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# Laser removal of copper particles from silicon wafers using UV, visible and IR radiation

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**Abstract.** Laser removal of small copper particles from silicon wafer surfaces was carried out using Nd:YAG laser radiation from near-infrared (1064 nm) through visible (532 nm) to ultraviolet (266 nm). It has been found that both 266 nm and 532 nm are successful in removing the particles from the surface whereas 1064 nm was shown to be ineffective in the removal of particles. The damage-threshold laser fluence at 266 nm was much higher than other wavelengths which provides a much wider regime for safe cleaning of the surface without causing any substrate damage. The cleaning efficiency was increased with a shorter wavelength. The effect of laser wavelength in the removal process is discussed by considering the adhesion force of the particle on the surface and the laser-induced cleaning forces for the three wavelengths.

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As semiconductor and microelectronic devices are becoming increasingly smaller, surface contamination of these devices is 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 production yield. For example, particles in the size of about 0.1 μm to several μm 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]. Those particles should be removed to ensure device quality and performance and reduce scrap rates. Conventional cleaning techniques such as wiping and scrubbing are often limited due to possible substrate damage caused by the mechanical action on the surface. Ultrasonic (or megasonic) and chemical flux as a more effective cleaning technique may also pose environmental problems due to the considerable water consumption and the discard of chemicals after use with an added disadvantage of hazard to human health.

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Recently lasers have been considered as a new promising technique, which may overcome the disadvantages induced by conventional cleaning techniques. This approach utilises the versatile, controllable, selective and environmentally friendly nature of the laser system to optimum effect [3, 4]. 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 particles from various surfaces in industry [5–8].

In this paper the removal of small copper particles with a diameter of 1 μm from silicon wafers has been carried out using a Q-switched Nd:YAG laser having three different wavelengths of 1064 nm (near-infrared), 532 nm (visible) and 266 nm (ultraviolet), produced by frequency harmonic generation. Quantitative analysis was carried out in order to determine the fluence values that induced substrate damage to the silicon wafer at each of the three wavelengths, which would then provide the maximum processing window for successful laser cleaning of semiconductors. 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 three wavelengths and compared with each other. In addition, particle adhesion force on the surface and cleaning force exerted at the particle–substrate interface were taken into account for the three different wavelengths in order to understand the effect of laser wavelength in the cleaning process.

## 1 Experimental

One of the most important issues in the cleaning of copper particles from semiconductors is preventing it from getting into the front-end processing where it could possibly destroy the integrity of the gate oxide and hence create leakage currents [1]. Surface defects could be also introduced such as roughening with the presence of copper contaminants, moreover copper 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 spherical copper particles on silicon wafer substrates was carried out. The wafer samples were coated with copper 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 visible and UV radiation were achieved by frequency doubling and 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 energies obtainable were 500 mJ, 250 mJ, and 50 mJ for 1064 nm, 532 nm and 266 nm, respectively. These three wavelengths were used to remove the copper 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.

## 2 Cleaning results

In order to determine the maximum laser fluence for successful removal of copper particles without causing substrate damage, damage-threshold fluences on uncoated Si wafer were determined. They were approximately 0.62 J/cm$^2$ for 1064 nm, 0.68 J/cm$^2$ for 532 nm and 1.2 J/cm$^2$ for 266 nm. Interestingly, the damage threshold is higher at the shorter wavelength. This is opposite to the behaviour from metal substrates, i.e. the damage threshold is higher at a longer wavelength since beam reflectivity on the metal surface increases with increasing the wavelength. On the contrary, the reflectivity of silicon decreases with increasing the wavelength, i.e. 0.73 for 266 nm, 0.37 for 532 nm and 0.32 for 1064 nm [9]. From the results, it can be seen that cleaning trials should be carried out below these threshold values to avoid substrate damage. Figure 1 shows the surface morphology of the damaged silicon substrate after the irradiation of three laser pulses with higher laser fluence of 0.8 J/cm$^2$ than the damage threshold at 1064 nm. The diameter of the damaged area on the silicon wafer is approximately 3 mm, which is the same as the laser spot size.

Figure 2 shows the silicon surfaces before and after laser treatment with a wavelength of 1064 nm. Ten laser pulses with a fluence of 0.60 J/cm$^2$ were used for the removal of copper particles from the surface. It can be seen that very few particles were removed at the fluence just below the damage-threshold fluence of the silicon substrate at 1064 nm. This implies that successful cleaning of copper is almost impossible without introducing damage on the substrate at 1064 nm. From this result, the wavelength of 1064 nm is not appropriate for successful removal of the copper particles from the silicon wafer.

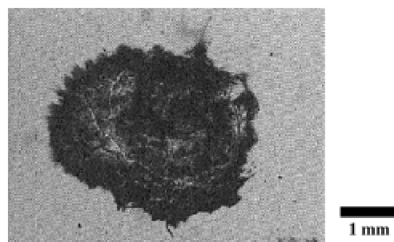


**Fig. 1.** Surface morphology of the damaged silicon wafer after the irradiation of three laser pulses with a fluence of 0.8 J/cm$^2$ at 1064 nm

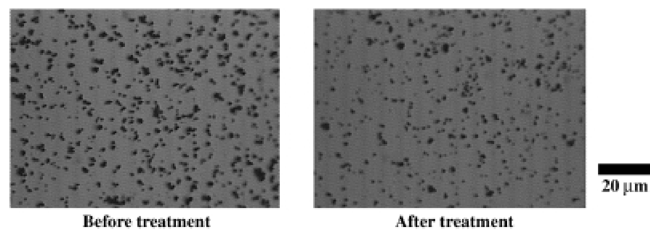


**Fig. 2.** Optical micrographs of silicon wafer surfaces before and after laser treatment with a wavelength of 1064 nm: 10 laser pulses with a fluence of 0.60 J/cm$^2$ were irradiated onto the surface

Figure 3 shows the silicon surfaces before and after laser cleaning with a wavelength of 532 nm. Ten laser pulses with fluences of 0.28 J/cm$^2$ and 0.46 J/cm$^2$ were used for the removal of copper particles from the silicon wafer. It can be seen that few particles were removed at the lower fluence of 0.28 J/cm$^2$ whereas a complete removal of all copper particles was achieved at the higher fluence of 0.46 J/cm$^2$, which is below the damage-threshold fluence. This implies that successful cleaning can be achieved at 532 nm wavelength without introducing damage to the wafer.

Figure 4 shows the silicon surfaces before and after laser cleaning with a wavelength of 266 nm. Ten laser pulses with fluences of 0.16 J/cm$^2$ and 0.18 J/cm$^2$ were used for removal of copper particles from the silicon wafer. 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 0.18 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. In addition, the complete removal of the particles occurs at a much lower fluence compared with the same result observed at 532 nm (0.46 J/cm$^2$). This implies that more effective energy coupling between the laser and the particles has been induced at 266 nm than at a wavelength of 532 nm.

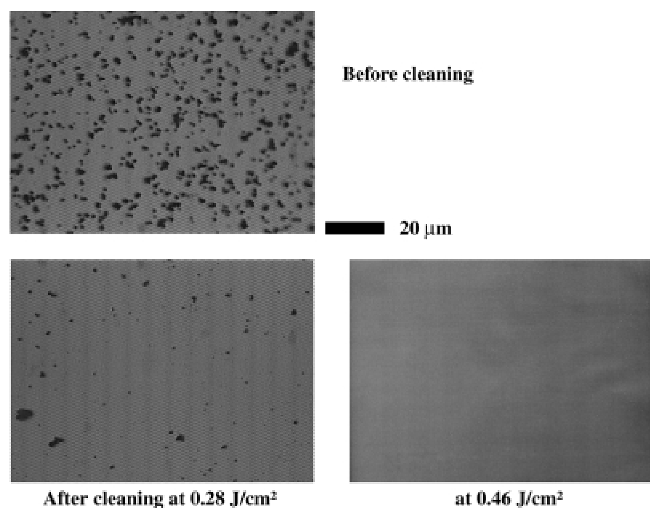


**Fig. 3.** Optical micrographs of silicon wafer surfaces before and after laser cleaning with a wavelength of 532 nm: 10 laser pulses were used

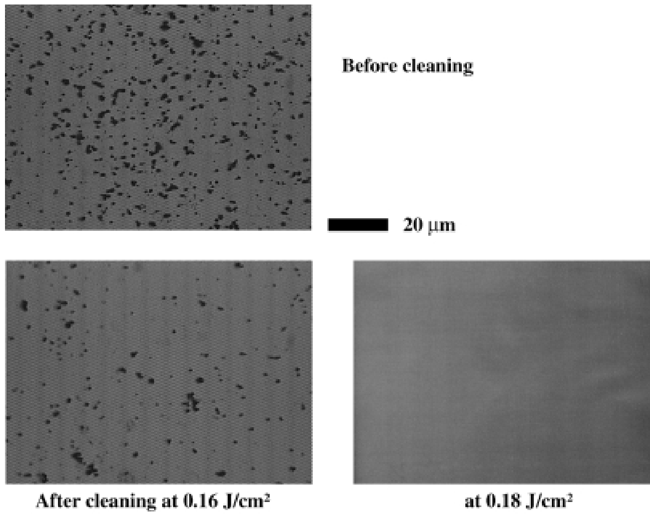


**Fig. 4.** Optical micrographs of silicon wafer surfaces before and after laser cleaning with a wavelength of 266 nm: 10 laser pulses were used

In order to understand the effects of laser fluence and laser wavelength clearly, the cleaning efficiency was investigated during laser cleaning, which is shown in Fig. 5. The cleaning efficiency is defined as the ratio of the number of copper particles cleaned away from the surface after the irradiation of ten 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 the laser fluence at all three wavelengths. Very little improvement in the cleaning efficiency was observed with an increase of laser fluence at 1064 nm. This implies that the 1064 nm wavelength is not effective for the removal of copper particles even with high laser fluences. However successful removal of copper particles is achieved at both 532 nm and 266 nm, i.e. 100% removal of the particles is obtained over $0.46\,\mathrm{J/cm^2}$ for 532 nm and $0.18\,\mathrm{J/cm^2}$ for 266 nm. These fluences are low enough to avoid substrate damage at both wavelengths. It is seen that these two wavelengths are suitable for the removal of copper particles from Si wafer surfaces. It was found previously that the damage thresholds of the silicon wafer were $0.68\,\mathrm{J/cm^2}$ and $1.2\,\mathrm{J/cm^2}$ for 532 nm and 266 nm, respectively. As a result the optimum processing window would be $0.46–0.68\,\mathrm{J/cm^2}$ for 532 nm and $0.18–1.2\,\mathrm{J/cm^2}$ for 266 nm for the successful removal of copper particles 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 $0.1\,\mathrm{J/cm^2}$ and $0.04\,\mathrm{J/cm^2}$ for 532 nm and 266 nm, respectively. This implies that a greater interaction between the incident laser beam and the copper particles might be induced and provides more effective removal at 266 nm than at 532 nm.

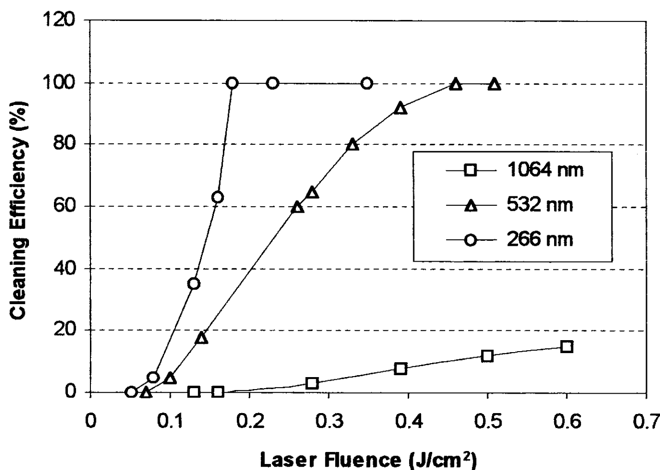


**Fig. 5.** Cleaning efficiency of copper particles on silicon substrates as a function of laser fluence at the wavelengths of 1064 nm, 532 nm and 266 nm

## 3 Discussion

### *3.1 Adhesion force*

The predominant adhesion force of small particles (μm) on a dry surface is due to Van der Waals force [10]. 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 [10]:

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

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 $h = 4\pi A/3$ [11, 12]. Since the Hamaker coefficients of a copper particle on a copper substrate and a silicon particle on a silicon substrate are $A_{Cu} = 40\times10^{-20}$ J and $A_{Si} = 25.6\times10^{-20}$ J, respectively, the Hamaker coefficient of copper particle on the silicon substrate $A_{Cu-Si}$ is approximately $32.0\times10^{-20}$ J based on the formula $A_{Cu-Si} = (A_{Cu}A_{Si})^{1/2}$. The Lifshitz–Van der Waals constant, $h$, for a copper particle on a silicon substrate is then $13.4\times10^{-19}$ J. For Van der Waals bonded crystals, $Z$ is approximately equal to 4 Å ($= 10^{-10}$ m) [10]. If it is assumed that the diameter of the copper particle is 1 μm and the diameter of the contact area between a copper particle and a copper substrate is 2% of the particle diameter, then $r$, $r_c$ are $5\times10^{-7}$ m and $0.1\times10^{-7}$ m, respectively. From (1) and the above constants, the adhesion force between the copper particle and the silicon substrate surface is approximately $1.6\times10^{-7}$ N for a point contact (without any deformation of the particle on the surface) and $2.4\times10^{-7}$ N with the contact area (or deformation) of 2%. These correspond to the forces per unit area of $2.0\times10^5$ Pa and $3.0\times10^5$ Pa, respectively.

### *3.2 Cleaning force*

The predominant cleaning force for the removal of small particles from a substrate surface is due to 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 surfaces. If a laser pulse with a pulse length of $t_p$ is absorbed by the particle and the substrate, then a temperature rise ($\Delta T$) at the interface between the particle and the substrate surface is induced.

In order to understand the effect of laser wavelength in the removal of copper particles from a silicon substrate surface, the cleaning forces induced by the different wavelengths were compared by obtaining each temperature rise at the interface with the three wavelengths. 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 wavelengths of 266 nm, 532 nm and 1064 nm. Surface reflectivities for copper are 0.33 for 266 nm, 0.62 for 532 nm and 0.97 for 1064 nm, and absorption coefficients are $7.9 \times 10^5$ ($\text{cm}^{-1}$) for 266 nm, $6.1 \times 10^5$ for 532 nm, $8.1 \times 10^5$ for 1064 nm, respectively [15]. The pulse length ($t_p$) of laser used in this work was 10 ns and the particle size was assumed to be 1 μm.

Figure 6 shows the temperature distribution with time for the three different wavelengths on the top surface of copper. The laser fluence used was 0.4 J/cm$^2$. It is shown that the surface temperature increases with time during laser irradiation and reaches peaks at the end of the laser pulse of 10 ns and then decreases with time. It is also seen that the shorter the wavelength the larger the temperature rise is, which results from higher laser absorption on the surface.

The temperature distribution with depth for the three wavelengths is shown in Fig. 7, which is a distribution of peak temperature at the time of 10 ns as shown in Fig. 6. It is shown that the temperature is maximum at the top surface of copper and decreases with the depth. At the depth of 1 μm ($\cong$ at the particle–substrate interface), the temperature rises are approximately 20 °C for 1064 nm, 230 °C for 532 nm and 390 °C for 266 nm, respectively. The temperature rise at the particle–substrate interface increases significantly at a shorter wavelength. This is because higher absorptivity at a shorter wavelength produces larger amounts of heat on the copper surface leading to a larger temperature rise at the interface.

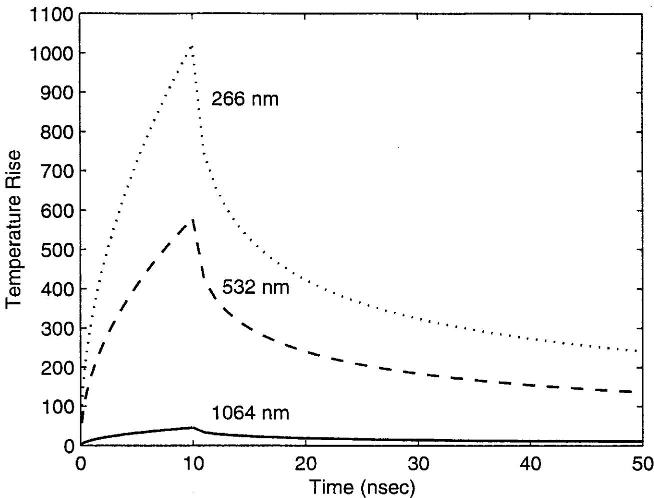


**Fig. 6.** Temperature rise as a function of time for the different wavelengths of 1064 nm, 532 nm and 266 nm on the top surface of copper at 0.4 J/cm$^2$

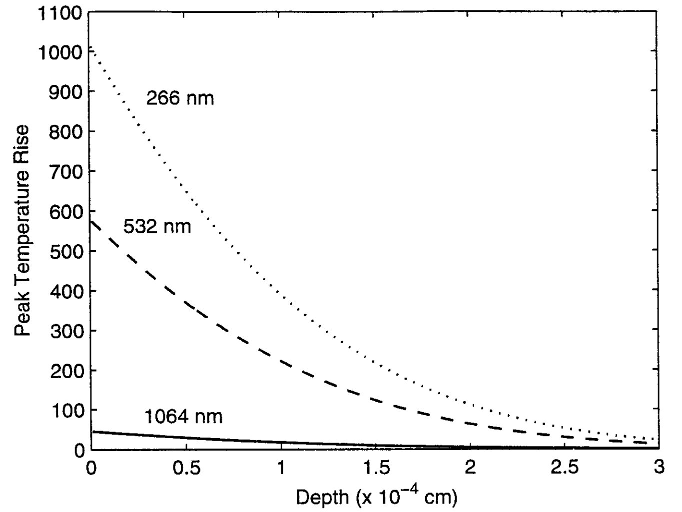


**Fig. 7.** Peak temperature rise as a function of depth in copper particle for the wavelengths of 1064 nm, 532 nm and 266 nm at 0.4 J/cm$^2$

The normal expansion of the surface ($\Delta l$) due to the temperature rise ($\Delta T$) is given by [13]:

$$\Delta l = \alpha \delta_p \Delta T \approx \alpha d \Delta T \tag{2}$$

where $\alpha$ is a thermal expansion coefficient and $\delta_p$ is a thermal diffusion length during the laser pulse. In the case of the small copper particle the thermal diffusion length should be replaced by the particle diameter ($d = 1.0 \times 10^{-6}$ m) since the diffusion length for copper is approximately $2.1 \times 10^{-6}$ m (calculated from $\delta_p = 2(kt_p)^{1/2}$ where the thermal diffusivity ($k$) for copper is about 1.16 cm$^2$/s [16]) which is larger than the particle size.

Using both the estimated temperature rises and the following linear thermal expansion coefficient for copper: $\alpha(10^{-6}\,\text{K}^{-1}) = 14.34 + 8.79 \times 10^{-3}T - 3.91 \times 10^{-6}T^2$ [17], the expansion amplitudes ($\Delta l$) can be estimated from (2) as $3.4 \times 10^{-10}$ m for 1064 nm, $4.4 \times 10^{-9}$ m for 532 nm and $8.0 \times 10^{-9}$ m for 266 nm. If the expansion is achieved during the pulse duration of 10 ns, the acceleration at the interface, $a$, resulting from the thermal expansion is approximately given by

$$a = \frac{\Delta l}{t_p^2} \, . \tag{3}$$

From (3) the accelerations at the interface are $3.4 \times 10^6$ m/s$^2$ for 1064 nm, $4.4 \times 10^7$ m/s$^2$ for 532 nm and $8.0 \times 10^7$ m/s$^2$ for 266 nm, respectively. Consequently, the thermo-elastic force, $F$, exerted on the particle at the interface is given by

$$F = ma \tag{4}$$

where $m$ is the mass of the copper particle, which can be calculated by $\varrho \times V$ : $\varrho$(density) $= 8.96$ g/cm$^3$ [16], $V$(particle volume) $= 5.24 \times 10^{-19}$ m$^3$. The resulting thermo-elastic forces at the particle–substrate interface for 1064 nm, 532 nm and 266 nm are $1.6 \times 10^{-8}$ N, $2.1 \times 10^{-7}$ N and $3.8 \times 10^{-7}$ N, respectively. These values correspond to forces per unit area of $0.2 \times 10^5$ Pa for 1064 nm, $2.6 \times 10^5$ Pa for 532 nm and $4.8 \times 10^5$ Pa for 266 nm. Figure 8 shows the

cleaning force per unit area with particle size for the three wavelengths at the laser fluence of $0.4\,\mathrm{J/cm^2}$, which was calculated numerically by using the temperature distribution of Fig. 7 and above equations.

From the approximately calculated values of cleaning forces for three wavelengths, it is seen that the thermo-elastic force at the particle–substrate interface for 266 nm is much larger than the estimated adhesion force between the particle and the substrate ($2.0 \sim 3.0 \times 10^5$ Pa) from (1) whereas the force at 1064 nm is much smaller than the adhesion force. The thermo-elastic force at 532 nm is taken to be $2.6 \times 10^5$ Pa which is between the adhesion force values for a point contact and 2% deformation. This implies that the cleaning force for 266 nm at $0.4\,\mathrm{J/cm^2}$ is high enough to break the adhesion bond thus detaching the particles from the surface; whereas the cleaning force for 1064 nm at $0.4\,\mathrm{J/cm^2}$ is not enough to break the bond and will need a much higher laser fluence to exceed the adhesion force. From Fig. 5, it was seen that complete removal of copper particles from the silicon substrate surface was achieved for 266 nm at $0.4\,\mathrm{J/cm^2}$, partial removal for 532 nm and the removal of the particles proved difficult at 1064 nm. It is also shown in Fig. 8 that the cleaning force is larger at shorter wavelengths and increases with an increase in particle size. This trend continues until the particle size approaches approximately 0.8 μm where the maximum cleaning force value is reached. After this peak the force steadily decreases with a continued increase in particle size. A larger cleaning force is associated with a shorter wavelength due to the fact that there is greater laser absorption on the surface of copper particle. This leads to a larger temperature rise at the particle–substrate interface producing a greater acceleration of the particle. The laser-induced temperature rise decreases with increased depth as shown in Fig. 7, thus resulting in reduced cleaning force at the interface with an increase in particle size. Moreover a reduction in cleaning force is seen with particles which are less than 1 μm in size. This is because the mass of the particle reduces significantly ($m \propto r^3$) with a decrease in particle size. From (1), it can be seen that the adhesion force per unit area increases significantly with decreasing the particle size (e.g. $22 \times 10^5$ Pa at the size of 0.1 μm with 2% deformation). This implies that very small metal particles of less size of 0.1 μm are difficult to remove from the surface by laser irradiation due to the combination of high adhesion force and poor cleaning force.

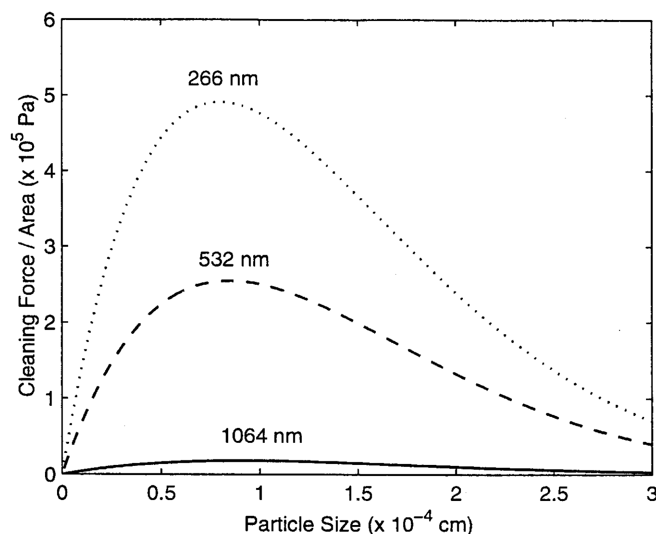


**Fig. 8.** Cleaning force per unit area exerted at the particle–substrate interface as a function of particle size (diameter) for the wavelengths of 1064 nm, 532 nm and 266 nm at $0.4\,\mathrm{J/cm^2}$

So far the effect of the wavelength in the removal of copper particles from silicon wafer surface has been investigated using a simple theoretical model under certain assumptions, which allowed the semi-quantitative understanding of the cleaning process. However a more reliable model can be developed by consideration of the following points in future. The contribution from an absorbing silicon substrate for the removal of the particles should be considered not only to calculate the accurate cleaning force exerted on the particle but also to understand the silicon substrate behaviour with wavelength. It can also be deduced from Fig. 5 that a partial removal (about 10%) of the particles at 1064 nm and $0.4\,\mathrm{J/cm^2}$ in spite of very poor laser absorption on the copper surface for the wavelength might be responsible for the absorption on the silicon substrate. In this work the particle is assumed to be plate-like in shape for a convenience for the calculation. However laser absorption on a small spherical particle should take the Mie theory into account where absorption cross-section change with wavelength, angle-dependent scattering functions and complex dielectric constants for a given wavelength are considered [18]. This is the case particularly for submicron particles which are much smaller than the laser wavelength. Here the beam absorption on the particle is dependent on the ratio of the particle diameter to the wavelength ($\sim d/\lambda$).

## 4 Conclusions

Laser removal of small copper particles from silicon wafer surfaces was carried out using a Q-switched Nd:YAG laser with wavelengths of 1064 nm (near-infrared), 532 nm (visible) and 266 nm (ultraviolet). Successful removal was achieved by laser irradiation at 532 nm and 266 nm whereas 1064 nm was found to be inappropriate for the particle removal. 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 particles from silicon wafers. The effect of laser wavelength in the removal process was investigated by experimental and theoretical analysis. More effective removal of the particles in terms of cleaning efficiency was found at a shorter wavelength. From the comparison between the adhesion force and laser-induced thermo-elastic force exerted at the particle–substrate interface for the different wavelengths, laser radiation with a shorter wavelength causes a larger absorption of laser energy on the surface and leads to a higher temperature rise at the interface producing a greater thermo-elastic force. This larger cleaning force increases the cleaning efficiency at a shorter wavelength. As a result, a shorter laser wavelength is much more beneficial for the removal of small particles from silicon wafers since it provides a higher cleaning efficiency as well as a wider safety regime for cleaning.

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