11-1-2002

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Removal versus ablation in KrF dry laser cleaning of polystyrene particles from silicon

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(Received 29 March 2002; accepted 9 July 2002)

Direct absorption and melting of 0.2, 0.5 and 1.1 μm polystyrene particles on a Si substrate irradiated by 248 nm excimer laser radiation was found to contribute to their dry laser removal via a ''hopping'' mechanism at cleaning thresholds of 0.05, 0.1, and 0.16 J/cm^2, respectively. Ablation of these particles, which starts near the beginning of substrate deceleration at fluences above 0.4–0.5 J/cm^2, suppresses particle removal due to ablative recoil momentum. At fluences above a second cleaning threshold of 0.7 J/cm^2 particles are completely evaporated without any visible surface damage of the Si substrate.
[DOI: 10.1063/1.1503854]

I. INTRODUCTION

Reduction of particulate contaminants is a basic requirement in the rapidly growing field of nanotechnology, especially in micro- and nanoelectronics. Different cleaning strategies (ultrasonic cleaning, wiping, brush scrubbing, high-pressure jet spraying, etching, and megasonic cleaning)[1] are currently being tested for removal of dust particles one fifth to one tenth the size of current 130 nm integrated circuits linewidths[2] from critical (predominantly silicon and lithographic mask) surfaces. An environmentally friendly, cost-effective noninvasive cleaning process with a high throughput will be required.

Dry laser cleaning (DLC) is a well-recognized technique for micron and submicron particle removal from semiconductor devices (e.g., Si wafers or lithography masks)[1–5] and high density memory devices.[6] Although DLC is frequently described as a ''trampoline''[1] or ''hopping'' effect[7] that occurs during fast thermal expansion of a nanosecond laser-heated substrate or an absorbing particle, respectively, a variety of optical, thermal, acoustic, mechanical, thermochemical, and mass transport phenomena are involved in the DLC process,[3–5] complicating its mechanism and development of a general theory of this phenomenon.[5] Laser beam characteristics (wavelength, pulse width, and intensity) and intrinsic material properties are key parameters in DLC, and they determine the predominance of optical or thermal phenomena.[4] For nanosecond laser pulses thermal aspects of laser–matter interaction such as, in order of increasing laser fluence, thermal expansion, melting, and ablation, seem to be more important. We report here the negative interference between DLC and laser ablation under nanosecond KrF excimer laser irradiation for micron and submicron absorbing polystyrene (PS) particles on Si substrates, and measure the relative density and actual size of PS particles as a function of incident laser fluence.

II. EXPERIMENT

In this work we used an excimer laser (Lambda Physik, LPX 210) with the following characteristics: wavelength of 248 nm, energy of 0.6 J/pulse ($\pm$3%), nearly rectangular and Gaussian fluence, F, distribution in horizontal and vertical directions, respectively, with characteristic dimensions of $x = 5$ mm and $\sigma_y = 1.5$ mm and pulse width τ [full width at half maximum (FWHM)] of 20 ns. The laser beam with a 1 cm wide vertical slit aperture in the center, was attenuated by UV transmitting color filters (Corning Glass Works) and was focused on the Si(100) wafer sample at normal incidence by a fused silica lens with a focal length $f = 8$ cm. The Si wafer was mounted on a three-dimensional stage and irradiated in a pattern of spots using single laser shots. Part of the beam was directed by a beam splitter to a pyroelectric detector (Gentec ED-500) for energy measurement of each pulse using a LeCroy 9360 storage oscilloscope. The excimer laser and oscilloscope were triggered manually in single-shot mode using a pulse generator (Stanford Research Systems DG 535).

Single-shot DLC was performed in ambient atmosphere for Si wafers covered with monodisperse PS particles of diameters, D = 0.2, 0.5, and 1.1 μm (Surf-Cal™ grade, density of 1.05 g/cm^3, relative standard deviation in D less than 1%) from Duke Scientific Corp. Particles were deposited on the Si wafer samples from a suspension of monodisperse PS particles in a water/ethanol mixture maintained at 55 °C using an airbrush.[8] Typical particle densities and average aggregation numbers for 0.2, 0.5, and 1.1 μm PS particles were

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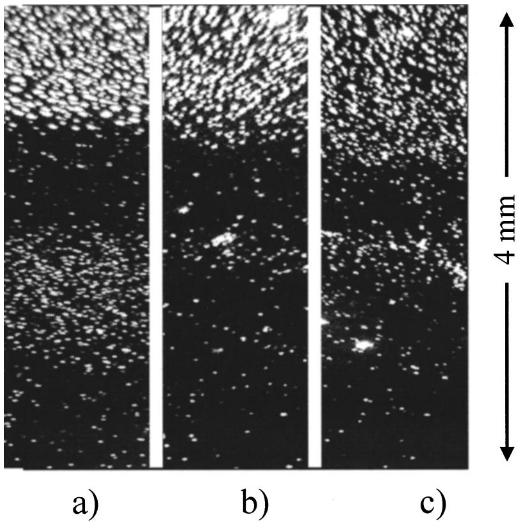

FIG. 1. Dark field optical microscopy images of the upper half of the axially symmetric, Gaussian lateral profile DLC spots: (a) 1.1, (b) 0.5, and (c) 0.2 μm PS particles on Si substrates.

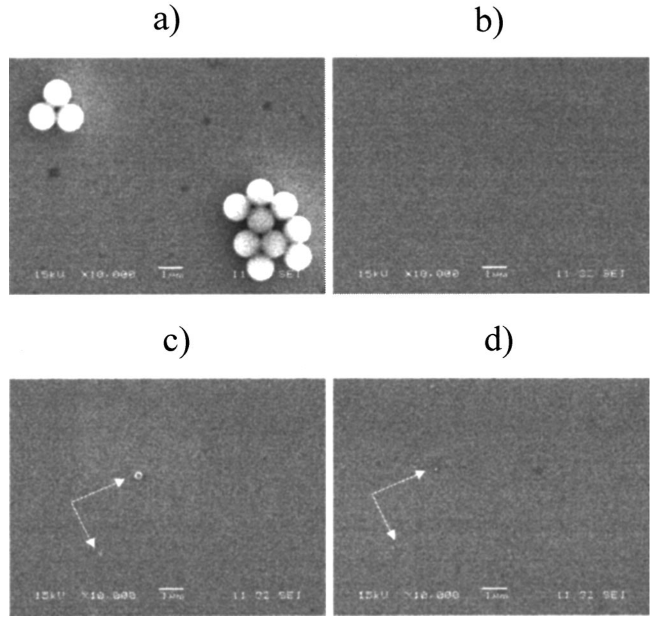

FIG. 2. SEM images (frame size 13×10 μm^2) of a (a) nonirradiated spot and (b)–(d) DLC spots of areas I–III, respectively for 1.1 μm PS particles on a Si substrate. The arrows point to partially ablated PS particles in (c) and (d).

about 10^4, 10^5, and 10^5 cm^{-2} and 3–4 particles/cluster, respectively. Since the particle deposition and removal experiments were done in normal laboratory air, the samples were occasionally contaminated by large dust particles several microns in size.

Analysis of laser-irradiated spots (including measurements of the size of the area cleaned, particle size, and density) was made using dark-field optical microscopy (Mitutoyo WH and Olympus BH-2 microscopes) and scanning electron microscopy (SEM) (JSM 5900). The right half of each irradiated spot was treated with acetone to dissolve the PS particles in order to test the Si substrate for surface damage underneath the particles. Digitized dark field images of scattered light from the irradiated spots were processed (including inversion and subtraction of background) using SCION IMAGE software (Scion Corp.). Spatial profiles of the normalized scattering intensity (the ratio of scattered light intensity taken vertically across laser-irradiated spots and an arbitrary unirradiated area) were used to measure the degree of DLC for different irradiated regions.

III. RESULTS AND DISCUSSION

The Gaussian fluence distribution in the vertical direction of the excimer laser beam and a single-shot exposure allowed the study of the phenomenological nature of DLC and measurement of the cleaning efficiency directly as a function of the fluence at one laser-irradiated site. As shown in Fig. 1, different surface topologies like the maximum lateral clean area (I), band-like area with particles (II), and center clean area (III) were revealed vertically across the Gaussian direction of the laser-irradiated spot for all three wafers covered by 1.1, 0.5, and 0.2 μm PS particles. Size-dependent DLC thresholds, F_1, measured at the distinct external edges of area I, are equal to 0.049±0.006, 0.1±0.01, and 0.16±0.02 J/cm^2 for 1.1, 0.5, and 0.2 μm PS particles, respectively, and are consistent with data in the literature for ambient conditions but at a laser wavelength of 532 nm and a pulse length of 7 ns (0.050±0.005, 0.074±0.009, and 0.154±0.008 J/cm^2 for the same particle sizes).[4] The agreement with prior experiments is quite good, although it is not expected that the thresholds will be the same for different laser irradiation conditions. More importantly, the expected trend toward higher removal thresholds for smaller particles is observed. Two prominent axially symmetric bands of PS particles (area II) nearer to the spot center and exhibiting well-defined, nearly size-independent thresholds F_2 of 0.43 J/cm^2 [0.37±0.04 (1.1 μm), 0.42±0.08 (0.5 μm), and 0.49 ±0.06 (0.2 μm) J/cm^2] were observed (Fig. 1). Finally, an apparently clean (area III) was found in the center of the irradiated spots at fluences above a size-independent threshold F_3 of 0.7 J/cm^2 (the corresponding F_3 values for 1.1, 0.5, and 0.2 μm PS particles are 0.70, 0.72, and 0.67 J/cm^2). The features observed were reproducible at five different peak fluences over the range of 0.45–2.4 J/cm^2.

Close inspection of the irradiated spots with SEM and optical microscopy has shown shrinking of the PS particles in areas II and III [Fig. 2(c) and 2(d)] relative to the initial particle size in Fig. 2(a). This effect was especially pronounced for separate particles observed in area III where the laser fluence was much higher. The blue spectral shift for visual white light scattering of particles (predominantly for 1.1 μm PS particles) that was observed in areas II and III is an additional indication of a postirradiation particle size decrease. At the same time, optical microscopy and SEM examination of acetone cleaned samples have not exhibited any micron-scale ($\geqslant$0.1 μm) damage in areas I–III [Fig. 2(b)] at fluences up to 2 J/cm^2, i.e., well above the Si melting threshold at 248 nm of 0.5–0.75 J/cm^2.[9] However, at the highest fluence of 2.4 J/cm^2 several nearly centrosymmetrical damaged spots 10–20 μm in size with radiating star-like cracks

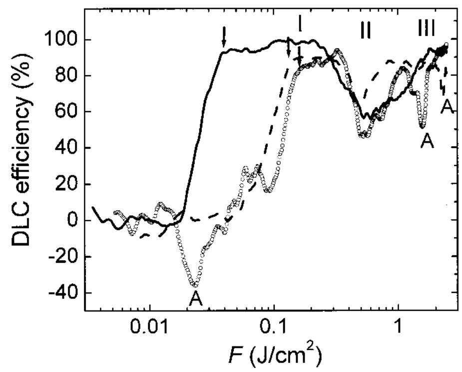

FIG. 3. DLC efficiency as a function of the laser fluence for the spots in Fig. 1 (solid curve, dashed curve, and open circles correspond to vertical scans across Figs. 1(a)–1(c), respectively). Areas I–III, artifact features, and the "first" DLC thresholds are marked by symbols, I, II, III, A and arrows, respectively.

were observed; they probably originated on large separate dust particles initially present on the substrate.

The dependence of cleaning efficiency on the laser fluence (Fig. 3) for PS particles of 0.2–1.1 μm was obtained from the spatial profiles of the normalized scattering intensity, considering an absence of light scattering as the result of complete cleaning. This assumption is not valid in area II where particle shrinkage influences light scattering considerably (Fig. 1). High DLC efficiency (near 90%) in a single shot was observed in area I for all particle sizes. The cleaning efficiency in area III was comparable. Additional artifact minima of these curves marked by the "A" resulted from the presence of single large dust particles [cf. Figs. 1(a)–1(c)] deposited occasionally during handling of the samples.

The main difference between the experimental conditions of this and previous work[4] on DLC of PS particles lies in the significant PS absorption at the 248 nm laser wavelength $[\alpha^{PS}(248\,\mathrm{nm}) = 6.3\times10^3\,\mathrm{cm}^{-1}]$[3,10] due to the $S_0 \rightarrow S_1$ electronic transition in a PS phenyl group[11] compared to negligible PS absorption at 532 nm.[4] In contrast to the observations at 532 nm of enhanced Si substrate damage under the PS particles,[4] no damage was observed on the particle-contaminated substrates irradiated by the 248 nm laser beam even well above the Si melting threshold. At 532 nm, the transparent PS particles can serve to "focus," i.e., locally enhance, the laser electromagnetic field, resulting in submicron-size damage (local melting and evaporation of the Si substrate) underneath particles.

Because of the PS absorption at 248 nm one may expect direct laser heating to result in the melting of PS particles at temperatures of 110–125 °C.[12] The 248 nm surface melting threshold for bulk polystyrene in air, F^M, is about 0.03 J/cm^2.[10] Size-dependent melting thresholds $F^M(D)$ of 0.05 (1.1 μm), 0.03 (0.5 μm), and 0.03 (0.2 μm) J/cm^2 as well as a value of $F^M \approx 0.03\,\mathrm{J/cm}^2$ were estimated from calculations of the maximum rise in temperature at the end of a excimer laser pulse on the front and back sides of PS particles using a simple linear absorption model,[13] heat capacity $C_p^{PS} \approx 1.6\,\mathrm{J/cm^3K}$, and thermal diffusivity $\chi^{PS} \sim 10^{-3}\,\mathrm{cm^2/s}$.[12] The effects of local scattering and thermal transport to the Si substrate were neglected in these rough temperature calculations. The large thermal coefficient of expansion for molten PS particles (typically $10^{-4}\,\mathrm{K}^{-1}$ relative to $10^{-6}\,\mathrm{K}^{-1}$ for Si)[12] may decrease their DLC thresholds because of an enhanced "hopping" effect. On the other hand, the motion of molten particles may be significantly damped by viscoplastic deformation of the molten particles. This last phenomenon has been used to explain difficulties in removal of molten metal particles from Si by DLC.[1] Nevertheless, because the "trampoline" effect of a Si substrate is weaker at 248 nm relative to that at 532 nm because of the lower substrate absorbance (0.4 for 248 nm, 0.63 for 532 nm) and longer excimer laser pulse (20 ns) compared to 7 ns in previous work,[4] the hopping effect for molten or near-molten PS particles seems to be significant enough to affect some DLC thresholds at these wavelengths.

Another consequence of PS absorption at 248 nm is shown in the laser ablation and of PS particles decomposition to styrene monomers[14] competing with DLC at fluences above the ablation threshold of the material in air of 0.1–0.12 J/cm^2.[9,13] For such a low thermal conductivity material as polystyrene, the onset of ablation near the threshold fluence occurs at the end of the pulse, even for 20 ns pulse lengths, since the material effectively stores the incident laser energy. For increasing total fluences, the onset of ablation shifts toward the beginning of the laser pulse. For a temporal profile of the excimer laser pulse at a total fluence of 0.4 J/cm^2, the onset of laser ablation is calculated to occur nearly simultaneously with the deceleration of the Si substrate.[4,5] Ablation may suppress DLC completely, and produce a high enough counterforce from the recoil momentum of ablation products from the top surface of the particles, particularly for the inhomogeneously heated large PS particles. Thus, the appearance of PS particles in area II at total fluences F_2 above 0.37–0.49 J/cm^2 may correspond to the ablative suppression of DLC. This ablation effect may also be influenced by Si substrate surface melting, which should occur at nearly the same fluence of 0.5 J/cm^2.[9,15] Si surface melting and the resulting contraction[9] would also decrease the maximum acceleration of the substrate and PS particles or increase the deceleration of the Si substrate,[9,15] depending on whether the Si melt threshold is reached in the acceleration or deceleration phase.

The second cleaning threshold, F_3, observed in area III, when multiplied by the effective absorption coefficient, $[1\text{-}R^{PS}(248\,\mathrm{nm})]\alpha^{PS}(248\,\mathrm{nm})$, where $R^{PS}(248\,\mathrm{nm})$ is the reflectivity and $\alpha^{PS}(248\,\mathrm{nm})$ the absorption coefficient of PS, respectively, corresponds to the volume energy density necessary to cause ablation. The energy needed to heat polystyrene to an ablation temperature of $1.2\times10^3\,°\mathrm{C}$,[16] and to evaporate it in the form of a styrene monomer (evaporation enthalpy $\Delta H_{evap} \approx 2.9\times10^3\,\mathrm{J/cm^3}$) is about $4.6\times10^3\,\mathrm{J/cm^3}$. The corresponding absorbed energy density calculated using the threshold fluence $F_3 \approx 0.7\,\mathrm{J/cm^2}$, the previously referenced absorption coefficient, and a reflectivity value characteristic for other polymers at 248 nm (6%),[17] is $4.2\times10^3\,\mathrm{J/cm^3}$ for all particle sizes used. These estimates are consistent with the observed ablation of PS particles in area III.

IV. CONCLUSIONS

Direct laser heating and melting of absorbing 0.2–1.1 μm PS particles on a highly absorbing Si substrate at a laser wavelength of 248 nm were found to be significant for the DLC process, decreasing the dry cleaning thresholds due to the higher thermal expansion of molten particles. Laser ablation of PS particles seems to suppress DLC at the nearly size-independent threshold (0.37–0.49 J/cm^2 for 0.2–1.1 μm PS particles) via ablative recoil momentum. At fluences above the second cleaning threshold of 0.7 J/cm^2 nearly complete ablation of PS particles is observed. The ''negative'' interference effect of laser ablation on DLC for PS particles on a Si substrate may provide a better understanding of the DLC dynamics. DLC and laser ablation of PS particles at 248 nm as well as surface melting of the Si substrate were found to occur without damage to the substrate up to a laser fluence of 2 J/cm^2.

ACKNOWLEDGMENTS

The authors acknowledge assistance with experiments by P. S. Davis and R. S. Kadambala.

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