance spectra of silicon, (b) the emission spectra of laser plasma.

3.2. Ionization effect of radiation light on the particles

The particles can be ionized and vaporized by absorbing the radiation of the laser plasma, which also facilitates the removal of the particles. The particles' electronic band properties rely on their size, based on the quantum size effect. Particles of a different size will possess different energy levels. The wide spectra of laser plasma are able to ionize particles of various sizes because different wavelengths of light will be absorbed by particles of different sizes. So the laser plasma is helpful in removing particles with various sizes. On the other hand, shorter-wavelength light has a greater capability to ionize particles and the radiation of laser plasma mostly lies within the visible spectra.[13,15] Thus, the laser plasma will ionize and vaporize the particles more easily than incident laser beam (1064 nm).[16]

4. The effects of a laser plasma shock wave

4.1. The particle removal mechanism

The LPSW particle removal mechanism can be divided into sliding and rolling. Sliding happens when the shock wave force overcomes the adhesion force between a particle and a surface, while rolling is based on the action of an impact moment from a shock wave.[6] The sliding and rolling models are illustrated in Fig. 5.

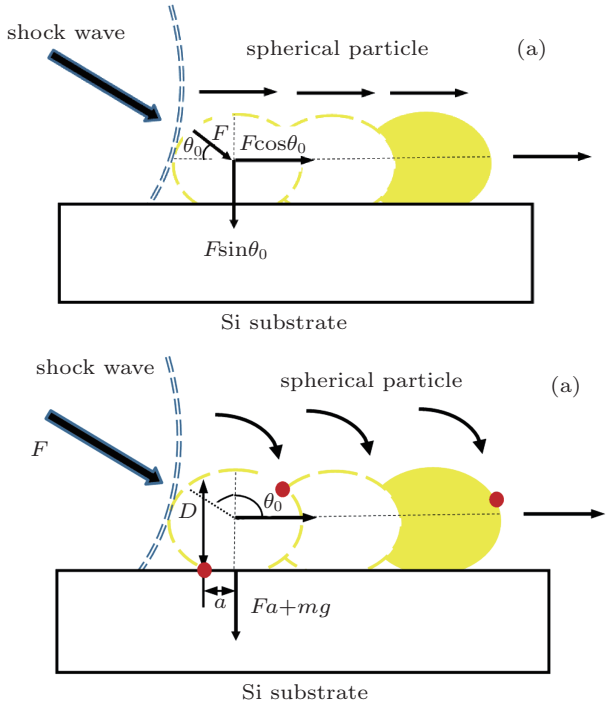


Fig. 5. (color online) Illustration of LPSW particle removal. (a) Sliding model. (b) Rolling model.

As for the sliding mechanism, the Van der Waals force plays a pivotal role in the adhesion of particles onto a surface.[17] The Van der Waals force between a sphere and a plane can be formulated as

$$F_{\mathrm{v}} = \frac{hR}{8\pi Z^2} + \frac{ha^2}{8\pi Z^3}, \tag{1}$$

where h is the material-dependent Lifshitz–Van der Waals constant, R is the particle radius, a is the radius of the adhesion surface area, and Z is the atomic separation between the substrate surface and the bottom surface of the particle, respectively. Hence, a pressure necessary to remove the particle is

$$\begin{aligned} P_{\mathrm{sliding}} &= F_{\mathrm{v}}/S = \left(\frac{hR}{8\pi Z^2} + \frac{ha^2}{8\pi Z^3}\right) \Big/ R \\ &= \frac{h}{8\pi^2 Z^2 R} + \frac{ha^2}{8\pi^2 Z^3 R^2}. \end{aligned} \tag{2}$$

In the process of rolling removal of particles, the moment of resistance comes from the particle's gravity and the adhesion between a particle and the substrate. Based on the

Johnson–Kendall–Roberts (JKR) model, the resistance can be describe as $F_A = \frac{3}{2}\pi W_A R$, where $W_A$is the work of adhesion and given by $W_A = 2.02 \times 10^{-2}$ J·m^{-2} under room conditions.[6]

Applying moment balance at point O, the critical pressure required for rolling removal of the particle can be obtained as

$$P_{\text{Rolling}} = \frac{a(F_A + mg)}{A_s(R|\cos\theta| - a\sin\theta)}, \tag{3}$$

where A_s is the hemispherical area (effective area) normal to the pressure of LPSW, mg is the gravity of particle, which is much lower than the adhesion for nanoparticles and can be neglected, and θ is the angle between the force of LPSW and substrate.[6]

It is clear that the critical pressures required to remove the particles in the sliding and rolling models are closely related to the size of the particles. Let h be 8.5 eV, Z be 0.4 nm, and a be 5% of the particle radius. Then the critical pressures for sliding and rolling model can be achieved according to the Eqs. (2) and (3), as shown in Fig. 6.

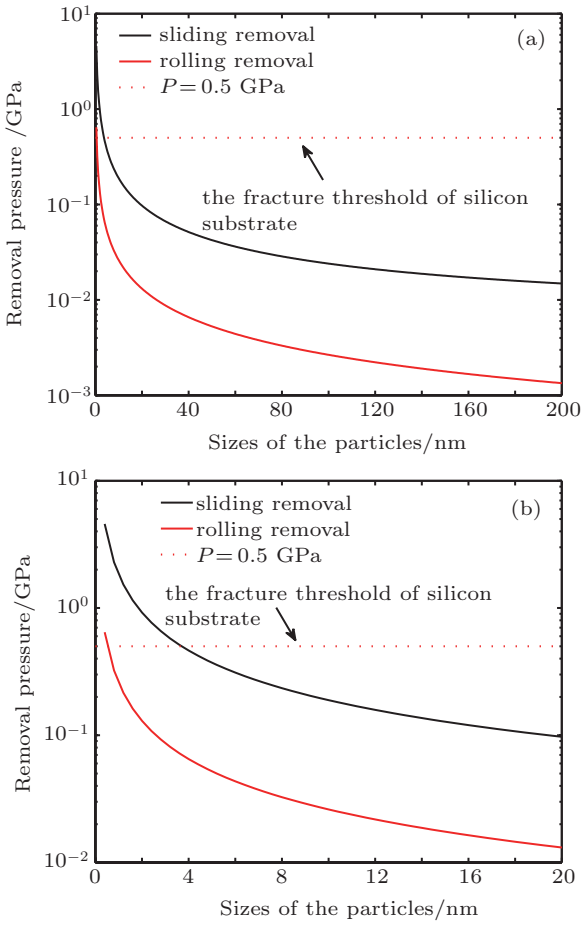


Fig. 6. (color online) The critical pressure required for particles with a size within 200 nm (a) and 20 nm (b).

Figure 6 shows that the critical pressure increases with the decrease in particle size, indicating that smaller particles are much more difficult to remove. In particular, for particles smaller than 20 nm, the pressure soars to 0.1 GPa and 0.01 GPa for sliding and rolling model, respectively. For particles of the same size, the rolling model has much lower critical pressure — sometimes by an order of magnitude — than the sliding model, so the dominant removal mechanism is assumed to be rolling. As an effective cleaning technique, it is required that the particles on a surface are removed without causing damage to the substrate. So the fracture threshold of substrate determines the maximum removal pressure, which corresponds to the minimum particle size. For the silicon substrate, the fracture threshold is about 0.5 GPa.[18] Thus the corresponding minimum particles that can be removed should be 0.5 nm for the rolling model and 4 nm for the sliding model.

4.2. The laser plasma's spatial distribution

The pressure of a laser plasma will affect the removal of particles. The plasma is ignited once the air at the focus is broken down by the laser beam. The energy of successive pulses is absorbed strongly by the plasma and the plasma is heated. As a result, the plasma extends outwards rapidly, and then the shock wave is generated and exploded. Ignoring the radiation loss, the pressure of plasma is described as[19]

$$R(t) = A\left(\frac{Q}{\rho_0}\right)^{1/5} t^{2/5}, \tag{4}$$

$$u(t) = \frac{2}{5}A\left(\frac{Q}{\rho_0}\right)^{1/5} t^{-3/5}, \tag{5}$$

$$p = \frac{\rho_0 u^2}{\gamma + 1}, \tag{6}$$

where Q is the energy deposition, R the radius of shock wave, t the time, $A \sim 0.98$, u the velocity of wave front. The density of plasma ρ_0 and the adiabatic coefficient γ can be set as 1.3 kg/m^3 and 4/3 respectively, when the plasma is approximated as an ideal gas. The absorptivity of the laser plasma can be taken to be 0.85.[20] Then the wave front of the plasma can be modeled as shown in Fig. 7, where the time interval is 20 ns.

As shown in Fig. 7(a), when the shock wave of a laser plasma expands outside from the focus point, the expansion distance in the same time interval decreases gradually, which means that the highest velocity exists at the center of the plasma and stably slows down with the time, as shown in Fig. 7(b). The velocity of the shock wave is also determined by the energy deposition of the laser pulse. The larger the energy deposition is, the higher velocity the shock wave has, as shown in Fig. 7(c). Generally, the duration of laser plasma is about 2 μs.[19] So the propagation distance of the shock wave is limited. The maximum distance of laser pulse energy is simulated in Fig. 7(d).

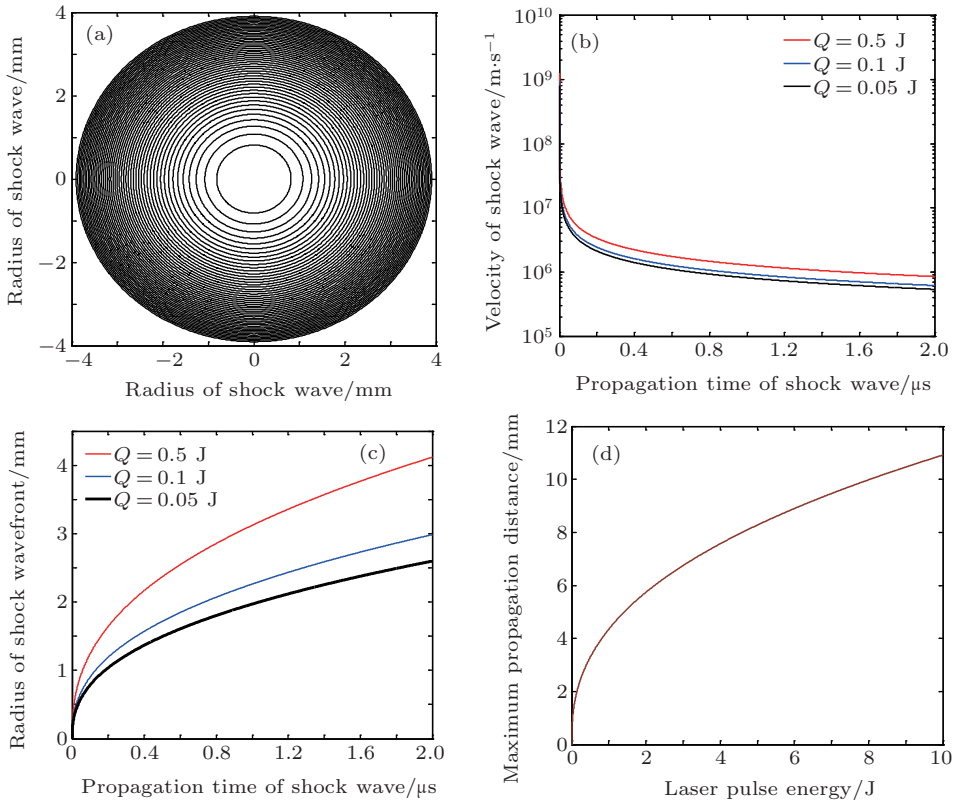


Fig. 7. (color online) The expansion of a laser plasma shock wave. (a) The radius of the shock wave front. (b) The velocity of shock wave versus time. (c) Expansion distance versus time. (d) The maximum expansion distance versus the energy of the laser pulse.

4.3. The working conditions for particle removal

The critical pressures for particles are determined by the size of the particles and the properties of the substrate surface. In other words, the force provided by the shock wave must reach the critical pressure for particles with the specific size.[21,22] The pressure of the shock wave is closely related to the expansion time and distance. So, in order to get the working condition for particles removal, the temporal and spatial characteristics of the pressure must be obtained based on Eqs. (4)–(6). The simulation results are demonstrated in Fig. 8.

Figure 8(a) shows that the pressure of the shock wave decreases with time. For a shock wave from a laser pulse with a higher energy deposition, the expansion time is longer, which corresponds to a longer expansion distance, as shown in Fig. 8(b). For particles with a specific size and removal pressure, we can get the corresponding force from shock wave by changing the laser pulse energy and expansion distance. In this way, the working conditions for particle removal can be obtained.

Figure 9 shows that for particles with a specific size, the working conditions can be achieved by selecting the laser pulse energy, and the gap between the focus of laser and the substrate. Due to the limited duration of a shock wave, the selection of laser parameters cannot exceed the maximum propagation distance of the shock wave. This limited condition can be used to explain the low removal rate of Fig. 2(b) in the experiment. For a laser pulse energy 0.5 J, the maximum propagation distance is about 4 mm. So for a gap of 5 mm, the

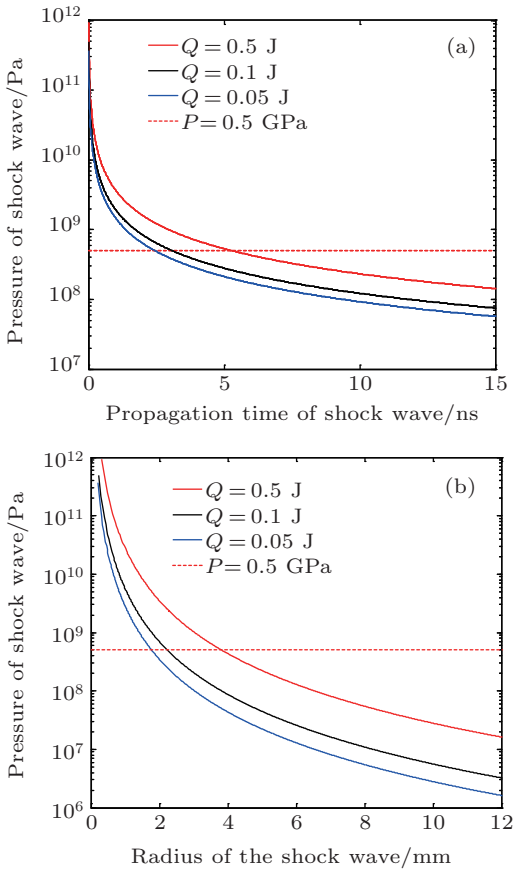


Fig. 8. (color online) The temporal (a) and spatial (b) distributions of pressure from a shock wave.

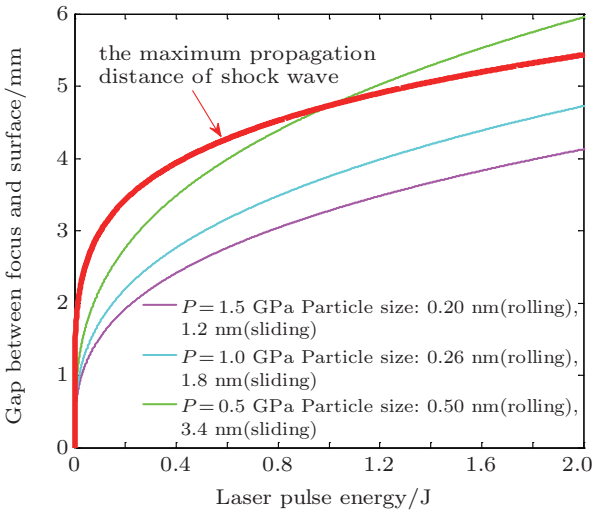


Fig. 9. (color online) The working conditions of particles removal.

shock wave has bad action effects.

In experiment, the breakdown threshold of air is about 0.08 J, so a laser pulse energy lower than 0.08 J cannot be taken into account. Considering the ionization effects and shock wave effects due to laser plasma, the focus of the laser cannot approach infinitely to the substrate surface, or the laser will easily cause damage. The gap should be longer than 0.5 mm. For complex influence factors, the actual size of the removal particle is larger than the theoretical prediction. However, they are expected to have the same order of magnitude, which offers a primary point of reference for actual operation.

5. Conclusion

Laser-induced plasma has shown increasing potential in removing micro-/nano-particles stuck onto the surface of precise components in nano-science and nano-technology. In our work, the mechanism of a technique to clean a silicon surface is elucidated in depth and thus the optimized conditions for laser plasma to flush the silicon surface is recommended. The results indicate that the visible light radiated from a laser plasma, in particular UV light, can be absorbed greatly by the contaminant particles and this will then heat the particles. Because of the difference in heat absorption between the particles and the silicon substrate, and therefore the different temperature and expansion coefficients, the particles can more readily be detached from the substrate. Furthermore, the Van der Waals force through which the particles are attached onto the substrate surface is balanced by the pressure of the shock wave from an expanding laser plasma, allowing us to more easily remove the particles by sliding or rolling. The removal pressure is related to the size of the particle. In general, the larger a particle is, the greater the pressure necessary to remove the particle will be. On the other hand, the pressure of laser plasma diminishes with propagation distance, so the substrates should be close to the laser plasma. But as the distance between plasma and the silicon surface decreases, the possibility of damage to the silicon substrate may rise owing to the extreme pressure of the plasma. Thus, in practice the right balance should be sought between particle removal and the maintenance of an undamaged substrate.

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