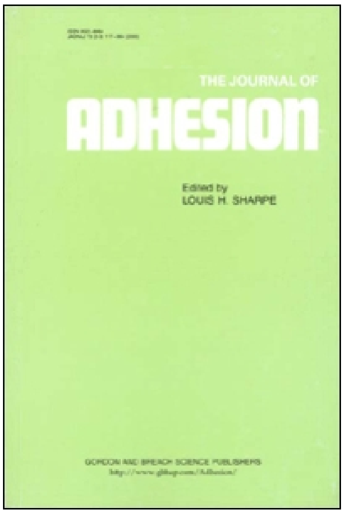

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Liquid Explosive Evaporative Removal of Submicron Particles from Hydrophilic Oxidized Silicon Surfaces*

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A pulsed CO_2 laser-based system, operating at a wavelength of 10.6 μm, was used as a cleaning tool to remove particles as small as 0.1 μm from hydrophilic, oxidized silicon surfaces. The laser beam served as a fast heating source to induce the explosive evaporation of a water film deposited on the particle-contaminated surface. The resulting explosive forces were high enough to expel particles from the surface efficiently. The contaminant particles used were 0.1 μm alumina, 0.1–0.2 μm silica, and 0.1 μm polystyrene latex.

For each of these, the cleaning efficiency was monitored as a function of the laser fluence, the thickness of the deposited water film and the number of cleaning cycles. Whatever the nature of the particles, the cleaning efficiency was characterized by an upper limit of the energy density, determined to be 1.5 J/cm^2, at which *substrate* damage occurred. At all lower laser fluences, the removal efficiency was *particle*-dependent.

The thickness of the deposited water film was varied by changing the time of exposure of the surface to water vapor, the vapor flow being fixed at 4700 ml/min. An exposure time of 1.5 s was found to be the most effective. Increasing the number of cleaning cycles permitted the evaluation of the effect of the zeta potentials of the particles with respect to that of the surface.

Keywords: Laser cleaning; liquid explosive evaporation; particle removal; adhesion; contamination; hydrophilic silicon surface

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INTRODUCTION

Efficient sub-half-micron particle removal is currently one of the most challenging tasks facing the microelectronics industry [1,2]. The conventional liquid chemicals-based cleaning techniques are no longer efficient for particles of 0.1µm and smaller. A review of these techniques, their advantages and shortcomings, may be found in References 3 and 4. The necessity of removing such small particles after each processing step requires the development of new cleaning techniques [4]. Among them, the laser-induced particle removal technique is one of the most promising [5–12].

In our approach, a pulsed CO_2 laser beam (at a wavelength of 10.6 µm) is used as a fast heating source to induce the explosive evaporation of a liquid water energy transfer medium, condensed from the vapor phase onto the contaminated surface: [5–9] the resulting forces are high enough to expel submicrometer particles efficiently from the surface.

Such an approach was previously used by us [8,9] to investigate thoroughly the cleaning of as-received silicon and other surfaces, none of which underwent any special cleaning treatment. However, rigorous, reproducible control of the natures of the surfaces of both substrates and contaminant particles is needed to permit in-depth investigations of the adhesion forces and removal mechanisms.

Particle adhesion arises from three sources [13]: i) van der Waals (more properly, London) forces; ii) electrostatic forces; iii) capillary forces (experimentally found for particles larger than those considered here). Reference 13 contains the results of adhesion calculations, based on adjustable parameters and supposing pure materials with uncontaminated, high energy surfaces; these results generally correspond to the values and trends found experimentally [13], and indicate that van der Waals forces predominate. However, the absence of contamination is the exception, rather than the rule, for high energy surfaces (both particles and substrates); this is because such surfaces are thermodynamically driven to reduce their surface free energies by reaction with the components of ambient air. Thus, gold, for example, with no stable oxide at room temperature, reacts with ambient hydrocarbon contaminants to form reticulated hydrocarbon overlayers [14, 15]; silicon, on the other hand, reacts with both hydrocarbon and oxygen contaminants [16, 17]. Further, in our laboratory we frequently use ultrapure inorganic and metallic standards; X-ray photoelectron spectroscopy (XPS), which probes the outer 50–100 Å of the surface, *invariably* shows these standards to be highly contaminated by carbon and oxygen, despite the fact that destructive analyses showed them to be ultrapure.

The results we report here deal with the laser-induced removal of particles from hydrophilic, oxidized silicon surfaces, obtained using a modified RCA cleaning proccess [3]. Substrate and particle surfaces were analyzed by XPS while the evolution of the wettability of the substrate surface was monitored by optical interferometry. Conditions leading to a well controlled, reproducible substrate surface were then adopted to investigate the roles of the nature of the contaminant, laser fluence, water film thickness and the number of cleaning cycles on the efficiency of cleaning. Some results emphasized the role of the zeta potentials of particle and substrate, while others suggested the existence of chemical reactions at the particle/substrate interface.

EXPERIMENTAL

The experimental set-up given in Figure 1 has been detailed elsewhere [8,9]. The 3×3 cm^2 square multimode beam from the pulsed CO_2 laser (Lumonics, TEA 841-2), with a pulse energy of 0.95 J and a duration of 0.2 µs, was focused onto the substrate surface. The substrate was mounted face down on a computer-controlled *XYZ* stage. The *XY* axes permitted the scanning of the surface to perform the cleaning of large areas, while the *Z* axis was used to vary the laser beam energy flux in the range 0.5–3 J/cm^2, with an estimated error of 10%. The deposition of the water film at the irradiated spot before the laser pulse triggering was accomplished using a stainless steel chamber, half-filled with deionized (DI) water; the water was heated to 37 °C using a stainless steel isolated heater. The temperature was measured using a stainless steel isolated thermometer. In this way, the water was in equilibrium with its saturated vapor. A nitrogen gas input of 4700 ml/min, connected to a flowmeter and valves, was used to carry a controlled volume of water vapor toward the gas output. This output was connected to a stainless steel nozzle, heated to about 40 °C, whose end was held near the surface to be cleaned. On reaching

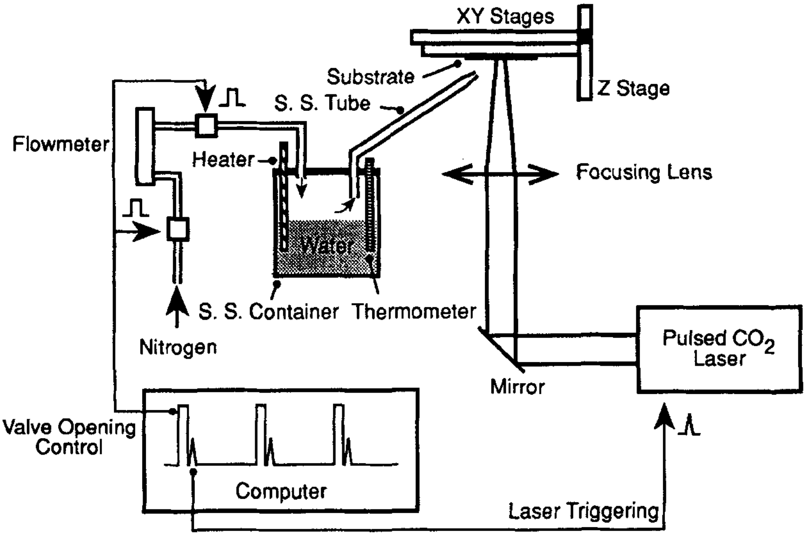

FIGURE 1 Schematic of the CO_2 laser-induced, vapor-assisted particle removal set-up; S.S.: stainless steel.

the colder target surface, the vapor condensed to a water film. A pulse-timing unit permitted the water vapor to be deposited for periods ranging between 0.5 and 3.5 s; 0.1 s later, four laser pulses were triggered at intervals of 0.1 s. To perform a cleaning over a sufficiently large area, the wafer was linearly stepped 3 mm after each vapor burst, four laser pulse, sequence. The area cleaned was a square 24×24 mm^2, whose center corresponded to that of the wafer. While the areas of adjacent spots overlapped, the extent of overlap varied with the laser beam flux, which was controlled by varying the Z axis, as described above; this overlap varied from $\sim$40% at higher fluxes to $\sim$75% at lower fluxes.

The substrates were 100 mm ⟨100⟩ Si wafers, whose surfaces were cleaned and made hydrophilic using a modified RCA recipe [3]. This consisted of (i) 0.05:1:5 SC1, 80 °C, 10 min; (ii) 1:1:6 SC2, 80 °C, 10 min; (iii) 0.5 % HF etch; (iv) boiling isopropyl alcohol, 2 min; (v) 0.05:1:5 SC1, 80 °C, 10 min. Here, SC1 (standard clean 1) refers to $NH_4OH{:}H_2O_2{:}H_2O$ and SC2, to $HCl{:}H_2O_2{:}H_2O$; SC1 is used to remove particles and organic contaminants and SC2, to remove metals.

To contaminate the surfaces artificially with particles, we used a particle generator (Particle Measuring Systems, Inc.). Filtered air was driven through a nebulizer with the desired particles suspended in DI water. The droplets so generated were carried through a tube and a drying chamber, resulting in particle-laden dry air. This air exited through a nozzle which could be manually moved over the wafer surface. To avoid any cross-contamination, a set of dedicated nebulizers, drying tubes and chambers was used for each type of contaminant particle. The actual particles used were: i) 0.1 μm alumina (Al_2O_3) from Beta Diamond Corp.; ii) 0.1–0.2 μm agglomerated silica (SiO_2) from Beta Diamond Corp.; iii) 0.1 μm polystyrene latex (PSL) from Particle Measuring Systems, Inc..

XPS and optical interferometry were used to characterize particle and substrate surfaces. Both a laser scanning surface inspection system (Particle Measuring Systems Inc., SAS 3600) and a dark-field optical microscope were used to characterize surface contamination and cleaning efficiency. The laser counter uses scattered light to classify particles according to their PSL-spherical equivalents, from 0.1 to 10 μm. It permitted us to perform quantitative measurements on particle removal efficiency over a defined analysis area, which was a circle 20 mm in diameter inside the 24 × 24 mm^2 cleaned square. Furthermore, dark-field optical microscopy was used, in conjunction with scanning electron microscopy, to investigate the quality of the substrate surface in order to define rigorously a process window in which defects were not induced at the surface by the laser beam.

RESULTS AND DISCUSSION

Surface Conditions and Contamination

Both the contaminant particles and the oxidized Si substrate were evaluated by XPS. The substrate surface was found to contain a small amount of surface carbon contaminant, as seen in the survey scan in Figure 2a. At higher resolution, Figure 2b, the C1s region has several components, at 285.0 eV (hydrocarbon), at 286.8 eV (hydroxyl or ether) and at 289.4 eV (acid or ester). Clearly, the surface is contaminated to some extent with a partially oxidized hydrocarbon layer. These studies were made within minutes of having prepared the surfaces.

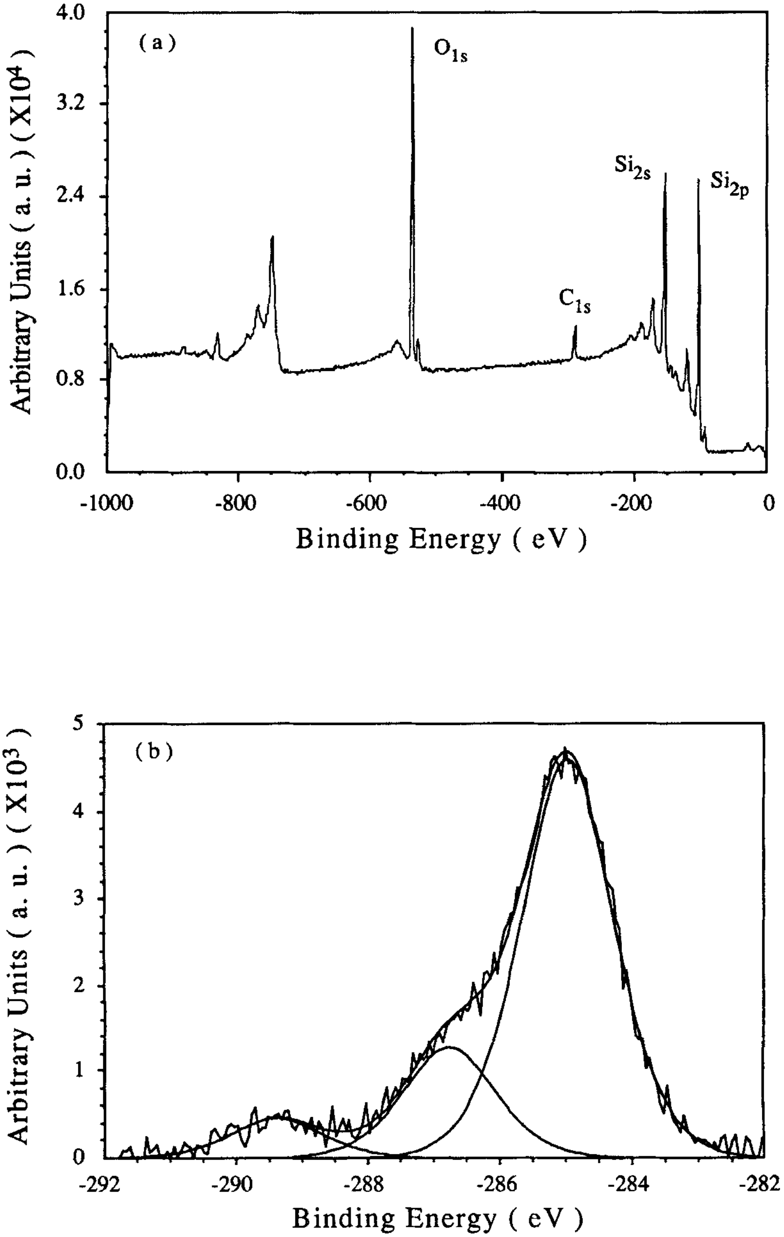

FIGURE 2 XPS spectrum of hydrophilic, oxidized Si substrate: a) survey scan; b) high resolution C1s scan.

Similar surface contamination results were found for the alumina and silica particles: each is contaminated with a thin, partially oxidized hydrocarbon layer. It is these surfaces which come in contact on particle deposition.

Using an optical interference set-up similar to that reported in Ref. 18, and a water vapor supply unit similar to that used in the experimental set-up described above, we were able to monitor the evolution of the wettability of the surfaces with time. Figure 3 contains two optical micrographs of a condensed water spot on our surface, two hours and eight hours after the oxidation step; the exposure of the surface to the vapor burst was 0.1 s. The interference fringes show constant thicknesses; the film becomes thinner from the center to the edge. Dry spots were observed within the water film; these spots first appeared as localized points (Fig. 3a), enlarging and increasing in number with time (Fig. 3b). These spots, not present on initial cleaning, are certainly due to the carbon contamination, which results in a decrease in the surface tension to the point where wettability is lost (water has a surface tension of $\sim$72 mJ/m^2, while that of a hydrocarbon surface is $\sim$34 mJ/m^2). Instead of a continuous film, the water condenses gradually as microdroplets, as is clearly seen at the upper periphery of Figure 3b. On the basis of these observations, to assure reproducible conditions, the particle contamination of the surfaces and the laser cleaning experiments were performed immediately after the surface oxidation step.

XPS of the hydrophilic, oxidized silicon surfaces has shown a trace of contaminant hydrocarbon at the surface. While the stability of such surfaces to further contamination varies with the cleaning procedure, [16] it is clear from our optical and XPS data that contamination proceeds quickly here, and that reproducibility required that substrates be used immediately after the RCA clean. The inorganic particles used to contaminate this surface are themselves already contaminated with organic surface layers, although these contaminant surface layers may not totally cover the particles.

Laser Particle Cleaning Efficiency

Figure 4 contains typical histograms of the number of particles on the surface, as a function of their size, before and after one laser cleaning

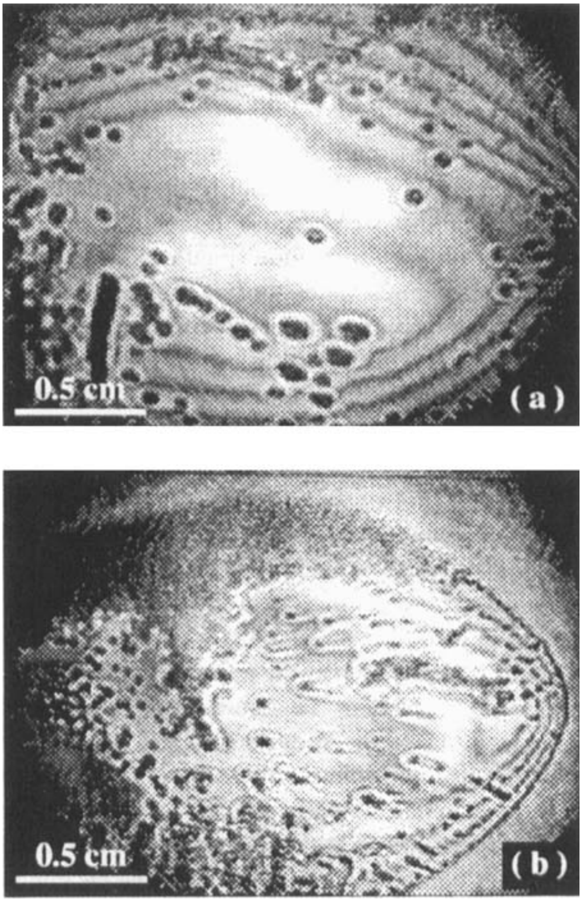

FIGURE 3 Optical micrographs of water spots condensed on oxidized silicon surface after a) 2 h and b) 8 h. Vapor burst duration: 0.1 s.

scan. The beam energy flux was 1 J/cm^2 and the nitrogen volume was 118 ml (a N_2 flow of 4700 m/min and a valve open time of 1.5 s). For silica, the initial distribution was centred at 0.1μm, with negligible particle clustering, as was the case for PSL particles. For alumina, some clustering was observed. After one laser cleaning scan, the number of particles was markedly reduced, whatever the nature of the contaminants. However, for alumina, counts for sizes larger than 0.2 μm were still not negligible. For the three kinds of particles, it should

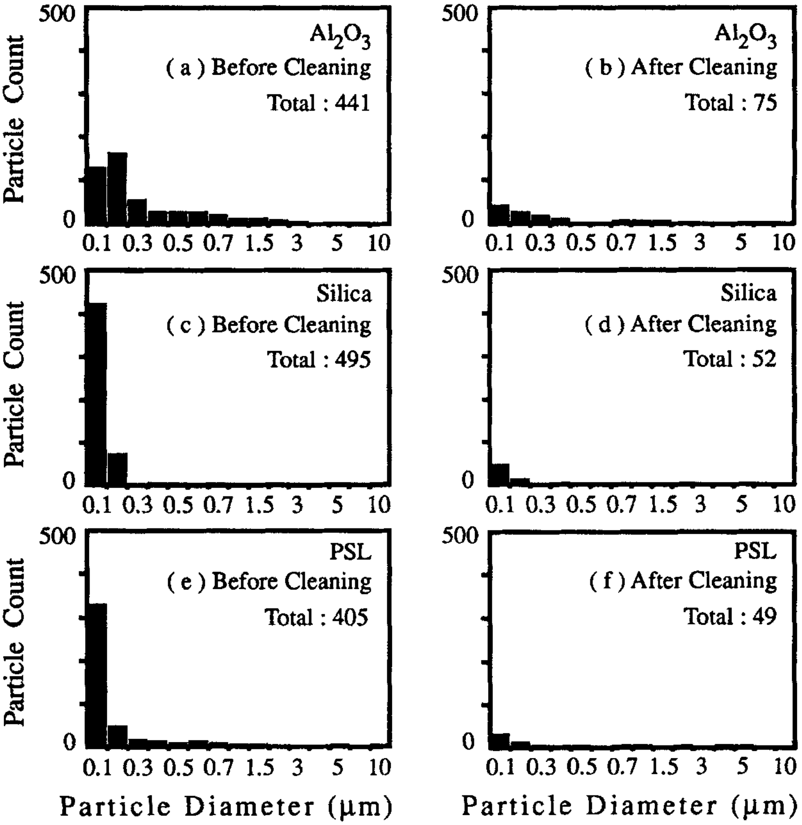

FIGURE 4 Size distribution of silica, alumina and PSL particles before and after one laser cleaning scan of the surface; energy beam density: 1 J/cm^2; vapor burst duration: 1.5 s.

be emphasized that the smallest size affected by the cleaning was 0.1 μm.

The effect of increasing the number of cleaning scans on the efficiency of the process is contrasted in Figure 5a for 0.1 μm silica and PSL and, in Figure 5b, for 0.1, 0.2 and 0.5 μm alumina. Increasing the number of cleaning scans had no effect in the case of silica and PSL particles, for which one scan was sufficient to reach a minimum level of about 40 particles (Fig. 5a). In the case of alumina, such a minimum was observed after 3 scans (Fig. 5b). The fact that a higher number of scans was required to reach the lower limit with alumina may be related to the fact that, at a pH of 7 (measured DI water pH), this

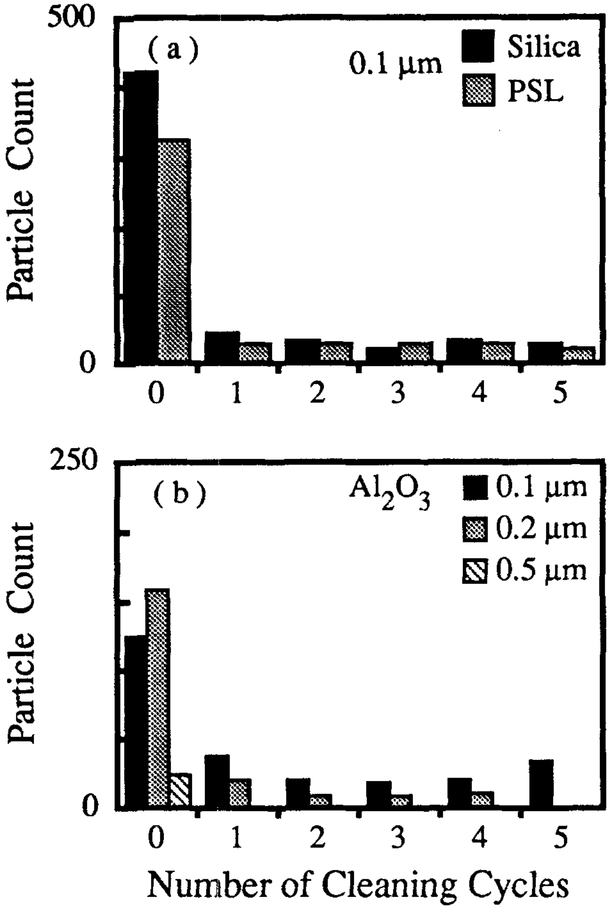

FIGURE 5 Influence of the number of scans on the cleaning efficiency of a) 0.1 μm silica and 0.1 μm PSL particles and b) 0.1, 0.2 and 0.5 alumina particles. Laser energy beam density: 1 J/cm^2; vapor burst duration: 1.5 s.

material has a positive zeta potential, of opposite sign to that of our oxidized surface [19, 20]. That is, the zeta potential at the isoelectric point (pH = 7.4–8.6 for alumina) is zero by definition, positive below and negative above; the isoelectric point of SiO_2 is at a pH of 1.8–2.2. The zeta potential of the PSL particles depends on the suspension solution history but, on the basis of our results, appears to be negative, leading, as for silica, to repulsive interactions with our surface.

The influence of the laser beam energy flux on the removal efficiency is presented in Figure 6 for a nitrogen volume of 118 ml and five cleaning scans. In the case of silica and PSL, the cleaning efficiency was almost the same whatever the beam energy flux, taken in the range 0.5–1.5 J/cm^2. The only exception was the removal of 0.1 μm silica particles at an energy flux of 0.5 J/cm^2, whose effectiveness was slightly reduced with respect to higher fluxes. We attribute this to

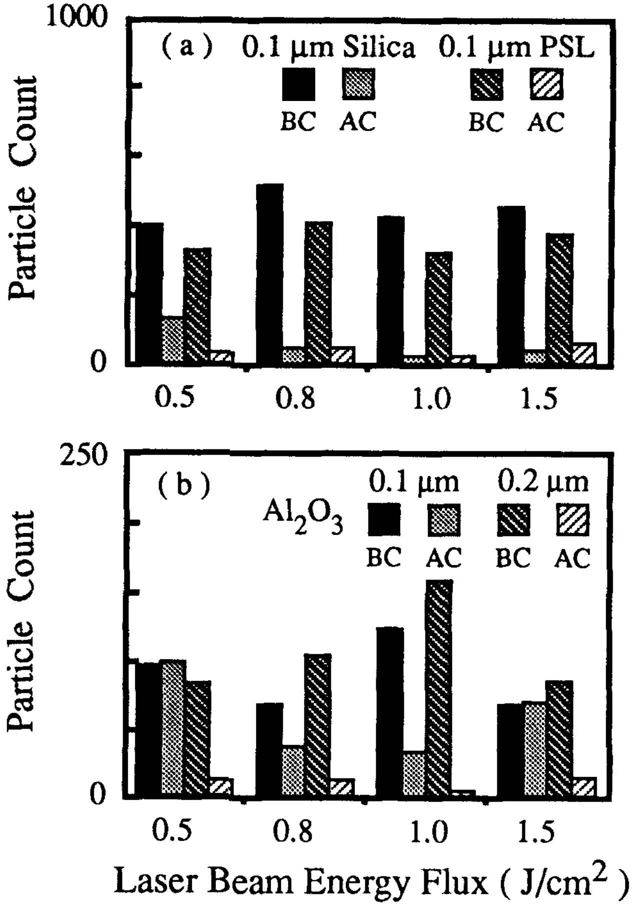

FIGURE 6 Influence of the beam energy density on the removal efficiency of 0.1 μm silica, PSL and alumina particles; vapor burst duration: 1.5 s; 5 cleaning scans; BC: before cleaning; AC: after cleaning.

reaction at the hydrated SiO_2/SiO_2 interface, which increased particle adhesion, requiring a higher laser flux.

Alumina particles were best removed at 0.8 and 1 J/cm^2. At 0.5 or 1.5 J/cm^2, the number of remaining particles was almost the same as that before cleaning. For the lowest energy flux, a connection with interaction at the hydrated interface is again suggested; the reason for the slight loss in efficiency at 1.5 J/cm^2 may be related to the onset of beam-induced localized surface modifications, which could enhance the interaction between the particles and the surface. The removal of 0.2 μm and larger Al_2O_3 particles was efficient and unaffected by varying the flux in the range investigated.

This less efficient removal of both silica and alumina particles suggests that, while both are covered with partially oxidized hydrocarbon layers, this coverage is not total. Thus, both silica and alumina are capable of hydrating to interact with the hydrated substrate surface, initially through hydrogen bond formation; indeed, this is the basis for reaction with silane ester adhesion promoters. To overcome such interactions requires an increased beam energy flux.

Beyond 1.5 J/cm^2, whatever the nature of the particles, defects were observed on the cleaned surface by both dark-field and scanning electron microscopies. These defects consisted of ripples and were similar to those reported in laser processing studies [21]. Such defects could be attributed to localized interference phenomena at the surface between incident and scattered radiation. A detailed description of these defects is beyond the scope of this article and will be included in a forthcoming publication.

Figure 7 shows the effect of varying the valve open time before firing the laser pulses. In this way, the thickness of the deposited water film was varied. The laser beam energy flux was 1 J/cm^2 and five cleaning scans were used. Whatever the nature of the particles, the best removal efficiency was obtained with a valve open time of 1.5 s, which corresponds to a nitrogen volume of 118 ml. For shorter open times, the thickness of the water film was probably not sufficient to assure an effective laser beam absorption to induce efficient film heating. The absorption depth of a beam of 10.6 μm wavelength in bulk water is 10 μm; we estimate the optimal thickness of the deposited water layer to be 8 μm. For longer open times, the thickness is larger than this absorption depth, so that effective laser-induced heating

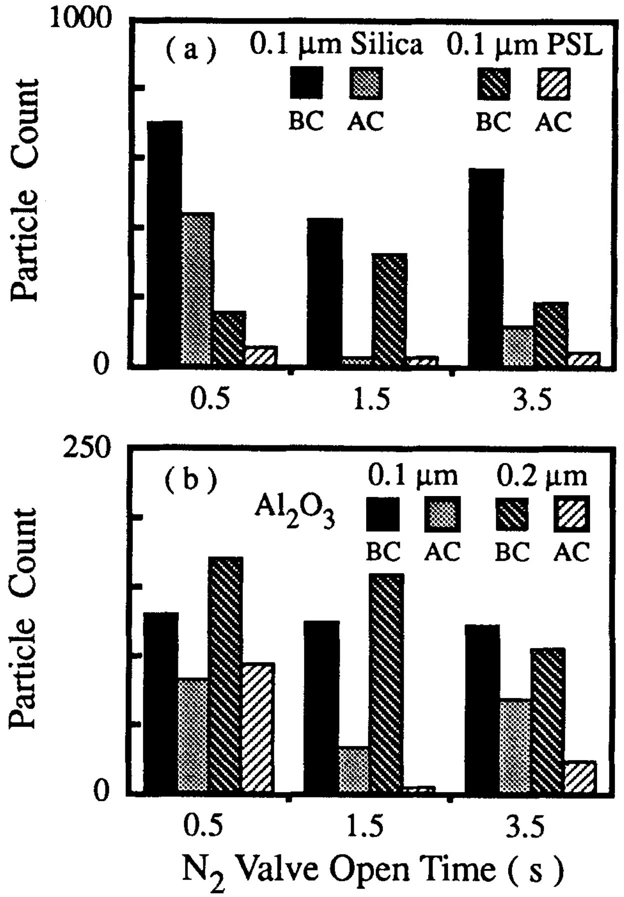

FIGURE 7 Influence of the vapor burst duration on the removal efficiency of 0.1 μm silica, PSL and alumina particles; beam energy density: 1 J/cm^2; 5 cleaning scans; BC: before cleaning; AC: after cleaning.

occurs mainly at the top of the water film, where explosive evaporation is less efficient in ejecting particles.

CONCLUSION

Our ability to control our surface in a reproducible, understandable manner, and to use pure, monodisperse (albeit contaminated) particles, has permitted us to identify several important features in our laser-based method of particle removal. First, by the laser flux must be greater than some minimum value (0.5 J/cm^2), so as to overcome particle-substrate interactions; this is followed by a slight decrease in particle removal efficiency for alumina and silica, just below the onset of the substrate damage threshold (1.5 J/cm^2). Secondly, an optimum thickness of the deposited water layer is required. Below this value, the amount of water deposited is not enough to clean the surface optimally while, above this value, the laser beam is absorbed by the outer surface and the explosion is not optimally directed.

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