

*Rapid communication***Universal threshold for the steam laser cleaning of submicron spherical particles from silicon**

M. Mosbacher*, V. Dobler, J. Boneberg, P. Leiderer

Universität Konstanz, Zentrum für Moderne Optik Konstanz, 78457 Konstanz, Germany

Received: 28 January 2000/Revised version: 28 March 2000/Published online: 11 May 2000 – © Springer-Verlag 2000

Abstract. The efficiency of the “steam laser cleaning” process is examined. For the investigation of the physics of particle removal from the particularly interesting surface of silicon we have deposited well-characterized spherical polymer and silica particles of different diameters ranging from several tens to hundreds of nanometers on commercial wafers. As a result of our systematic study we observe a sharp threshold of the steam cleaning process at 110 mJ/cm^2 ($\lambda = 532 \text{ nm}$, $\text{FWHM} = 7 \text{ ns}$) which is independent of the size (for particles with diameters as small as 60 nm) and material of the particles. An efficiency above 90% after 20 cleaning steps is reached at a laser fluence of 170 mJ/cm^2 . Experiments with irregularly shaped alumina particles exhibit the same threshold as for spherical particles.

PACS: 81.65.C; 79.60.Bm

The removal of submicron particles from highly damageable surfaces poses an increasing challenge to engineers worldwide. Unless removed, these particles are responsible for production losses or malfunctions, e.g. in electronic circuits [1]. One way to overcome the strong adhesion forces acting on the particles is to make use of inertia effects. High accelerations on the order of 10^6 g are needed for particle removal [2] which cannot be provided by conventional methods such as ultrasonics [3]. It has recently been demonstrated that particles (Al_2O_3 , SiO_2 , MgO , SiC , CeO_2 , BC) as small as 100 nm in diameter can efficiently be removed by laser cleaning [4–10]. In this “steam laser cleaning” process, a thin liquid film is condensed onto the substrate and then evaporated momentarily by irradiating the surface with a short laser pulse. The energy absorption in the substrate leads to a fast temperature increase both in the substrate and, due to heat transport, in the liquid film. Bubble nucleation at the solid/liquid interface and the subsequent explosive vaporization of the liquid cause the removal of contaminants.

Previous investigations focused on the demonstration of the cleaning effect itself [4–7] and on the study of the bubble nucleation and growth process [12–14]. To the best of our knowledge only a few quantitative measurements on the influence of the process parameters of the steam laser cleaning (laser fluence, particle size and material) on the cleaning efficiency have been reported. However, these experiments were performed either with irregularly shaped particles that tend to form coagulates and thus inhibit a quantitative analysis of single particle removal [8–11] or the cleaning efficiency was investigated only for a few different kinds of particles [9, 10]. For a systematic investigation of the underlying physical processes on the cleaning behaviour we changed [15] from the irregularly shaped alumina particles commonly used as test particles to small monodisperse polystyrene (PS) or silica (SiO_2) spheres [16] with diameters in a range from 60 nm up to 800 nm. This allows studies on the size and material dependence of the cleaning efficiency. Preliminary results for PS particles with diameters of 800 nm have already been presented in [17].

1 Sample preparation—colloidal particles as model contaminants

After rarefaction with isopropyl alcohol (IPA) the particle suspension was deposited onto the wafer surface by spin coating. Since we were interested in the preparation of samples with isolated particles, high evaporation rates and low concentrations of colloids were chosen for drying in order to keep coagulation to a minimum. We were able to prepare samples with essentially isolated spheres (> 95% for particles with diameter > 300 nm) at high particle densities. The percentage of isolated particles increases with particle diameter. An example of PS particles with diameters of 480 nm is shown in Fig. 1.

For a comparison with previous studies [4–6, 8–11] we have in addition chosen commercially available micropolish powder [18] with a mean diameter of 300 nm as a source of alumina (Al_2O_3) particles that were applied to the sample in

*Corresponding author. (E-mail: mario.mosbacher@uni-konstanz.de)

the same way as the spherical particles. However, the percentage of coagulates was quite high, indicating that these samples were not suitable for obtaining quantitative information on the removal process of single particles.

2 Experimental setup

A Nd:YAG laser ($\lambda = 532$ nm, FWHM = 7 ns) with a Gaussian beam profile was used for cleaning an area of about 1 mm². This area was much larger than the area in which particle removal was monitored (diameter ≤ 0.5 mm). For this reason the laser fluence in the test area can be considered as homogeneous.

The calibration of the laser fluences in the monitored area was carried out applying three independent methods: the first one, based on an approach by Liu [19], uses a phase transformation of a thin (approx. 50 nm) GeSb film on a glass substrate, as described in detail elsewhere [20, 21]. Secondly we used a pinhole that allowed only the center part of the beam to pass (where the laser fluence is quite uniform) and derived the energy density from the measured transmitted light pulse and the known pinhole area. As a third, independent method we determined the threshold cleaning fluence relative to the melting threshold of Si, monitored in the same experiment via ns time-resolved reflectivity measurements. The laser fluence necessary for the onset of melting of the Si surface is well known [23–25], and it constitutes a critical value, to which all the fluences used in laser cleaning of silicon should be compared, because for all practical applications melting has to be strictly avoided.

Similar to earlier work [6] the liquid film (thickness 200–400 nm) required for the steam cleaning was obtained by condensing a burst of water/alcohol (25% isopropanol for enhanced wetting) vapor supplied through a nozzle above the wafer surface just before the pulse.

In order to evaluate cleaning efficiency we followed two different methods of particle detection, namely direct observation in a microscope and light scattering by the particles.

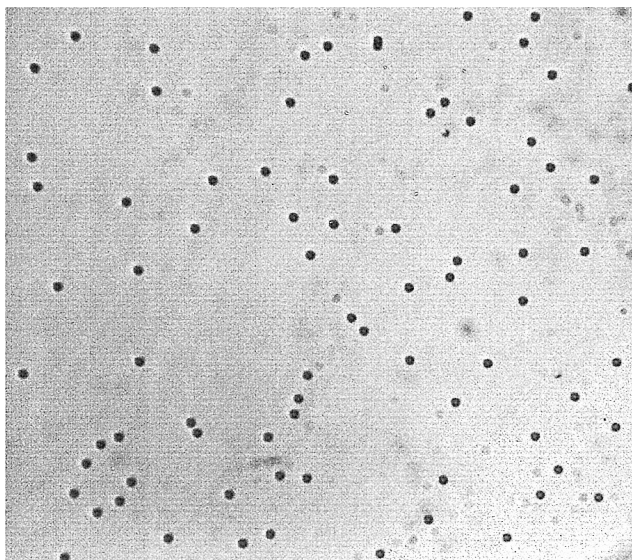


Fig. 1. A typical sample ($4.3 \mu\text{m} \times 5 \mu\text{m}$) before cleaning showing a random distribution of isolated colloidal PS spheres with a diameter of 480 nm

Using microscopes [optical microscope and scanning electron microscope (SEM) depending on the particle diameter] it is possible to monitor the particle concentration in the cleaned area. Figure 2 shows the same area of a sample contaminated with PS spheres (800 nm diameter) before (Fig. 2a) and after (Fig. 2b) one cleaning step (application of vapor and subsequent laser pulse). Particle removal is clearly visible. As the applied laser fluence was only slightly higher than the cleaning threshold, not all particles were removed. Those which are left on the surface remain in their position indicating that there was no recontamination in the monitored area. SEM images also demonstrate this cleaning effect for distinctly smaller particles (Fig. 3). The picture shows the edge of the region irradiated by the cleaning laser pulse (marked by the white line) of a sample prepared with PS particles which are 60 nm in diameter. Cleaning is obvious on the left-hand side. Outside the cleaned region, the original colloidal particles can be seen. To our knowledge, this is the smallest size of particles ever removed by laser cleaning.

Although the application of microscopes provides a direct image of the cleaned regions we applied a different method for the analysis of the process in our systematic studies: a measurement of the particle concentration via light scattering yields the same quantitative information but increases the speed of data analysis. Using a photomultiplier we were able to detect scattered light from particles with diameters as small as 60 nm. The detection of the scattered light from these particles represents the detection limit of our present setup, but might be extended to even smaller sizes by the application of lasers with higher intensity and smaller wavelengths.

A 5-mW HeNe laser illuminated a spot with a diameter of < 0.5 mm which corresponds to several hundred particles at the particle concentration used. This high number of spheres ensured a small statistical error in our experiments as we were able to monitor several hundred lift off processes at the same time. Since the prepared samples consist of mainly isolated particles that are not geometrically correlated the scattered intensity I is directly proportional to the number N of adherent particles in the scattering area. A comparison be-

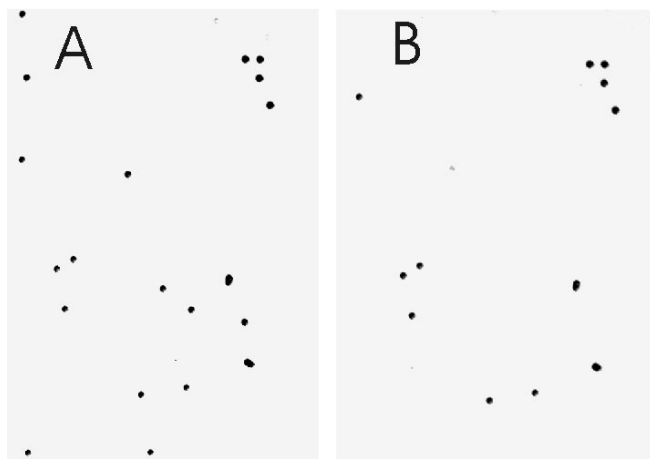


Fig. 2a,b. A typical site of a sample ($34 \mu\text{m} \times 49 \mu\text{m}$) contaminated with PS spheres of diameter 800 nm. The reduction from 20 to 12 in the number of particles before (a) and after (b) one cleaning step (application of steam and subsequent laser pulse) corresponds very well with the decrease of the scattered intensity to 54% after the cleaning. The particles visible in the picture are single spheres besides two dimers

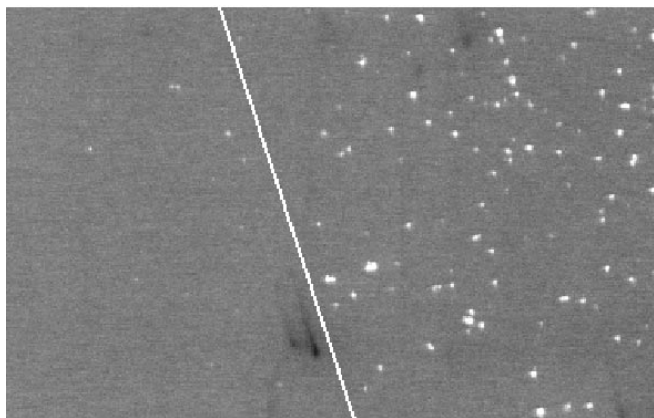


Fig. 3. The edge (indicated by a white line) of the cleaned area ($10\ \mu\text{m} \times 6.5\ \mu\text{m}$) of a sample contaminated with PS particles 60 nm in diameter as seen in the SEM. Cleaning of single spheres is clearly visible, the percentage of coagulated spheres is higher for these small particles than for larger ones

tween the microscopic and light scattering measurement of the particle removal shows a very good agreement of both methods. The number of adherent point scatterers in Fig. 2 is reduced from $N_0 = 20$ to $N = 12$ corresponding to a cleaning efficiency of $(1 - N/N_0) = 40\%$, whereas the scattered intensity of the HeNe laser measured for the same sample exhibited a reduction of 44%. This close agreement shows that the application of the scattering intensity for the detection of the number of particles on the sample is justified. We will therefore denote in the following the quantity $(1 - I/I_0)$ as “cleaning efficiency” where I_0 and I denote the measured scattered intensity before and after the cleaning, respectively.

3 Experimental results

Results of the energy dependence of particle removal by the steam laser cleaning process for PS spheres with diameters of 800 nm, 500 nm, and 60 nm are plotted in Fig. 4. As already shown in a previous investigation [15] the ablation process for our samples is completely statistical making quantitative studies feasible. With regard to a better illustration of the cleaning behavior the results for 20 cleaning steps are plotted.

For all sizes we obtain a similar behavior of the efficiency as a function of the laser fluence: a steep increase in the cleaning efficiency at a laser fluence of $F = 110\ \text{mJ}/\text{cm}^2$. This absolute value of the threshold fluence was determined by the three methods [22] described in Sect. 2. From the GeSb method we obtained a value of $110 \pm 15\ \text{mJ}/\text{cm}^2$, the calibration via determination of the irradiated area gave a value of $100\text{--}110\ \text{mJ}/\text{cm}^2$. A comparison of the laser fluence needed for cleaning to the one necessary for melting resulted in a value of 0.35 which corresponds to a cleaning threshold fluence of about $110\ \text{mJ}/\text{cm}^2$ deduced from the known fluence [23–25] of about $310\ \text{mJ}/\text{cm}^2$ for melting of a surface layer corresponding to the optical penetration depth of molten Si.

The same cleaning threshold was found for PS spheres with diameters of 235 nm and 300 nm. These results are not shown in the graph for the sake of clarity. At fluences above

$170\ \text{mJ}/\text{cm}^2$ more than 90% of the particles are removed after 20 cleaning steps. For comparison, the threshold where a (bare) Si surface would start to melt at the laser parameters used here is $270\ \text{mJ}/\text{cm}^2$. The difference of a factor of 3 in the cleaning and melting threshold is a considerable advantage with respect to industrial application where surface damage has to be strictly avoided.

In order to study the influence of the particle material on the cleaning efficiency we used silica spheres with diameters of 800 nm and 500 nm and alumina particles with a mean diameter of 300 nm. Once again we obtain the same threshold as for PS spheres (Fig. 5) and the same dependence of the cleaning efficiency on the laser fluence. Thus the cleaning threshold is independent of both particle size and material for the particles investigated. Experiments using slightly different laser parameters ($\lambda = 583\ \text{nm}$, FWHM = 2.5 ns and 7 ns, as well as $\lambda = 532\ \text{nm}$ and FWHM = 2.5 ns) revealed again the same cleaning threshold as reported above [17].

4 Discussion and conclusion

The objective of the experiments presented here was to investigate the physics of particle removal during the steam laser cleaning process. In order to control the particle properties (size, material) we chose monodisperse spherical particles as contaminants. From the identical results obtained for these spheres and the irregularly shaped Al_2O_3 particles (see Figs. 4, 5) we infer that colloids are a realistic model system. Application of these spherical particles that were dispersed as isolated contaminants on the sample allowed us to obtain quantitative information on the cleaning efficiency for a specific particle size as we did not face the problem of agglomeration of the species common for the Al_2O_3 particles [29].

We have investigated the cleaning efficiency of the steam laser cleaning process as a function of laser fluence ($\lambda = 532\ \text{nm}$, FWHM = 7 ns) for different particle sizes ranging from 60 nm to 800 nm and for PS and SiO_2 spheres. In contrast to observations in a different “dry” laser cleaning process [4] we did not find different cleaning thresholds for the different particles, but one universal threshold for all inves-

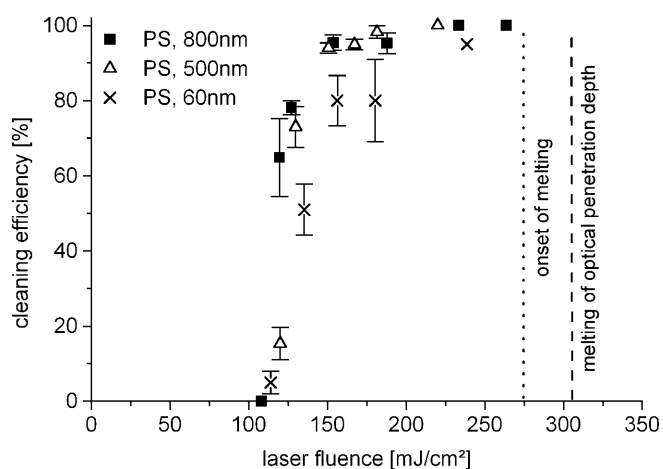


Fig. 4. Experimentally determined cleaning efficiency as a function of applied laser fluence for various PS spheres. The cleaning threshold is size-independent and exhibits a steep increase above the onset of cleaning

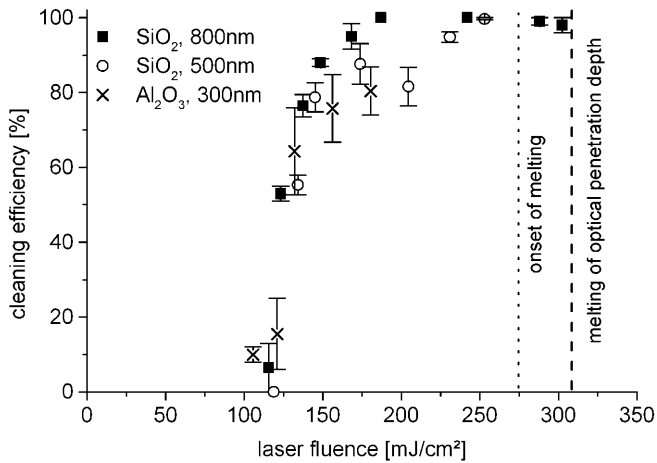


Fig. 5. Experimentally determined cleaning efficiency as a function of applied laser fluence for particles of different geometry, material and size. A material- and size-independent threshold and a steep increase of the cleaning efficiency was monitored

tigated contaminants at a laser fluence of 110 mJ/cm². This observation is also in contrast to a recent theoretically predicted particle-dependent cleaning threshold for the steam laser cleaning by Lu and coworkers [28] and to experimental findings of She and coworkers [11] regarding the removal of Al₂O₃ particles where lower thresholds for larger particles are reported. However, these larger particles were agglomerates of smaller, arbitrarily shaped Al₂O₃ particles and a thicker (μm) liquid layer was used which makes a direct comparison with our experiments difficult and might be an explanation for the different results.

Previous studies [27] on bubble nucleation on bare surfaces have shown that the liquid has to be superheated to a certain extent before bubbles are formed. Numerical computations of temperature profiles for the liquid layer implementing the 1D heat equation [26] and temperature-dependent material properties yield a laser fluence of about 50 mJ/cm² to reach the boiling temperature of the liquid and thus allow bubble nucleation. As the liquid temperature at 110 mJ/cm² is much higher we assume a scenario of superheating also for our experiments and conclude that the value of the universal cleaning threshold of 110 mJ/cm² is determined only by the onset of bubble nucleation. The universality of the threshold in the steam laser cleaning process implies that the maximum acting forces in this process are well above the adhesion forces. Cleaning efficiencies of more than 90% were reached at fluence levels of 170 mJ/cm², well below the onset of melting of a bare [30] Si surface of 270 mJ/cm².

The universal cleaning threshold and the distinct difference between cleaning and melting threshold are considerable advantages with respect to possible applications over the so-called dry laser cleaning where the threshold is size- and material-dependent [4] and the efficiencies are lower [31]. Thus, steam laser cleaning allows particle removal at lower and therefore safer laser fluences, which is essential for avoiding surface modifications.

Acknowledgements. This work was supported by the Optik-Zentrum Konstanz and the EU (TMR ERB-CT98-0188 "Modeling and diagnostic of pulsed laser-solid interactions: applications to laser cleaning"). Wacker Silicon supplied the industrial silicon wafers. We would like to thank the group of C.N. Afonso, Instituto de Optica, CSIC, Madrid, for supply with GeSb-films and valuable discussions.

References

1. R. DeJulee, Semiconductor International August (1998) 64
2. V. Dobler, R. Oltra, J.P. Boquillon, M. Mosbacher, J. Boneberg, P. Leiderer: Appl. Phys. A **69**, S335 (1999)
3. J. Bardina: In *Particles on surfaces*, ed. by K.L. Mittal (Plenum, New York 1988) p. 329
4. W. Zapka, W. Ziemlich: Appl. Phys. Lett. **58**(20), 2217 (1991)
5. K. Imen, J. Lee, S.D. Allen: Appl. Phys. Lett. **58**(2), 203 (1991)
6. A.C. Tam, W.P. Leung, W. Zapka, W. Ziemlich: J. Appl. Phys. **71**(7), 3515 (1992)
7. A.C. Tam, H.K. Park, C.P. Grigoropoulos: Appl. Surf. Sci. **127-129**, 721 (1998)
8. J.B. Heroux, S. Boughaba, I. Ressejac, E. Sacher, M. Meunier: J. Appl. Phys. **79**, 2857 (1996)
9. S. Boughaba, X. Wu, E. Sacher, M. Meunier: J. Adhesion **61**, 293 (1997)
10. Y.F. Lu, W.D. Song, Y. Zhang, T.S. Low: SPIE **3550**, 7 (1998)
11. M. She, D. Kim, C.P. Grigoropoulos: J. Appl. Phys. **86**(11), 6519 (1999)
12. O. Yavas, P. Leiderer, H.K. Park, C.P. Grigoropoulos, C.C. Poon, W.P. Leung, N. Do, A.C. Tam: Phys. Rev. Lett. **70**, 1830 (1993)
13. A. Schilling, O. Yavas, J. Bischof, J. Boneberg, P. Leiderer: Appl. Phys. Lett. **69**(27), 4159 (1996)
14. O. Yavas, A. Schilling, J. Bischof, J. Boneberg, P. Leiderer: Appl. Phys. A **64**, 331 (1997)
15. P. Leiderer, J. Boneberg, M. Mosbacher, A. Schilling, O. Yavas: Proc. SPIE **3274**, 68 (1998)
16. SiO₂ 800 nm, 500 nm, PS 800 nm: Bangs Laboratories Inc., Fishers, Illinois, USA; PS 500 nm, PS 235 nm: Agar; PS 60 nm: Seradyn, Indianapolis, Indiana, USA
17. M. Mosbacher, N. Chaoui, J. Siegel, V. Dobler, J. Solis, J. Boneberg, C.N. Afonso, P. Leiderer: Appl. Phys. A **69**, S331 (1999)
18. Buehler Micropolish, Buehler LTD., Evanston, Illinois, USA
19. J.M. Liu: Opt. Lett. **7**(5), 196 (1982)
20. J. Siegel: In *Structural transformation dynamics in Ge films upon ultrashort laser pulse irradiation*, PhD thesis at Universidad Autonoma de Madrid (1999)
21. J. Solis, C.N. Afonso, S.C.W. Hyde, N.P. Barry, P.M.W. French: Phys. Rev. Lett. **76**(14), 2519 (1999)
22. In a recent publication [17] we reported an incorrect threshold of 50 mJ/cm² for steam laser cleaning with 8 ns pulses FWHM, λ = 532 nm, due to an erroneous calibration.
23. H. Kurz, L.A. Lompré, J.M. Liu: J. de Physique **10**(44), C5-23 (1983)
24. D.H. Lowndes, R.F. Wood, D. Westbrook: Appl. Phys. Lett. **43**, 258 (1983)
25. J. Boneberg: In *Dynamische Verfestigung von Halbleiterschichten nach ns-Laser-Annealing*, PhD thesis at University of Konstanz (1993)
26. J. Bischof: In *Metallische Dünnschmelzen nach Puls laserbestrahlung: Phasenumwandlungen und Instabilitäten*, PhD thesis at University of Konstanz (1996)
27. O. Yavas, P. Leiderer, H.K. Park, C.P. Grigoropoulos, C.C. Poon, W.P. Leung, N. Do, A.C. Tam: Appl. Phys. A **58**, 407 (1994)
28. Y.F. Lu, Y. Zhang, Y.H. Wan, W.D. Song: Appl. Surf. Sci. **138-139**, 140 (1999)
29. D.R. Halfpenny, D.M. Kane: J. Appl. Phys. **86**(12), 6641 (1999)
30. It should be pointed out that the light intensity underneath the particles will be locally increased due to focusing effects. Studies of this phenomenon are in progress
31. M. Mosbacher, V. Dobler, J. Boneberg, P. Leiderer, CLEO/Europe - EQEC '98, CPD2.12 (1998)