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Laser removal of oxides and particles from copper surfaces for microelectronic fabrication

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Abstract: Laser removal of surface oxides and small particles from copper surfaces is carried out using a Q-switched Nd:YAG radiation. The oxides and the small particles on copper surfaces should be removed for the improvement of solder quality on printed circuit boards (PCBs) and for the prevention of the circuit failure or loss of production yield during the fabrication of microelectronic devices. A selective removal of surface oxides from copper surface was achieved by the laser treatment, which can be confirmed by on-line acoustic monitoring of the process. Angular laser cleaning technique in which the laser irradiates a surface at a glancing angle was used for effective removal of the particles from the surface. The unique characteristics of this technique and the cleaning mechanism are discussed.

OCIS codes: (140.3390) Laser materials processing; (120.4610) Optical fabrication

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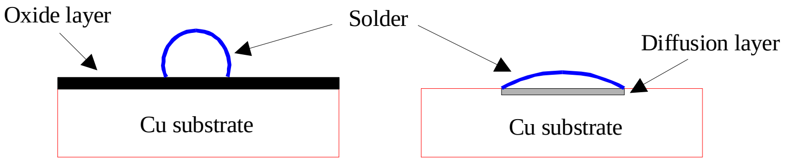
1. Introduction

Laser surface cleaning has attracted a considerable amount of interest recently as a new revolutionary technique to replace conventional cleaning methods such as wet chemicals employing solvents and mechanical cleaning involving air abrasive, scrubbing. Laser offers many advantages as a soft and environment-friendly cleaning tool since it is a non-contact and dry process. This unique process has been finding successful applications in industry, which include the removal of adherent particles from semiconductors [1], various contaminants from magnetic media surfaces [2], ablation debris from laser-etched vias [3], contaminants from astronomical telescope mirror [4], cleaning of moulds in the manufacturing of tyres [5] and paint stripping of aircraft [6]. In all its applications, a successful cleaning is defined as complete removal of the surface contamination while there is minimal damage to the underlying substrate material. Since laser cleaning is a physical process which is applied under conditions in which there is a strictly limited interaction with the substrate material, the procedure is more effective, more controllable and more flexible than conventional cleaning methods based on chemical and mechanical actions [7,8].

In this paper, laser techniques for the removal of surface oxides and small particles from copper surfaces are described for the applications of microelectronic device fabrication. The feasibility of selective removal of copper oxides from a copper printed circuit board was also investigated by acoustic monitoring. Laser irradiation to the surface at a glancing angle called "angular laser cleaning" was found to be very effective for the removal of small particles from a metal surface and compared to typical laser cleaning employing a perpendicular angle of incidence. The cleaning mechanism is discussed by considering laser-matter interactions and laser-induced cleaning forces during the process.

2. Laser removal of copper oxides

The process of removing the oxide layers from copper printed circuit board (PCB) is advantageous in the electronics industry in obtaining a good quality soldered joint with high bond strength by improving the surface wetability [9]. The soldering features before and after cleaning the surface are illustrated in Fig. 1. Normally, most portion of the copper surface is composed of copper oxides. These copper oxide layers should be removed in order to achieve good quality solders. Currently, acids in flux are used to clean the oxide layers from the PCBs. However the use of acids causes many problems, of which the environmental impact of discarding the flux after use. It is also difficult to use flux when it is necessary to solder complex structures or modules that cannot tolerate solvents and thermal stress. Furthermore, it is expected that European legislation will limit the use of fluxes in soldering. Substituting this traditional method with a laser process would overcome those problems in an environment-friendly way and offer the added advantages of easy automation and incorporation into existing laser soldering processes.



(a) before cleaning **(b) after cleaning**

Fig. 1. Soldering features before and after cleaning the surface

In order to prepare oxidised copper samples artificially, the plates of copper foil were baked in oven at 250 ^{o}C for 20 min when the colour of the samples has been changed from shiny surface to dark brown which is similar to that of severely oxidised printed circuit board.

The removal of copper oxides from a copper surface was carried out using a Q-switched Nd:YAG laser (a Paragon 2XL laser from Lynton Lasers) having a wavelength of 1064 nm, a pulse length of around 10 nsec and multi-mode cylindrical optics which produced a non-Gaussian beam with a ‘top-hat’ shape.

Fig. 2 shows the laser craters on the oxidised copper surface with the sequence of the number of laser pulses with a fluence of 3.5 J/cm^2. The first crater at the right end is the crater produced by one laser pulse, the second by two laser pulses etc., up to four laser pulses. It is shown that after one laser pulse the brown oxidised copper surface was changed to a dark black colour. This might be caused by further oxidation of the Cu_2O to CuO [10]. Two laser pulses revealed a well-cleaned and shiny copper surface, which was confirmed by SIMS (Secondary Ion Mass Spectroscopy). The laser crater was not significantly changed by further laser pulses.

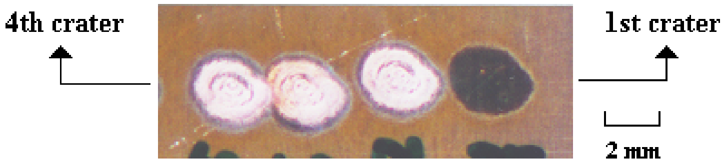


Fig. 2. Laser craters on an oxidised copper surface with the sequence of the number of laser pulses with 3.5 J/cm^2 at 1064 nm

2.1 On-line monitoring of the process

In order to correlate between surface conditions and acoustic emission during the removal of copper oxides, the same laser parameters are used as those in Fig. 2. The acoustic waves were detected by a wide-band microphone with a frequency response of 10 Hz – 15 kHz placing 10 cm away from the laser spot.

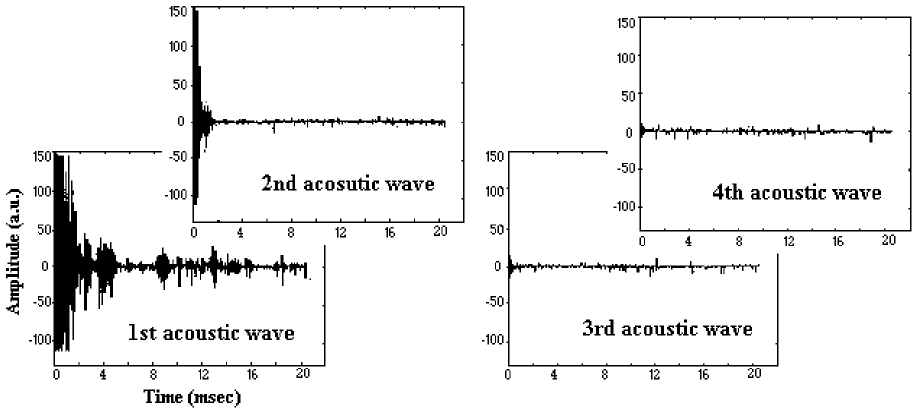


Fig. 3. Acoustic waves emitted from an oxidised copper substrate under laser irradiation from the 1st to 4th pulse respectively

Fig. 3 shows the acoustic waves emitted from an oxidised copper substrate under the laser irradiation from the first (a) to the fourth (d) pulse respectively on the same spot. When the first laser pulse is irradiated on the surface, a very strong acoustic wave is observed. This strong acoustic wave implies that the surface was contaminated with copper oxides and the laser pulse interacted strongly with the surface oxides. Due to the short laser pulse length (10 nsec), the acoustic wave emission is especially strong in the initial time period and decays rapidly. When the second laser pulse is applied on the surface, the overall signal intensity decreases although initial intensity is still large. This implies that surface oxides remain after the irradiation of the first laser pulse. The acoustic wave induced by the third laser pulse decreased drastically and became quite small. This very weak intensity implies that there are little oxides to interact with laser pulse on the surface. When the fourth laser pulse was applied, the acoustic waveform does not change any more. From these results, acoustic emission provides a clear indication of different levels of surface cleanliness, i.e. heavy oxide, slight oxide and clean surface.

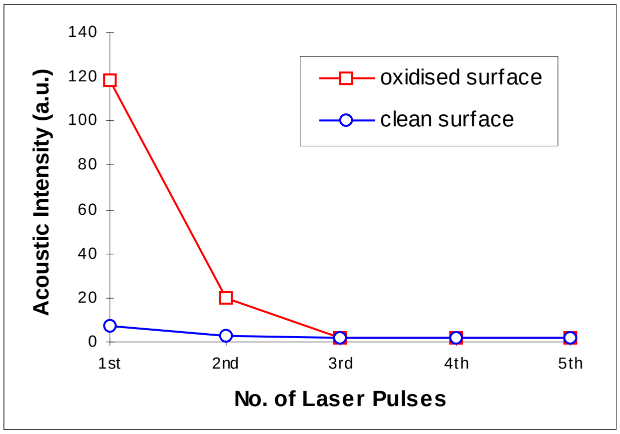


Fig. 4. Acoustic emission intensity as a function of the number of laser pulses from an oxidised copper surface and a clean (non-oxidised) copper surface

In order to understand clearly the change of the acoustic spectra with the number of laser pulses, overall acoustic emission intensity was obtained by calculating the mean signal strength. Fig. 4 shows the acoustic emission intensity as a function of the number of laser pulses in the laser cleaning of an oxidised copper surface and a clean (non-oxidised) copper surface in the laser fluence of 3.5 J/cm^2. In the cleaning of the oxidised copper surface, very strong acoustic shock waves were observed which decreased with subsequent pulses until the third acoustic pulse after which the signal did not change and had a value similar to clean copper. Meanwhile, there is no obvious change of the intensity arising from a clean copper surface. The curves in Fig. 4 demonstrate the selective removal of copper oxides from the surface. It is clear that strong absorption and interaction between the laser and the oxides leads to the generation of plasma and the ejection of sufficient oxide particles creating a intense acoustic shock wave in the air. Once the oxides have been removed and the underlying shiny copper surface exposed the acoustic shock wave is diminished or fails to occur and the signal does not change with further laser pulses. From these results, it is seen that acoustic emission intensity can give a criterion of the surface cleanliness for surface monitoring during laser cleaning of copper. This monitoring system may be also utilised to control the laser cleaning process in real-time.

3. Laser removal of small copper particles

Copper is known to be one of the important particles to remove from the surface of semiconductors and microelectronic devices where it can destroy the integrity of the gate oxide, create leakage currents and induce surface defects such as roughening [11]. Normally, the material used in the microelectronic industry for the production of electrical contacts for semiconductors and for high current transmission contacts is high quality copper. The substrate used in this experiment was high purity copper foil (Cu > 99.9 %). The copper particles were introduced by coating the copper substrate with an ethanol suspension of the particles. The substrate was left in air for a few hours to evaporate the ethanol. A strong hot air jet from a heat gun was then applied to ensure the complete evaporation of the ethanol as well as to remove all the loose particles.

The removal of small copper particles (~ tens of µm diameter) from a copper substrate surface was carried out using a visible laser radiation (532 nm) generated by frequency doubling of a fundamental Nd:YAG wavelength of 1064 nm. The laser has a pulse length of 10 nsec and a beam shape of near Gaussian profile.

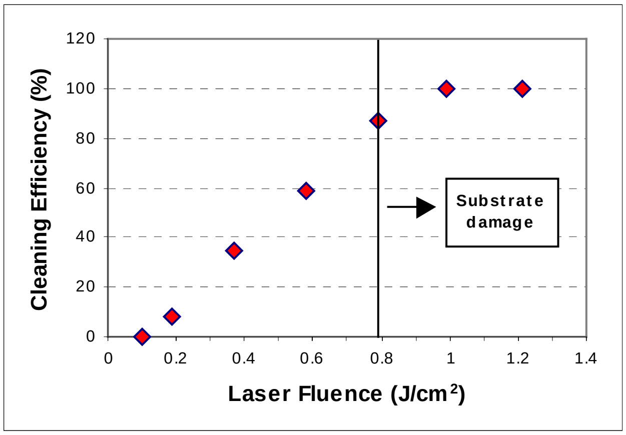


Fig. 5. Laser cleaning efficiency as a function of the laser fluence

Fig. 5 shows the laser cleaning efficiency as a function of the laser fluence. The cleaning efficiency is calculated by dividing the actual cleaned area by the laser spot area after irradiation by 10 laser pulses on the same spot (100% means that the laser-cleaned area is equal to the laser irradiated spot on the surface). It is seen that there is a threshold laser fluence for the removal of the copper particle of around 0.15 J/cm^2 and that the laser cleaning efficiency increases uniformly with increasing the laser fluence reaching 100 % at a fluence of 1.0 J/cm^2. However it was found that substrate damage was induced at around 0.8 J/cm^2. This implies that complete removal (100%) of the copper particles from the surface is difficult to achieve without causing some copper substrate damage. Fig. 6 shows the copper surface after the laser treatment at 1.0 J/cm^2, where the visible substrate damage is shown in the middle of the laser-cleaned area. This might be the result of the higher energy density in the middle of the Gaussian laser beam.

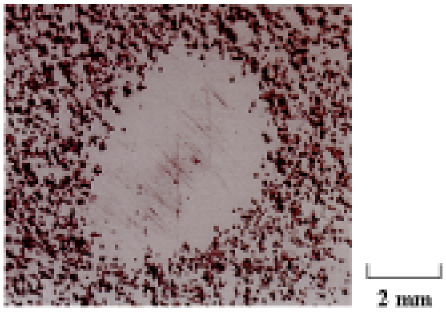


Fig. 6. Copper surface morphology after 10 laser pulses at 1.0 J/cm^2

3.1 Angular irradiation technique

A serious problem for laser removal of the copper particles is substrate damage as shown in Fig. 6. In order to tackle this problem the laser irradiates a surface at a glancing angle in contrast with typical laser cleaning using a perpendicular angle of incidence. The illustration of the angular laser cleaning technique is shown schematically in Fig. 7 where the beam directed to the surface at two different angles, i.e. one is perpendicular to the surface ($\theta = 90^o$) as for typical laser cleaning and the other is nearly parallel to the surface with a glancing angle ($\theta = 10^o$).

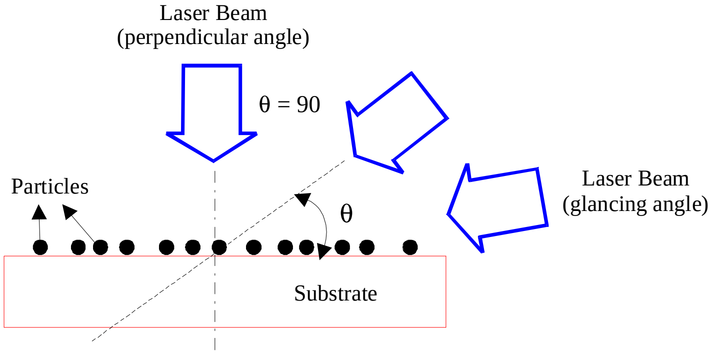


Fig. 7. Illustration of angular laser cleaning

The effect of angle of laser incidence on the copper surface is shown in Fig. 8. The cleaned surfaces were achieved after 10 laser pulses with a pulse energy of 0.14 J. It is shown interestingly that the laser-cleaned area at the glancing angle of 10^o is around ten times larger than that at the perpendicular angle of 90^o, i.e. the cleaned areas at 10^o and 90^o are 1.35 cm^2 and 0.13 cm^2 respectively. This implies that the cleaning efficiency in term of area is much larger at the glancing angle. Thus this new technique offers an advantage in speed of cleaning large areas.

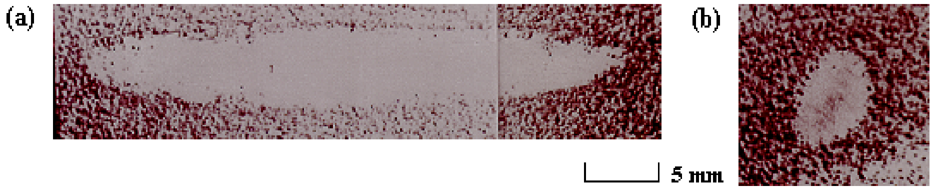


Fig. 8. Copper surfaces after 10 laser pulses at 0.14 J for (a) the glancing angle of 10^o and (b) the perpendicular angle of 90^o

Fig. 9 shows the laser cleaning efficiency as a function of the laser fluence at the glancing angle of 10^o to the surface after 10 laser pulses. It is shown that the laser cleaning efficiency uniformly increases with increasing laser fluence. Interestingly, the efficiency can reach over 100 % above 0.08 J/cm^2 e.g. 130 % at 0.15 J/cm^2. This implies that the laser-cleaned area is larger than the laser-irradiated area for the laser fluence above a certain value when operating at glancing angles. It is also seen that the threshold laser fluence at the glancing angle is around 0.01 J/cm^2, which is one order of magnitude smaller than for the perpendicular angle (0.15 J/cm^2). Thus laser cleaning at a glancing angle is much more efficient in terms of energy and can remove the particles from the surface more easily and effectively without causing any substrate damage.

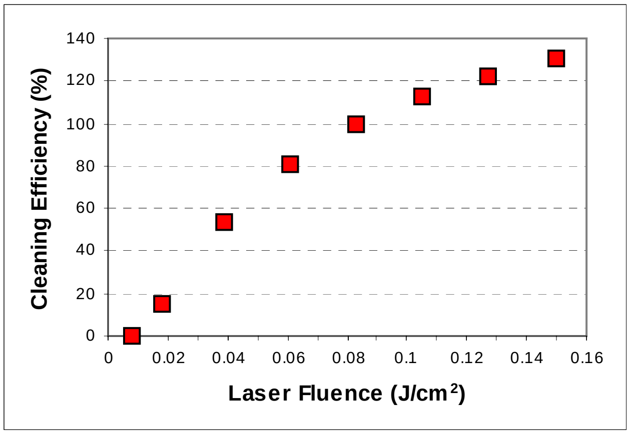


Fig. 9. Laser cleaning efficiency as a function of the laser fluence at the glancing angle of incidence

3.2 The process mechanism

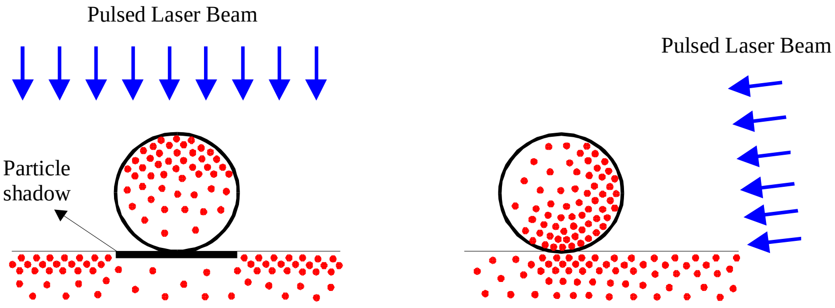
The predominant adhesion force of tiny particles smaller than 50 μm on a dry surface is due to Van der Waals force [12]. The adhesion force, F_a, for a spherical particle on a flat substrate surface with a certain deformation at the particle-substrate interface is given by [12]

$$F_a = \frac{h\,r}{8\pi Z^2} + \frac{h\,r_a^2}{8\pi Z^3} \tag{1}$$

where h is the material-dependent Lifshitz-Van der Waals constant, r is the particle radius, r_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. The Lifshitz-Van der Waals constant, h, for a copper particle on a copper substrate is 8.5 eV [12], which corresponds to 13.6×10^{-19} J. For Van der Waals bonded crystals, Z is approximately equal to 4 Å [12]. Assuming that the diameter of the copper particle is 10 μm and the diameter of adhesion area between a copper particle and a copper substrate is 5 % of particle diameter, then r, r_a are 5.0×10^{-4} cm and 0.25×10^{-4} cm respectively. From Eq. (1) and the above values, the adhesion force between the copper particle and the copper substrate is approximately 5.5 dyne.

The predominant cleaning force for the removal of small particles from a substrate surface is known to be a thermo-elastic force [13,14]. This force is caused by the rapid thermal expansion of the particle and the substrate resulting from the absorption of the laser radiation on the surface. If a laser pulse with a pulse length of t_p is absorbed on the particle and the substrate, then a temperature rise (ΔT) at the interface between the particle and the substrate surface is induced. The incident angle of the laser beam makes a geometrically difference in the laser absorption on the surfaces of the particle and the substrate and thus produces a different temperature rise at the interface. This is schematically illustrated in Fig. 10 for the perpendicular angle (a) and the glancing angle (b). It is clearly seen that at the glancing angle direct absorption at the interface between particles and substrate is possible. This absorption can be enhanced by multiple reflections and the increased absorption for polarisation in the plane of laser incidence. However at the perpendicular angle, the temperature rise at the interface is restricted by the absorption on the top surface of the particle and the particle induced shadow on the substrate, as shown in Fig. 10 (a).

If it is assumed that the particle is plate-like and most of the laser radiation is effectively absorbed at the interface at the glancing angle as shown in Fig. 10 (b), the temperature rise at the interface can be simply estimated by a one-dimensional heat equation and be compared for the two different incident angles. The laser absorptivity for copper at the wavelength of 532 nm is 0.38 [15] and the pulse length (t_p) of laser used in this work was 10 nsec. It is assumed that the particle size was 10 μm and the laser absorptivity increased to 0.8 at glancing angles of incidence. Consequently, the temperature rise for the perpendicular angle was estimated to be approximately 10 ^{o}C at the particle-substrate interface (≅ the depth of 10 μm from the surface) for a laser fluence of 0.1 J/cm^2 while the rise for the glancing angle case was around 240 ^{o}C at the interface. This is a significant difference.



(a) Perpendicular angle of incidence **(b) Glancing angle of incidence**

Fig. 10. Illustration of the laser absorption on the surfaces of the particle and the substrate for different laser incident angles (The density of “dots” indicates the amount of heating due to the laser absorption on the surfaces)

The normal expansion of the surface (Δl) due to the temperature rise (ΔT) is given by [13]

$$\Delta l \quad = \quad \alpha\,\delta\,\Delta T \qquad (2)$$

where α is the thermal expansion coefficient and δ is thermal diffusion length during the laser pulse. Inserting both the estimated temperature rises and the following typical numerical values for copper: $\alpha = 17.0\times10^{-6}$ K^{-1}, $\delta = 2.1\times10^{-4}$ cm [16], the expansion amplitudes (Δl) are estimated from Eq. (2) as 3.6×10^{-8} cm and 8.6×10^{-7} cm for the perpendicular and the glancing angle respectively. If the expansion is achieved during the pulse duration of 10 nsec, the acceleration at the interface, a, resulting from the thermal expansion is approximately given by

$$a \quad = \quad \frac{\Delta l}{t_p^{\,2}} \qquad (3)$$

From the Eq. (3) the accelerations at the interface are 3.6×10^{8} cm/s^2 and 8.6×10^{9} cm/s^2 for the perpendicular and the glancing angle respectively. Consequently, the thermo-elastic force, F, exerted at the interface is given by

$$F \quad = \quad m\,a \qquad (4)$$

where m is the mass of the copper particle, which can be calculated by $\rho\times V$: ρ (density) = 8.96 g/cm^3 [16], V (particle volume) = 5.24×10^{-10} cm^3. The resulting thermo-elastic forces at the particle-substrate interface for perpendicular and glancing angles are 1.7 dyne and 40.4 dyne respectively.

From these approximately calculated values both of adhesion force and cleaning force, it is seen that the thermo-elastic force at the glancing angle of laser incidence with a fluence of

0.1 J/cm^2 is much larger than the adhesion force between the copper particle and the substrate whereas the force at the perpendicular angle is smaller than the adhesion force. This implies that the cleaning force at 0.1 J/cm^2 and a glancing angle is high enough to break the adhesion bond thus detaching the particles from the surface; while the cleaning force at 0.1 J/cm^2 and a perpendicular angle is not high enough to break the bond and will need much higher laser fluence to exceed the adhesion force. From Fig. 5, the removal of copper particles from the copper substrate surface was impossible at 0.1 J/cm^2 since this is lower than the cleaning threshold of 0.15 J/cm^2 for a perpendicular angle of laser incidence. From Fig. 9, it was also shown that successful removal of the particles has been carried out at 0.1 J/cm^2 since this is much higher than the cleaning threshold of 0.01 J/cm^2 for a glancing angle of laser incidence. As a result, the process mechanism discussed above is appropriate to account for the effect of incident angle in laser cleaning.

4. Conclusions

Successful removal of surface oxides and small particles from copper surfaces was achieved by using a Q-switched Nd:YAG laser radiation. It was shown that the copper oxides could be removed selectively from the surface since more effective interactions between the laser and the oxide are induced due to its higher laser absorptivity. This was also demonstrated by acoustic monitoring. The acoustic emission was well consistent with the surface conditions so this can be used to monitor the surface cleanliness during the process. A dramatic improvement of cleaning efficiency in the removal of small particles from a copper surface has been found at the glancing angle of laser incidence to the surface. This angular cleaning technique provides much larger cleaned area and higher energy efficiency compared to the typical laser cleaning employing a perpendicular laser incidence, which offer advantages of high cleaning speed and safe cleaning of the surface without causing any substrate damage. The process mechanism has been described by considering the adhesion and the laser-induced cleaning forces for the different incident angles.