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Influence of storage time on laser cleaning of SiO_2 on Si

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ABSTRACT The influence of the 'storage time' τ_s on the threshold fluence ϕ_{cl} and the efficiency in dry laser cleaning is investigated. τ_s denotes the time between the deposition of particles and the cleaning. As a model system we employed silica spheres with diameters of 500 nm and 1500 nm on commercial silicon wafers and single-pulse KrF excimer laser radiation ($\tau_{FWHM} = 28$ ns). For the 1500-nm silica spheres, ϕ_{cl} was found to increase from about 65 mJ/cm^2 to 125 mJ/cm^2 for storage times of 4 h and 362 h, respectively. For 500-nm silica spheres the increase in the threshold fluence was less than 20% for storage times up to 386 h.

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1 Introduction

Dry laser cleaning (DLC) is a technology for the removal of particles or thin contamination layers from solid surfaces. Among the most important parameters are the laser fluence and wavelength, the pulse duration, the particle size, the type of particle, the substrate material, etc. Note that in the past DLC experiments were just performed in ambient atmosphere, although humidity has a significant influence on the cleaning process.

Adhesion of particles to surfaces is a complex phenomenon [1]. It plays an important role in different fields like semiconductor fabrication, micromechanics, optics, pharmacology, etc. [2]. In laser cleaning applications, the adhesion of particles to the substrate has to be overcome to provide particle removal [3].

Dry laser cleaning is normally optimized by increasing the cleaning forces via tuning the laser power, wavelength, pulse duration, and/or the pulse shape. Obviously, the cleaning efficiency depends on the strength of adhesion which, for a particular system, usually does not depend on time. For particles smaller than 10 microns in diameter, the Van der Waals force is the dominant adhesion force. This force causes deformation of the particle and/or the substrate. It can be elastic or plastic [4], depending on their tensile strengths. Plastic deformations are well known for systems where the particles and/or the substrate have low yield strength.

Even with the investigated system, which consists of such firm materials as silica spheres on silicon wafers, non-equilibrium, time-dependent deformation plays an important role. It significantly increases the laser cleaning threshold fluence. Deformation of the spheres has been observed directly by means of scanning electron microscopy (SEM).

2 Experimental setup

Cleaning was performed in vacuum with a KrF excimer laser (Lambda Physik LPX 205) which has a wavelength of 248 nm and a pulse duration of 28 ns (FWHM). The pulse energy is controlled by an adjustable dielectric attenuator. A beam splitter, which is placed between the attenuator and the target, enables in situ measurements of the pulse energy. The experiments were performed in a vacuum chamber. Prior to irradiation, the chamber was evacuated for 3 h and heated during the first 35 min of pumping to 37.7 ± 0.5 °C to lower residual adsorbents, in particular water. Cleaning was performed at 26.5 ± 1.5 °C and a pressure lower than 2×10^{-4} mbar.

The substrates used were (100) silicon wafers (Wacker Siltronic). The SiO_2 particles were supplied by Bangs Laboratory Ltd. These particles have a size distribution which is specified to be between 1% and 10% of the average size. It should be noted that at present about 50 short-range orders are known for SiO_2 and that different structures result in different material parameters.

The particles were deposited on the Si wafer by spin coating. The delivered colloidal solution was rarefied in isopropanol. Mostly, single 1500-nm silica spheres were homogeneously distributed on the wafer. Spin coating turned out to be less satisfactory for smaller particles. The ratio of single particles vs. particles in clusters was lower for the 500-nm particles.

The cleaning efficiency was determined by counting the particles with digitizing software. In each counting process, a digitized image is created, which makes it possible to compare exactly the same position on the sample before and after cleaning. As a consequence, low cleaning efficiencies can be

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detected, though relative uncertainties are quite large in this region.

3 Results

3.1 *Silica spheres with* 1500-nm *diameter*

After deposition of particles, the samples were stored up to nearly 800 h. Equilibrium is reached after about 400 h of storage, where no further increase in the laser cleaning threshold fluence was observed. No significant change in the cleaning behavior was found during the first 100 h of storage. For all storage times, it was possible to reach nearly 100% cleaning efficiency, but the laser cleaning threshold fluence increased from $\phi_{cl} = 65 \pm 5\,\mathrm{mJ/cm^2}$ to $125 \pm 8\,\mathrm{mJ/cm^2}$ (Fig. 1). Deformation of 1500-nm silica spheres takes place mainly during times between about 100 h and 400 h after deposition. Before and after this period, ϕ_{cl} remains constant within the accuracy of the measurements (Fig. 2).

The dependence of ϕ_{cl} on τ_s is a typical s-shaped curve. This may indicate that a transition from one equilibrium state to another equilibrium state takes place. The simplest approximation which describes such a transition with an exponential departure and approach to the equilibrium points $\phi_{cl}(0)$ and $\phi_{cl}(\infty)$ is given by

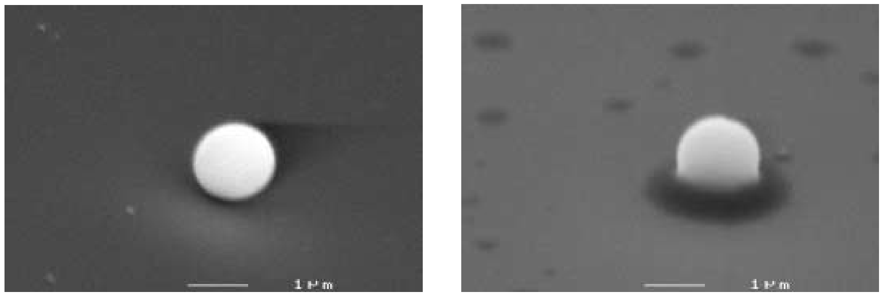

FIGURE 3 SEM pictures of 1500-nm SiO_2 particles for **a** $\tau_s = 17$ h and **b** $\tau_s = 1350$ h. The tilting angle was in all cases 60°

$$\phi_{cl}(\tau_s) = \phi(0) + \frac{\phi(\infty) - \phi(0)}{\exp\left((\tau_{tr} - \tau_s)/\Delta\tau\right) + 1} \quad (1)$$

A fit to the data yields $\phi_{cl}(0) = 62\,\mathrm{mJ/cm^2}$ and $\phi_{cl}(\infty) = 129\,\mathrm{mJ/cm^2}$, with a transition time $\tau_{tr} = 250$ h, and the transition time scale $\Delta\tau = 48$ h. The transition times for 500-nm particles are comparable, while the change in threshold is significantly lower.

Deformation is clearly seen in the SEM pictures (compare Figs. 3a and b). For better visibility, the pictures were taken at an angle of incidence of 60°. The deformation is most probably plastic and develops over the large storage times investigated in the experiments. A separate question is what causes this deformation? Plastic deformation may be related to the poor tensile strength of the silica spheres, which by no means consist of stoichiometric fused quartz. It may contain a significant percentage of hydrogen. The density of such microspheres was reported to be $1.96\,\mathrm{g/cm^3}$ (manufacturer information – Bangs Laboratories) vs. $2.2\,\mathrm{g/cm^3}$ for bulk quartz.

For fused quartz, compressive and tensile strengths are $1.1 \times 10^{10}\,\mathrm{dyne/cm^2}$ and $4.8 \times 10^8\,\mathrm{dyne/cm^2}$, respectively [5]. In the region of adhesive contact, both compressive and tensile stresses exist. Their values can be estimated from

$$p_{VdW} \sim \frac{F_0}{S_{ad}} \sim \frac{2\pi r\varphi}{2\pi r h_0} \sim \left(\frac{Y_{avg}}{2\pi}\right)^{2/3} \varphi^{1/3} r^{-1/3} \quad (2)$$

Here, φ is the work of adhesion, S_{ad} is the contact area, and Y_{avg} is the average Young modulus of the substrate and the particle with radius r. For details see [6]. For typical values and $d = 1500$-nm particles, this yields $2.2 \times 10^9\,\mathrm{dyne/cm^2}$. This is larger than the tensile strength of bulk fused quartz. This dependence on particle radius suggests that plastic deformation should be larger for smaller spheres (for $d = 500$-nm particles $p_{VdW} \sim$

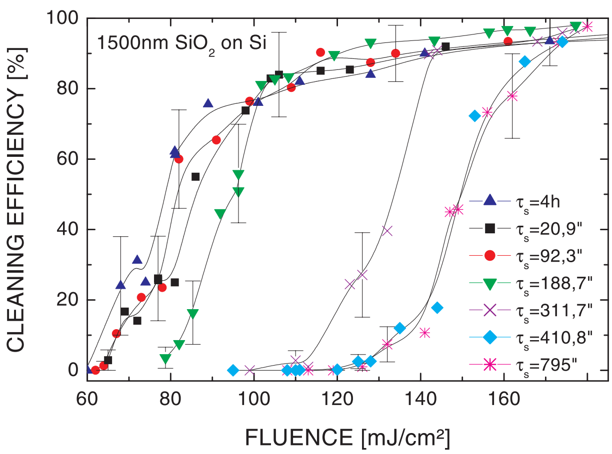

FIGURE 1 Cleaning efficiency vs. storage time for 1500-nm SiO_2 on (100) Si and 248-nm KrF laser radiation ($\tau = 28$ ns). The pressure within the chamber was $p < 1.6 \times 10^{-4}$ mbar after 3 h pumping and heating to 37.9 ± 0.3 celsius

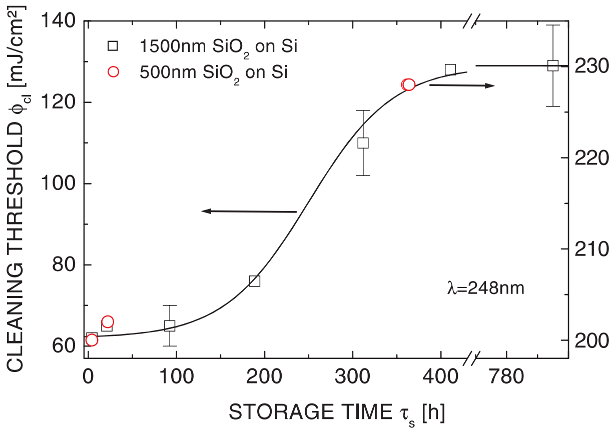

FIGURE 2 Dependence of the cleaning threshold on storage time derived from the data in Figs. 1 and 4. The *solid curve* is calculated from (1)

3.2×10^9 dyne/cm^2). This is in contrast to the experiments.

Another reason for the changes in shape (Fig. 3) could be related to the formation of chemical bonds between the particles and the native oxide layer on the silicon surface. Such a chemical reaction will lead to an increase in adhesion on its own, i.e. an effective increase of surface energy φ with time τ_s. Furthermore, it will increase deformation and stresses, which may finally again result in plastic deformation.

The third possibility is the chemical build up of SiO_2 in the interstice between the particle and the surface, which probably includes solid-state diffusion in the oxide film or in the particle.

3.2 *Silica spheres with* 500-nm *diameter*

The maximum storage time investigated for these particles was almost 400 h. The laser cleaning threshold fluence increased from $\phi_{cl} = 200 \pm 10\,\mathrm{mJ/cm^2}$ to $228 \pm 10\,\mathrm{mJ/cm^2}$ for times τ_s of 4 h and 364 h, respectively (Fig. 4). This is in agreement with SEM images, which indicated that the shape of 500-nm silica spheres does not change significantly for different storage times. The maximum increase of the laser cleaning threshold fluence is less than 20% for times τ_s such that 4 h $\leq \tau_s \leq$ 364 h.

The efficiency plots for the 500-nm particles should be taken with caution. The fraction of objects that can be perceived as single particles in optical investigations was typically 10%–20%. The majority of objects were agglomerates of two to five particles. Note that one cannot unambiguously identify the shape of particles by optical means in this size range. To prepare a sample with a large concentration of isolated 500-nm particles is difficult, as the particles start agglomerating already in the solution.

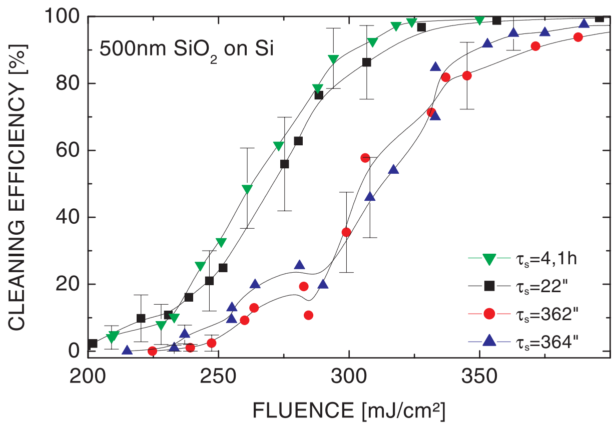

FIGURE 4 Cleaning efficiency vs. storage time for 500-nm SiO_2 on (100) Si and 248-nm KrF laser radiation ($\tau = 28$ ns). The pressure within the chamber was $p < 2 \times 10^{-4}$ mbar after 3 h pumping and heating to 37.7 celsius

Investigations with digitizing software suggest that smaller objects get cleaned somewhat earlier. At the same time both 0% and 100% cleaning efficiencies can be established pretty accurately. In the first case the pre- and post-cleaning pictures are identical. Thus (hypothetical) single particle cleaning efficiency curves should have marginally smaller thresholds, and they should be shifted to somewhat lower fluences for the intermediate efficiencies. Probably, a somewhat sharper increase in the initial stage can be expected.

4 Conclusions

It is demonstrated that deformation is relevant even in DLC of firm materials such as silica spheres on silicon substrates. The increase in the contact area results in stronger adhesion and higher laser cleaning threshold fluences. Deformation is more pronounced for 1500-nm particles and directly detectable via SEM investigations. For 500-nm particles, deformation was detected only indirectly via a shift in the laser cleaning threshold fluence. Deformation of the silicon substrate was not observed with the techniques employed in the present experiments.

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