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Ultraviolet laser removal of small metallic particles from silicon wafers

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Abstract

Laser removal of small 1 μm sized copper, gold and tungsten particles from silicon wafer surfaces was carried out using ultraviolet radiation at 266 nm generated by Nd:YAG harmonic generation. Successful removal of both copper and gold particles from the surface was achieved whereas tungsten particles proved to be difficult to remove. The cleaning efficiency was increased with an increase of laser fluence. The optimum processing window for safe cleaning of the surface without any substrate damage was determined by measuring the damage threshold laser fluence on the silicon substrate and the required fluence for complete removal of the particles. The different cleaning efficiencies with particle type are discussed by considering the adhesion force of the particle on the surface and the laser-induced cleaning force for the three different particles. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Laser cleaning; Adhesion force; Cleaning force; Particle removal

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1. Introduction

There proves to be a continual need to develop effective techniques for the removal of small particles in the semiconductor industry. As semiconductor and microelectronic devices are becoming increasingly smaller, surface contamination of these devices is becoming an increasing problem for manufacturers due to the adverse effects that micron and submicron particles have on the device performance [1,2]. In some cases they act as a potential source of circuit failure, threatening

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production yield. For example, particles in the size of about 0.1 μm to several microns possibly deposited on surfaces from air, liquids and humans in the processing environment are considered to have killer defects for the generation of dynamic random access memory (DRAM) and microprocessors [2]. The use of wet-chemical techniques for particle removal poses environmental problems due to the vast quantities of water that are used and also the discard of the chemicals themselves. Moreover, the chemicals could prove hazardous to human health. Other conventional cleaning techniques such as wiping and scrubbing are often limited due to possible substrate damage caused by the mechanical action on the surface.

Recently, a non-contact dry laser cleaning technique, using a short-pulse (in the order of ns) laser irradiation on the surface, has been demonstrated as a potential solution for the removal of particles from critical surfaces [3–6]. This novel technique has the capacity to clean submicron particulates and has unique advantages over conventional methods. This approach utilises the versatile, controllable, selective and environmentally friendly nature of the laser system to optimum effect [7,8]. It is seen to be non-obtrusive in the production process since no vacuum or special protective atmospheres are required and the beam of the laser can be highly localised allowing specific areas of contamination to be targeted. These unique characteristics of laser cleaning have been demonstrating an effective removal of contaminants from various surfaces in industry [9–14].

In this paper the removal of small copper, gold and tungsten particles with a diameter of 1 μm from silicon wafers has been carried out using ultraviolet radiation of 266 nm. It is known that metal particles absorb more laser energy at shorter wavelengths and the thermal damage threshold fluence for silicon increases at shorter wavelengths. When both of the above are taken into consideration shorter wavelength lasers (UV lasers) are more effective for the removal of metallic particles from silicon wafers without inducing substrate damage. Thus the ultraviolet laser, with a wavelength of 266 nm, produced by frequency harmonic generation of the fundamental Nd:YAG radiation of 1064 nm was used in this work. Quantitative analysis was carried out in order to determine the fluence values that induced substrate damage to the silicon wafer at this wavelength and the threshold fluence values above which surface cleaning was observed were also found by surface analysis. The cleaning efficiency with laser fluence was measured for the different particles and compared with each other. In addition theoretical analysis was carried out for the different particle/substrate combinations in order to understand the effect of particle type in the laser cleaning process.

2. Experiments

One of the most important issues in the removal of metallic particles from semiconductors is preventing them from getting into the front-end processing where they could possibly destroy the integrity of the gate oxide and hence create leakage currents [1]. Surface defects could also be introduced such as roughening in the presence of the metal particles, moreover the particles can flake off the back of a wafer in solution leading to back-to-front-end contamination. In this work, the laser removal of 1 μm sized copper, gold and tungsten particles from silicon wafers was carried out. The wafer samples were coated with different spherical particles using a spinning slurry deposition technique (supplied by MATS UK).

A Q-switched Nd:YAG laser (a Paragon 2XL laser) was used as the cleaning source. The ultraviolet radiation was achieved by frequency quadrupling of the fundamental wavelength of 1064 nm after passing through a KTP ($KTiOPO_4$) crystal. The laser has a pulse length of 10 ns. The maximum pulse energy obtained was 50 mJ at 266 nm. This wavelength was used to remove the different particles from the silicon wafer by placing it on an X–Y stage. A particle counter software package was used to determine the number of particles present on the surface. The cleaning efficiency was achieved by determining the number of particles before and after the laser treatment.

3. Cleaning results

In order to determine the maximum laser fluence for successful removal of the different particles without causing substrate damage, the damage threshold fluence on pure silicon wafer was determined. This was ~0.70 J/cm^2 for 266 nm. From this result, it can be seen that cleaning trials should be carried out below this threshold value to avoid substrate damage.

Fig. 1 shows the silicon surfaces before and after laser removal of copper particles from the silicon wafer surface. Ten laser pulses with fluences of 0.16 and 0.20 J/cm^2

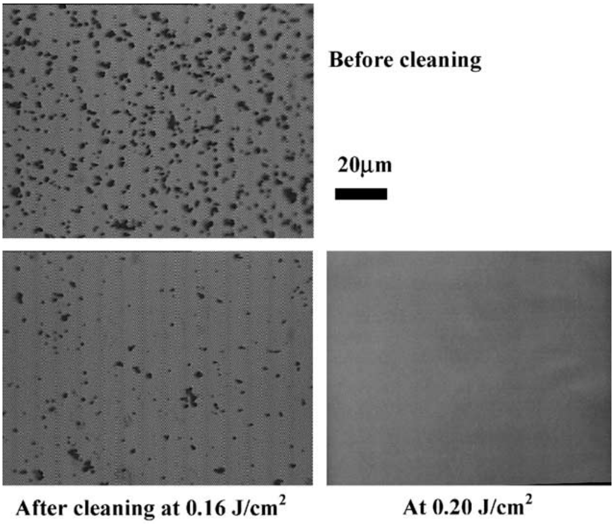
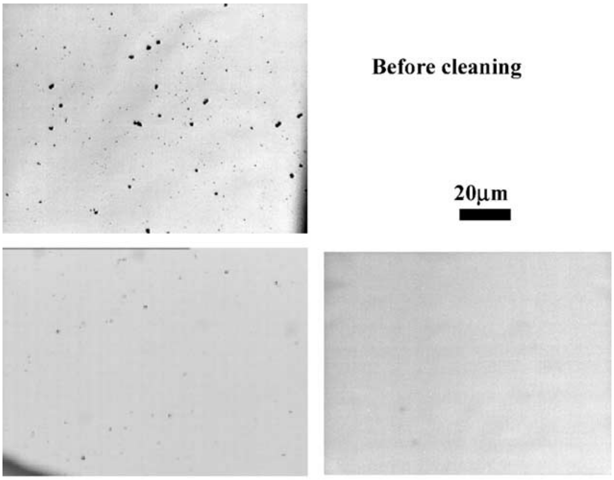


Fig. 1. Optical micrographs of copper particles on silicon wafer surfaces before and after laser with a wavelength of 266 nm: 10 laser pulses were used.

were used at 266 nm. It can clearly be seen that over half the particles have been removed at a fluence of 0.16 J/cm^2 and all particles appear to be removed from the surface at a slightly higher fluence of 0.20 J/cm^2. These fluence values are well below that of the damage threshold at 266 nm and no possible damage could have incurred on the surface during cleaning. This implies that effective energy coupling between the laser and the copper particles has been induced at 266 nm.

Fig. 2 shows the silicon surfaces before and after laser removal of gold particles from silicon wafer at 266 nm. Ten laser pulses with fluences of 0.05 and 0.08 J/cm^2 were used. It can be seen that a large number of particles were removed at the lower fluence of 0.05 J/cm^2 while a complete removal of all gold particles was achieved at the higher fluence of 0.08 J/cm^2, which is far below the damage threshold fluence. It was seen that successful removal of gold particles could also be achieved at 266 nm wavelength without introducing damage to the wafer. In addition a much smaller fluence was required for complete removal of gold than that for copper. This implies that there is more effective energy coupling between the laser and the gold particles than the copper particles.

Fig. 3 shows the silicon surfaces before and after laser removal of tungsten particles from silicon wafer at 266 nm. Ten laser pulses with a fluence of 0.65 J/cm^2 were used. It can be seen that very few particles were removed at the fluence just below the damage threshold fluence of the silicon substrate at 266 nm. This implies that successful removal of tungsten particles might be impossible without introducing damage on the substrate. It can be also deduced that the interactions between the laser and the tungsten particles is relatively weaker than that of the copper and gold particles.



After cleaning at 0.05 J/cm^2

At 0.08 J/cm^2

Fig. 2. Optical micrographs of gold particles on silicon wafer surfaces before and after laser with a wavelength of 266 nm: 10 laser pulses were used.

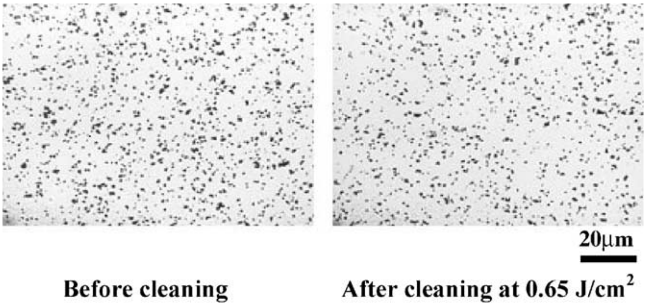


Fig. 3. Optical micrographs of tungsten particles on silicon wafer surfaces before and after laser with a wavelength of 266 nm: 10 laser pulses were used.

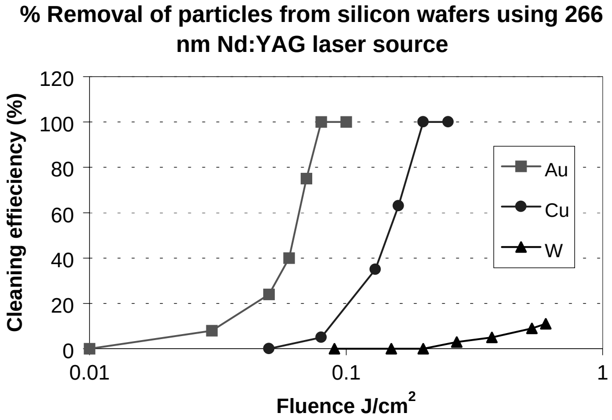


Fig. 4. Cleaning efficiency of different particles on silicon substrates as a function of laser fluence at a wavelength of 266 nm.

In order to understand the dependency of particle type in the removal process, the cleaning efficiency was investigated as a function of the laser fluence, which is shown in Fig. 4. The cleaning efficiency is defined as the ratio of the number of particles cleaned away from the surface after the irradiation of 10 laser pulses to the total number of particles before laser cleaning, which is measured by a particle counter. It is shown overall that the cleaning efficiency increases with increasing laser fluence for all particle types. Successful removal of copper and gold particles is achieved, i.e. 100% removal of the particles is obtained over 0.20 and 0.08 J/cm^2 at 266 nm for copper and gold, respectively. These fluences are low enough to avoid silicon substrate damage, which was found previously to be ~0.70 J/cm^2. As a result the optimum processing window would be 0.20–0.70 and 0.08–0.70 J/cm^2 for the successful removal of copper and gold particles, respectively, from the silicon wafer surface without causing any substrate damage. It was also found that the cleaning thresholds (above which the removal of particles takes place) were ~0.08 and 0.03 J/cm^2 for copper and gold, respectively. This implies that a greater interaction between the incident laser beam and the gold particles might be induced and provides more effective removal from the surface compared with that of copper. Moreover, little improvement in the cleaning efficiency with fluence was observed for the tungsten particles. This implies that even high fluences (just below the damage threshold) are not high enough to remove the tungsten particles successfully. As a result, the tungsten particles are found to be the most difficult to remove from the silicon surface, even using the ultraviolet laser radiation with high fluence.

4. Discussion

The predominant adhesion force of small particles (microns) on a dry surface is due to van der Waals force [15,16]. 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 [15]

$$F_a = \frac{hr}{8\pi Z^2} + \frac{hr_c^2}{8\pi Z^3}, \tag{1}$$

where h is the material-dependent Lifshitz–van der Waals constant, r is the particle radius, r_c is the radius of the contact 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, is related to the Hamaker constant, A, by the equation $h = 4\pi A/3$ [16,17]. The Hamaker coefficients of a copper particle on a copper substrate, a gold particle on a gold substrate and a tungsten particle on a tungsten substrate are almost same as $A_{\mathrm{Metal}} = 40 \times 10^{-20}$ J while the coefficient of a silicon particle on a silicon substrate is $A_{\mathrm{Si}} = 25.6 \times 10^{-20}$ J [16]. Then, the Hamaker coefficient of the metal particle on the silicon substrate $A_{\mathrm{Metal-Si}}$ is $\sim 32.0 \times 10^{-20}$ J based on the formula $A_{\mathrm{Metal-Si}} = (A_{\mathrm{Metal}} A_{\mathrm{Si}})^{1/2}$. The Lifshitz–van der Waals constant, h, for the metal particle on the silicon substrate is then 13.4×10^{-19} J. For van der Waals bonded crystals, Z is approximately equal to 4 Å (= 10^{-10} m) [15]. If it is assumed that the diameter of the metal particle is 1 μm and the diameter of the maximum contact area between the metal particle and the silicon substrate is 2% of the particle diameter, then r, r_c are 5×10^{-7} and 0.1×10^{-7} m, respectively. From Eq. (1) and the above constants, the adhesion force between the metal particle and the silicon substrate surface is $\sim 1.6 \times 10^{-7}$ N for a point contact (without any deformation of the particle on the surface) and 2.4×10^{-7} N with the contact area (or deformation) of 2%. It is seen that the adhesion force increases with an increase in contact area. Most importantly, the estimated adhesion force for the 1 μm sized metal particle on the silicon surface is tremendous, which is greater than the gravitational force acting on the particle by a factor of 10^7.

The predominant cleaning force for the removal of small particles from a substrate surface is due to a thermo-elastic force [18,19]. 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 surfaces. If a laser pulse with a pulse length of t_p is absorbed by the particle and the substrate, then a temperature rise (ΔT) at the interface between the particle and the substrate surface is induced.

In order to understand the effect of particle type in the laser cleaning of silicon surfaces, the cleaning forces induced by the laser absorption on the particle surface at 266 nm were compared for the different metallic particles by obtaining each temperature rise at the interface. If the particle is assumed to be plate-like (although the shape is spherical) and most of the laser radiation is effectively absorbed on the surface of the particle, the temperature rise at the interface can be simply estimated by a one-dimensional heat equation and can be compared with the different particles of copper, gold and tungsten. Surface reflectivities at 266 nm are 0.33 for copper, 0.36 for gold and 0.46 for tungsten [20]. The pulse length (t_p) of laser used in this work was 10 ns and the particle size was assumed to be 1 μm.

Fig. 5 shows the peak temperature distribution with depth for the three different particles at the end of the laser pulse (10 ns). The laser fluence used was 0.3 J/cm^2. It is shown that the temperature is at its maximum at the top surface of the particle and decreases with the depth. At the depth of 1 μm ($\cong$ at the particle–substrate interface), the temperature rises are ~235°C for copper, 309°C for gold and 224°C for tungsten, respectively. A large temperature rise is induced at the interface during the short pulse duration. The peak temperature rise at the depth of 1 μm as a function of the laser fluence is shown in Fig. 6. It is clearly seen that the temperature

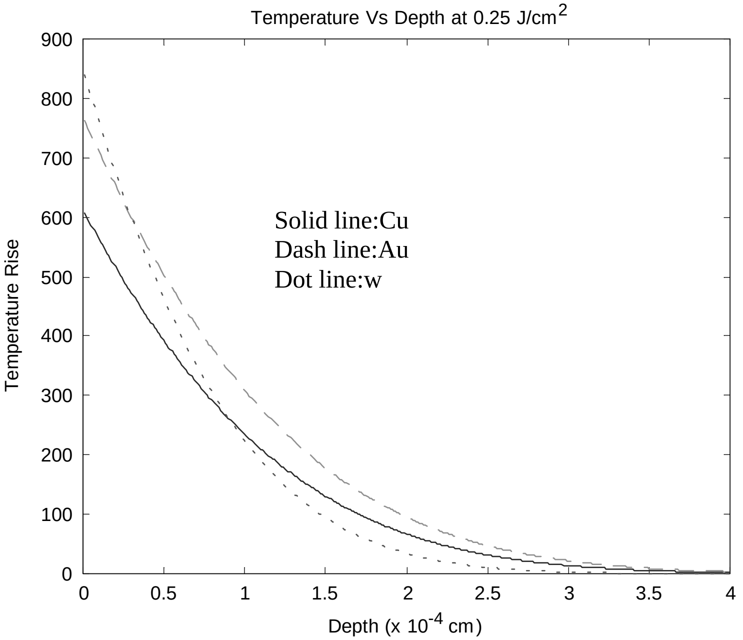


Fig. 5. Peak temperature distribution with depth for the three different particles at the end of the laser pulse (10 ns).

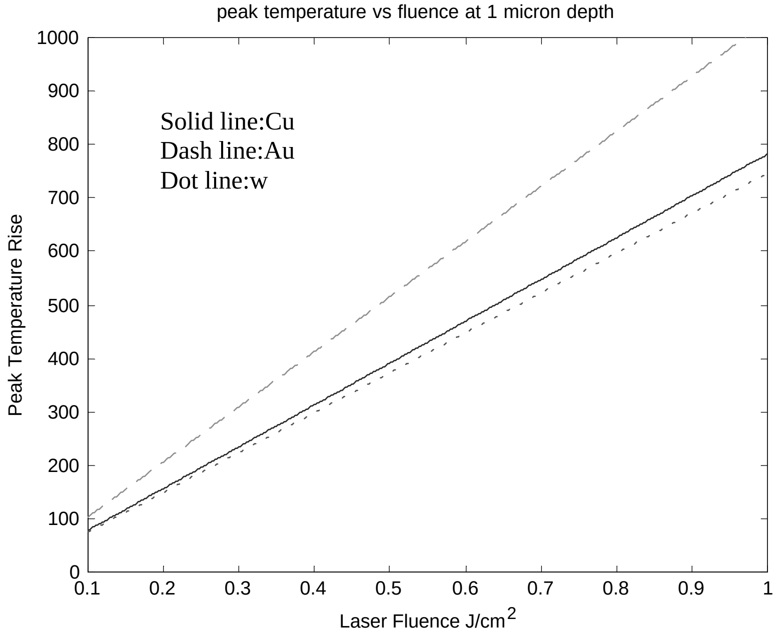


Fig. 6. Peak temperature rise at the depth of 1 μm as a function of the laser fluence.

rise at the interface increases with an increase in laser fluence due to the increased amount of laser energy absorbed on the surface.

The normal expansion of the surface (Δl) due to the temperature rise (ΔT) is given by [18]

$$\Delta l = \gamma \delta_{\mathrm{p}} \Delta T \approx \gamma \mathrm{d}\, \Delta T, \tag{2}$$

where γ is a thermal expansion coefficient and δ_{p} is a thermal diffusion length during laser pulse. In the case of the small metallic particles, the thermal diffusion length should be replaced by the particle diameter ($d = 1.0 \times 10^{-6}\,\mathrm{m}$) since the diffusion length ($\delta_{\mathrm{p}} = 2(kt_{\mathrm{p}})^{1/2}$, where k is a thermal diffusivity) is $\sim 2.1 \times 10^{-6}\,\mathrm{m}$ for copper, $2.2 \times 10^{-6}\,\mathrm{m}$ for gold, $1.6 \times 10^{-6}\,\mathrm{m}$ for tungsten, which is larger than the particle size. Using both the estimated temperature rises at the particle–substrate interface and the average thermal expansion coefficients for the different metals: γ_{Cu} $(10^{-6}\,\mathrm{K}^{-1}) = 17.0$, $\gamma_{\mathrm{Au}} = 14.1$, $\gamma_{\mathrm{W}} = 4.5$ [21], the expansion amplitude (Δl) can be estimated from Eq. (2). If the expansion is achieved within the pulse duration of 10 ns, the thermo-elastic force, F, exerted in the particle at the interface resulting from the rapid thermal expansion is approximately given by

$$F = ma = \rho V \frac{\Delta l}{t_{\mathrm{p}}^2}, \tag{3}$$

where m, a, ρ, V is mass, acceleration, density and volume of the particle. The resulting thermo-elastic forces for copper, gold and tungsten with laser fluence are

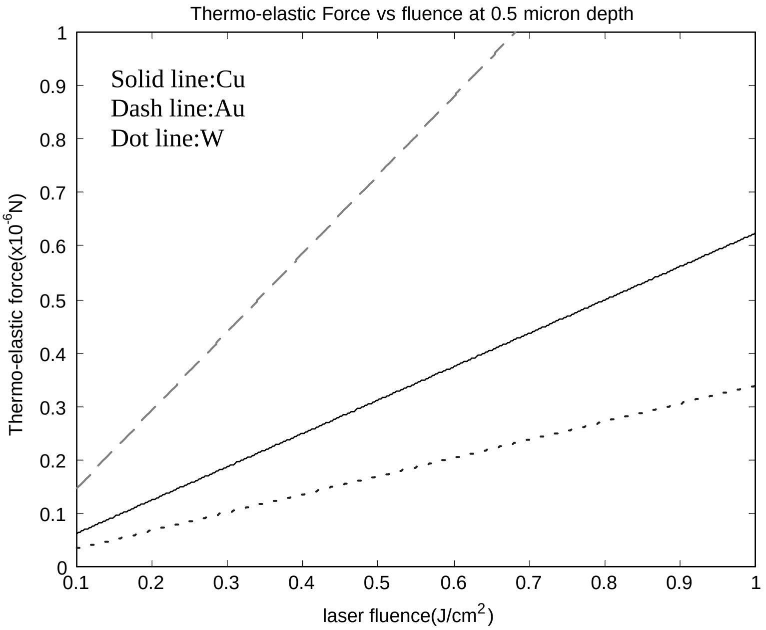


Fig. 7. The resulting thermo-elastic forces for copper, gold and tungsten with laser fluence.

shown in Fig. 7, which were calculated numerically by using the temperature distribution of Fig. 6 and the above equation.

From the approximately calculated cleaning forces for three different particles, it is seen that the thermo-elastic force at the particle–substrate interface increases with an increase in laser fluence. It is also apparent that the greatest force is induced with the gold particle and the smallest is with the tungsten particle under the same laser fluence. This implies that the gold particle is the easiest to remove from the surface while the tungsten particle is most difficult to remove under the same conditions. This result is consistent with the cleaning experiments described in the previous section. If it is assumed that the complete removal of the particles from the silicon surface occurs when the cleaning force is larger than the maximum adhesion force ($F > F_{\text{a(max)}}$), the required laser fluences for the complete removal of copper and gold particles can be determined from Fig. 7. It was found from Eq. (1) that the maximum adhesion force (2% deformation) for the particles on the silicon surface was $\sim 2.4 \times 10^{-7}$ N. Then, the corresponding laser fluences to the adhesion forces are 0.38 J/cm^2 for copper and 0.16 J/cm^2 for gold according to Fig. 7. It was also found from Fig. 4 that the experimental laser fluences for the complete removal of copper and gold particles are 0.20 and 0.08 J/cm^2, respectively. From the comparison, the estimated fluences are ~ 2 times larger than the actual experimental fluences. This difference might be due to the contribution of the silicon substrate expansion during the laser pulse, which was not taken into account in this work. The particle was also assumed to be plate-like in shape for a convenience of the calculation in this work.

However, since the particle is spherical and small, light scattering and increased laser absorption due to the spherical geometry may enhance the temperature near the particle–substrate interface. Both consideration of substrate absorption and Mie's scattering theory [22] would be a next step in order to develop a more reliable model.

5. Conclusions

Laser removal of small metallic particles of copper, gold and tungsten from silicon wafer surfaces was carried out using ultraviolet radiation at 266 nm. Successful removal of copper and gold particles from the surface was achieved by laser irradiation whereas tungsten particles proved difficult to remove successfully without causing any substrate damage. From the experiments, the damage threshold laser fluences and the fluences above which complete removal occurs were found and then provided an optimum processing window for the removal of copper and gold particles from silicon wafers. The effect of the particle type in the cleaning process was investigated experimentally and theoretically. Most effective removal in terms of cleaning efficiency was found with gold particles and the least effective with tungsten particles. From looking at the comparison between the adhesion force and laser-induced thermo-elastic force exerted at the particle–substrate interface for the different metallic particles, it is seen that gold and copper particles have superior elastic and thermal properties compared with tungsten particles and hence cause a greater thermo-elastic force which leads to more effective removal of particles from the surface.

References

[1] DeJule R. Semiconductor International, August 1998. p. 64–8.
[2] Walz JY. Photonic Spectra, January 1997. p. 116–20.
[3] Lu YF, Sung WD, Hong MH, et al. J Appl Phys 1996;80(1):499.
[4] Lee JM, Watkins KG. Optics express (special focus issue), vol. 7, No. 2, p. 69–76, http://www.Opticsexpress.org/oearchieve/source/22798.htm.
[5] Tam AC, Park HK, Grigoropoulos CP. Appl Surf Sci 1998;721:127–9.
[6] Vereecke G, Rohr E, Heyns MM. J Appl Phys 1999;85(7):3837.
[7] Lee JM, Watkins KG. The laser industrial user, vol. 18, February 2000. p. 29–30.
[8] Lee JM. In-process and intelligent monitoring systems for laser cleaning process. Ph.D. thesis, The University of Liverpool, UK, 1999 [chapter 1].
[9] Tam AC, Leung WP, Zapka W, et al. J Appl Phys 1992;71(7):3515.
[10] Zapka W, Ziemlich W, Tam AC. Microelectron Eng 1993;20:171–83.
[11] Zapka W, Ziemlich W, Tam AC. Appl Phys Lett 1991;58:2217–9.
[12] Imen K, Lee SJ, Allen SD. Appl Phys Lett 1991;58:203–5.
[13] Lee SJ, Imen K, Allen SD. Appl Phys Lett 1992;61:2314–6.
[14] Lee JM, Watkins KG. Lasers Eng 1999;8(3):229–39.
[15] Bowling RA. In: Mittal KL, editor. Particles on surfaces, vol. 1. New York: Plenum, 1988. p. 129–42.
[16] Osborne-Lee IW. In: Mittal KL, editor. Particles on surfaces, vol. 1. New York: Plenum, 1988. p. 77–90.

[17] Ranade MB, Menon VB, Mullins ME, Debler VL. In: Mittal KL, editor. Particles on surfaces, vol. 1. New York: Plenum, 1988. p. 179–91.
[18] Tam AC, Leung WP, Zapka W, et al. J Appl Phys 1992;71(7):3515.
[19] Lu YF, Song WD, Ang BW, et al. Appl Phys A 1997;65:9.
[20] Edwards DF. In: Palik ED, editor. Handbook of optical constants of solids. New York: Academic Press, 1985.
[21] Brandes EA, Brook GB, editors. Smithells metals reference book. London: Butterworths–Heinemann, 1992 [chapter 14].
[22] Bohren CF, Huffman DR. Absorption and scattering of light by small particles. New York: Wiley, 1998[chapters 4&5].