CO_2 laser-assisted removal of submicron particles from solid surfaces

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(Received 11 September 1995; accepted for publication 12 December 1995)

A CO_2 laser-based system was used to provoke the vapor-assisted removal of contaminating particles from different kinds of surfaces. Particles of alumina, silicon carbide, boron carbide, and cerium dioxide, with a size as small as 0.1 μm, have been efficiently removed from silicon, gold, and silicon dioxide surfaces. The dependence of the cleaning efficiency on the laser fluence was investigated; a threshold was found at 0.65 J/cm^2 and the efficiency was highest for a fluence ranging from 2.9 to 3.2 J/cm^2 for silicon, and 3.2 J/cm^2 for gold and silicon dioxide surfaces. The amount of the water vapor which condenses at the surface was also found to play a major role, the best results being obtained with a condensed thickness calculated to be 6 μm. The zeta potential value of the contaminant particles with respect to that of the surface greatly influences the cleaning process. © *1996 American Institute of Physics.* [S0021-8979(96)05806-2]

I. INTRODUCTION

Surface contamination by particles is one of the most serious problems faced by the microelectronic industry,[1] and more than 50% of yield losses may be attributed to it.[2] As device features shrink, smaller and smaller particles become potential killer defects. In today's submicron integrated circuit technology, particles of 0.1 μm diameter or less are potential sources of circuit failure.[3,4]

Because the total elimination of contamination sources during IC processing operations is not presently achievable,[4] surface cleaning is the most frequently applied step during circuit manufacture. The most widespread cleaning techniques in the industry make use of liquid chemicals[5] which are themselves sources of contamination.[4] While ultrapure, low particulate grade chemicals and water could be used, they suffer from the drawback of increased cost. Moreover, these wet cleaning methods are not compatible with the process integration trend in which cluster tools play a major role. Another shortcoming of these techniques is their inability to efficiently remove particles of 0.1 μm size and smaller.

Over the last few years, the development of new, liquid chemicals free, cleaning techniques has attracted an increasing interest.[6] Laser cleaning is one of these promising new dry techniques. A pulsed laser beam irradiating a surface is used as a fast, localized heating tool to expel the contaminating particulates. An energy transfer medium is generally used at the surface to improve the process efficiency. Using water as such a medium, the first studies were carried out by Allen and co-workers,[7–9], where a CO_2 laser (10.6 μm) removed 1 μm Al_2O_3 particles from silicon substrates: the laser radiation was absorbed by deposited water which explosively evaporated, generating forces sufficient to expel the particles. In a similar fashion, Zapka and co-workers[10–13] used an excimer laser (248 nm); the main difference here lies in the fact that the liquid energy transfer medium was transparent to the laser beam, which was absorbed by the substrate surface that, in turn, transferred energy to the liquid film. In this case, it was demonstrated that the fluence required for efficient cleaning was far smaller than in the case of CO_2-based process.[12] However, the use of a CO_2 laser is more attractive because it makes the cleaning process independent of the nature of the substrate surface. This advantage caused us to adopt it.

For both series of studies described above, the experimental investigations focused on the monitoring and characterization (nucleation, particle removal threshold and shock wave generation) of the explosive evaporation, in order to understand the particle removal mechanism;[7–9, 10–13] no quantitative data were presented on the concentration of particles on the contaminated and post-cleaned surfaces, and only low magnification scanning electron microscope micrographs were shown. Moreover, particulate types were limited to alumina, polystyrene latex, and gold, while the effect of the nature of the contaminants on the cleaning process efficiency was not discussed. Furthermore, in the case of the CO_2 laser-based process, the investigation was limited to 1 μm and larger alumina particles.

In the work we report here, the CO_2 laser-induced, water vapor-assisted, removal of particles of size ranging from 0.1 to 10 μm was thoroughly investigated as a function of the laser fluence, the thickness of the energy transfer medium (water in our case) and the nature of the surfaces and particles. Silicon (Si), aluminum (Al), gold (Au), and silicon dioxide (SiO_2) surfaces were considered. Alumina (Al_2O_3), magnesium oxide (MgO), silicon carbide (SiC), cerium dioxide (CeO_2), boron carbide (BC), and diamond (C) particles were used as contaminants.

II. EXPERIMENT

The experimental setup is presented in Fig. 1. A TEA CO_2 laser (Lumonics 840), emitting at 10.6 μm in the pulsed mode was used. The output energy was 0.9 J, with a pulse duration of 0.25 μs. The multimode beam was vertically deflected with a mirror at 45° and then focused on the sample surface with a converging lens whose focal length was 30 cm.

To deposit the water film in a reproducible manner only at the irradiation location, a volume of nitrogen gas was sent through a container, half-filled with deionized (DI) water heated to 40 °C, to carry the vapor to a heated (50 °C) copper

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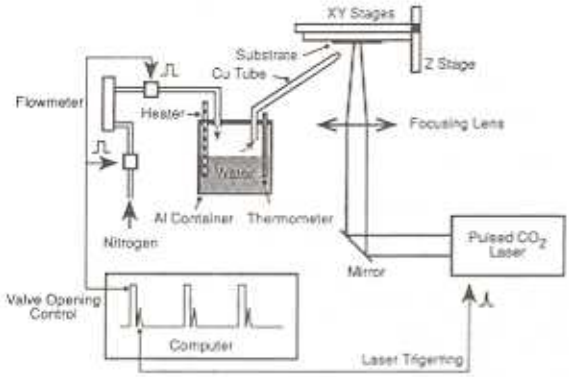

FIG. 1. Schematic of the CO_2 laser-induced, vapor-assisted particle removal setup.

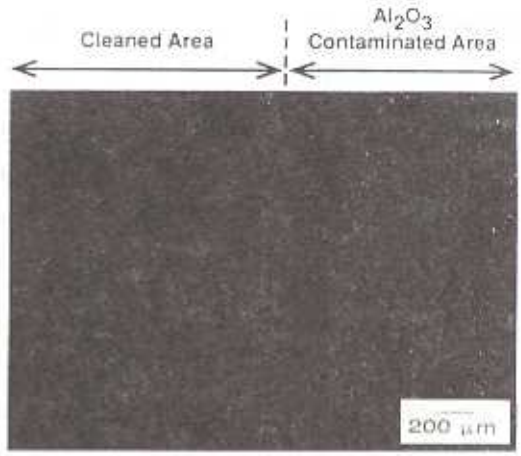

FIG. 2. Dark-field optical micrograph (50×) of a Si surface contaminat with 0.1 μm-diam Al_2O_3 particles. The edge of the cleaned region is show Laser fluence: 2.9 J/cm^2.

nozzle held near the surface to be cleaned. A pulse-timing unit permitted first nitrogen to expel the water vapor for a given time, varying between 0.1 and 2.5 s, resulting in condensation on the colder target surface. The laser irradiation was then triggered; absorption of the beam by the water film led to explosive evaporation, generating forces of sufficient magnitude to eject particles from the surface.

The sample was mounted face down on a computer-controlled XYZ stage. Displacement perpendicular to the optical axis (XY) was used to scan the wafer surface in order to clean large areas, while displacement along the optical axis (Z) was used to vary the laser fluence from 0.5 to 25 J/cm^2. The laser fluence values were determined by dividing the laser pulse energy by the laser spot area at the substrate surface. The error in such a determination was calculated to be of 10%.

To reduce the probability of contamination by ambient air, the experimental setup was located in a class 500 cleanroom, under laminar flow hoods which provide a class 10 working zone.

The samples used were bare 100-mm-diam (100) Si wafers, some of which were covered with a 100 nm thermally grown SiO_2 layer to provide SiO_2 surfaces (O_2-N_2 atmosphere, 1280 °C). Aluminum- and gold-coated surfaces were obtained by evaporating about 100 nm of these materials on bare Si wafers. The particles used to contaminate the surfaces were Al_2O_3, MgO, SiC, CeO_2, BC, and C, all supplied by the Beta Diamond Corp.

The deposition of the particles was carried out using two different methods: electrostatic attraction or colloidal solution spinning. For electrostatic attraction, a potential of 3 kV was applied to the substrate and particles held on a spatula were gently moved a few centimeters away from the surface. The resulting concentration of deposited particles was sufficiently large to permit the observation of the localized cleaned region. To obtain lower and more uniform particles concentration, less than 1 mg of particles powder was mixed with 100 ml of DI water; drops of this colloidal solution were deposited to form uniform film on the surface and spun at 4000 rpm.

To observe particles on any kind of surfaces, an optical microscope (Nikon, MM-11U) in either bright- or dark-field mode was used at magnifications ranging from 50× 1000×. The bright-field illumination was used to dete damage to the surface as well as film contamination. TI dark-field mode was used to detect submicron particles ov large areas (about 9 mm^2). To obtain quantitative data particle contamination on Si surfaces over large areas, a las scanning particle counter (Particle Measuring Systems, Inc SAS 3600) was used. This tool uses scattered light to classi particles according to their spherical equivalents from 0.1 10 μm. It must be emphasized that the counter is calibrate for polystyrene latex (PSL) spheres; because of the diffe ences in the optical properties of the contaminants and th calibrating PSL, the diameters obtained are PSL-sphe equivalent.

III. RESULTS AND DISCUSSION

Static laser cleaning was carried out by first sending burst of vapor to the substrate surface; the vapor pulse dura tion was 1 s and a flow rate of 5000 ml/min was used, givin a volume of nitrogen of 83 ml. Precisely 0.2 s after the vapo burst, three laser pulses were triggered at intervals of 1 s assure that all the water had been removed; an interval of 1 between the successive pulses was chosen to avoid excessiv heating of the substrate. This procedure was repeated fiv times for a complete cleaning of the irradiated spot whos size was 7×7 mm^2 for a fluence of 2.9 J/cm^2. Figure 2 show a typical dark-field optical micrograph of the edge of a re gion cleaned using a laser fluence of 2.9 J/cm^2. The particle used were 0.1 μm Al_2O_3 and the surface was silicon. Th right side of the micrograph corresponds to the originall contaminated surface, while the left side is a region of th cleaned area.

Cleaning by laser rastering was done by moving th sample 3 mm in a straight line after every burst of vapor an three laser pulses. This was repeated over a 24×24 mm square and analysis was carried out with the particle counte in a circle 20 mm in diameter inside the cleaned square. I

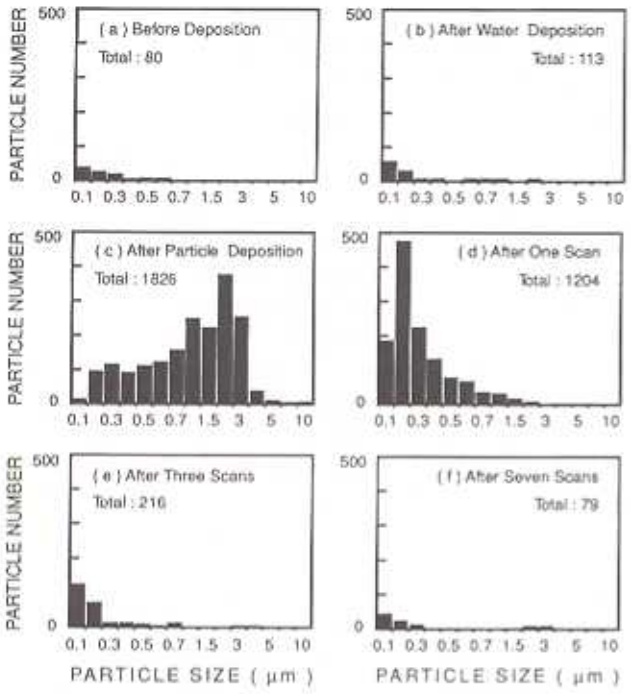

FIG. 3. Histograms obtained with the particle counter, showing 0.1 μm Al_2O_3 particles on a Si substrate (a) before treatment, (b) after deposition of DI water only, (c) after deposition of particles, and (d)–(f) after cleaning by laser rastering.

Fig. 3, histograms of the numbers of particles on the surface are given as a function of their size in microns. The laser fluence used for the cleaning is 2.9 J/cm^2. Eighty particles, all smaller than 1 μm, were counted on the original surface [Fig. 3(a)]. DI water deposition without particles resulted in only a slight increase in the number of particles [Fig. 3(b)], whereas deposition of the 0.1-μm-based Al_2O_3 colloidal solution resulted in a large number of particles deposited [Fig. 3(c)]. The particles distribution was centered at a size of 2 μm. Such a shift with respect to 0.1 μm was attributed to the formation of clusters during deposition due to the high concentration of particles in the colloidal solution. Moreover, the concentration of these clusters was high enough to veil the particles which appear on the surface before deposition. As a consequence, the laser counter was not able to detect them and a reduction in the number of 0.1 μm particles was observed after the Al_2O_3 deposition [Fig. 3(c)]. After one cleaning scan [Fig. 3(d)], some particles were removed, the clusters become smaller and the largest number of particles corresponded to a size of 0.2 μm. After three scans [Fig. 3(e)], the distribution of the particle sizes had its maximum at 0.1 μm. Following seven scans [Fig. 3(f)], the number of particles reached a lower limit essentially equal to that before deposition, although, a few particles larger than 1 μm remained on the surface. These results clearly show that laser cleaning is efficient in removing alumina particles as small as 0.1 μm.

A. Variation of the amount of water

Table I shows results obtained on the removal of 0.1 μm Al_2O_3 particles from a Si substrate when the volume of nitrogen was varied by changing the vapor burst pulse duration. The data represent the number of particles after deposition and after four laser cleaning scans. For a nitrogen volume of 20 ml, cleaning was clearly inefficient because the amount of water was too small, although cleaning was efficient for volumes of 80 and 170 ml. When the nitrogen volume reached 200 ml, the amount of water on the surface became too large, and it was not completely removed during laser irradiation.

TABLE I. Influence of the flowing nitrogen volume on the number of particles on silicon surfaces before and after cleaning. The contaminant was 0.1 μm Al_2O_3. Laser fluence: 2.9 J/cm^2. Number of cleaning scans: 4. The data were obtained using the particle counter.

Volume of nitrogen	Number of particles after contamination	Number of particles after four cleaning scannings
20 ml	1965	1480
80 ml	1969	345
170 ml	1959	76
200 ml	1386	926

The minimum nitrogen volume giving adequate cleaning, around 80 ml (Fig. 3), corresponds to an estimated water thickness of 6 μm, calculated for an area of the vapor circle of 10 cm^2. The requirement of a minimum water film thickness more than 60 times the particle diameter is probably due to an incomplete coverage of the Si surface for smaller film thicknesses due to larger spacing between the condensed microdroplets. To confirm this hypothesis, we attempted particle removal with a nitrogen volume of 80 ml from a Si substrate made hydrophobic by HF etching. As can be seen in Fig. 4, cleaning was inefficient because the surface was

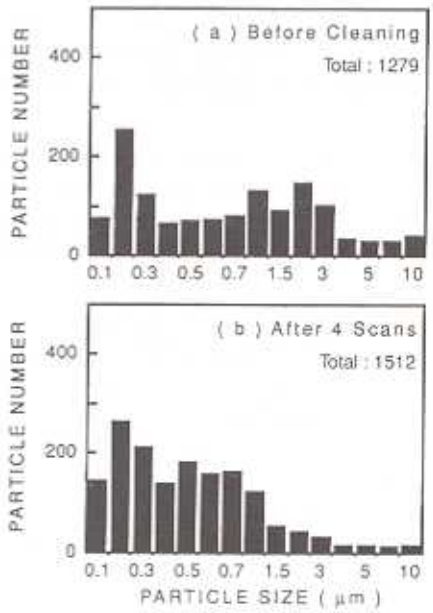

FIG. 4. Histograms obtained with the particle counter before (above) and after (below) cleaning of a hydrophobic Si substrate. Initial contamination was 0.1 μm Al_2O_3 particles.

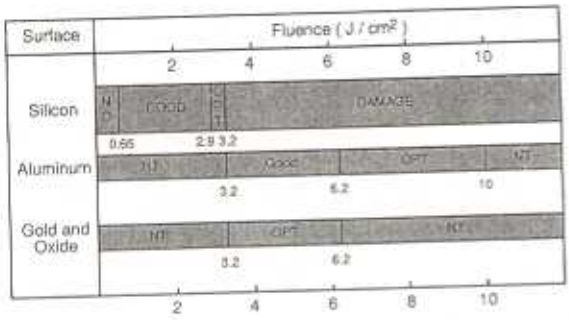

FIG. 5. Influence of the laser fluence on the cleaning efficiency for different surfaces. NO: inefficient cleaning; OPT: optimal cleaning; NT: not treated.

not uniformly covered by water, i.e., there were interstices between droplets, due to the high contact angle.

For spherical water droplets of about 10 μm in diameter irradiated by a CO_2 beam (10.6 μm), Dusel *et al.*[14] showed that the maximum temperature elevation occurred at the back (opposite to the irradiated side) of the droplet. Therefore another possible explanation of the nitrogen volume threshold is that a minimum water amount is required to obtain liquid droplets on the surface that focus the laser beam and induce a maximum film heating close to the substrate, ejecting particles more efficiently.

B. Variation of the fluence and the nature of the surface

Figure 5 shows the results for the variation of the laser fluence on different surfaces. For bare Si substrates, the results were recorded with both the optical microscope and the particle counter. For the latter, the cleanliness was assumed to be optimal when the amount of particles remaining on the surface after cleaning was essentially the same as before particle deposition. For all other surfaces, only the microscope was used because the particle counter was calibrated for Si substrates. In this case, optimal cleaning was defined as the case for which there were essentially no particles visible in dark-field mode at a magnification of 50× as shown on the left side of Fig. 2, which should be compared to the right side. Good cleaning is defined as the case in which the initial concentration is partially reduced by the cleaning process.

For Si, there is a threshold at 0.65 J/cm^2, under which cleaning is inefficient. The cleaning was good between 0.65 and 2.9 J/cm^2 and optimal between 2.9 and 3.2 J/cm^2. Over 3.2 J/cm^2, damage to the surface was observed with the optical microscope. The cleaning threshold value measured (0.65 J/cm^2) is lower than that obtained by Allen *et al.* (1.4 J/cm^2) for 1 μm Al_2O_3 particles.[8] This threshold at 0.65 J/cm^2 may correspond to the limit below which the heating of the liquid film was nonuniform and occurred only at the surface. It may also be the minimum power necessary to produce an acoustic wave at the front of the film which would be reflected by the substrate, thus ejecting water and particles. Alternatively, it may be associated with the maximum temperature that the water may reach without boiling; this temperature is given by $T_{max}=0.97T_c=309$ °C, where T_c is the critical temperature of the water.[15] Beyond 3.2 J/cm^2, ripples on the substrate surface were observed with the optical microscope. Such surface defects are similar to those widely reported in laser processing studies[16–18] and may result from interference phenomena between incident and scattered radiation at the surface.

On gold and SiO_2, cleaning was optimal between 3.2 and 6.2 J/cm^2, which means that dark-field micrographs were comparable to those obtained for Si at the optimal fluence (left side of Fig. 2). However, the cleaning of aluminum was optimal for a fluence of at least 6.2 J/cm^2, and only good at 3.2 J/cm^2. The reason for this different behavior for the aluminum surface is not yet understood; the optical and thermal properties of this material are similar to those of gold, for which the cleaning was optimal at 3.2 J/cm^2. It must be emphasized that with the dark-field microscope at a high magnification, a large amount of small scattering centers was observed at the aluminum surface which may possibly indicate an extensive roughness of the surface. The effect of roughness on van der Waals attraction forces depends on the

TABLE II. Number of contaminating particles on silicon surfaces before and after cleaning, as a function of the nature of the contaminants. Laser fluence: 2.9 J/cm^2. The data were obtained using the particle counter. The isoelectric points of some materials are also given.

Particles (Diameter)	Number of particles after contamination	Number of particles after four cleaning scannings: Size ≤1 μm	Number of particles after four cleaning scannings: Size >1 μm	Isoelectric point (pH)[a]
Al_2O_3 (1 μm)	741	88	3	5–9.2
MgO (1–5 μm)	1270	365	33	12.4±0.3
Diamond (≈0.2 μm)	818	319	0	...
CeO_2 (1 μm)	705	127	0	6.75
SiC (1 μm)	709	131	0	...
BC (1 μm)	978	180	0	...

[a]Reference 21.

TABLE III. Van der Vaals adhesion forces between 1 μm particle and a plane surface in air medium with a particle-surface separation assumed to be 1 nm. The hardness of the particles materials is also given.

Particle material on surface material	Hamaker constant[a] A_{132} (10^{-20} J)	Force[a] (nN)	Hardness of the particles materials[b] (Moh hardness scale)
Al_2O_3 on Si	19.1	16	
Al_2O_3 on Al_2O_3	14	12	9.0
Al_2O_3 on metals	20.5–27.7	17–23	
MgO on Si	17.7	15	6.0
SiC on Si	23.9	20	9.2
Diamond on Si	29.3	24	...
BC	...	...	9.3

[a]Reference 23.
[b]Reference 24.

nature of the roughness.[19] In the case of surface asperities larger than the contaminating particle size, these forces are reinforced since the effective contact area is increased. Such extended asperities may affect our aluminum surfaces and account for the particular behavior of these surfaces with regard to the cleaning efficiency.

If one considers the optical (at 10.6 μm) absorption and reflectivity, and thermal conductivity of each surface material,[20] no relationship between cleaning efficiency and these properties could be established. Such a result was expected since the radiation is absorbed in the liquid. These results confirm that CO_2 laser cleaning has the potential to remove particles on surfaces of different natures.

C. Variation of the nature of the particles

Table II shows that among all the particles used on Si surfaces, only MgO was removed with a significantly lower efficiency than Al_2O_3. The total number of MgO particles was reduced, but it was the only material for which tens of remaining particles of sizes larger than 1 μm were detected.

Taking into account the optical (at 10.6 μm) and thermal properties of the particles used,[20] no correlation between these parameters and cleaning efficiency was obvious. The thermal expansion of particles, as described by Kelley and Hovis[22] for a YAG laser, is not a dominant mechanism for CO_2 laser particle removal. Although one may suppose that the adhesion forces are functions of the nature of particles, Table III indicates that there is no relationship between our results and the calculated adhesion forces. The given values are calculated for materials in air; the presence of a liquid film may reduce the magnitude of these forces by a factor of 3–5 (Ref. 25) but should not influence their relative values. An increase of these adhesion forces through particle deformation has also to be ruled out on the basis of the hardness data given in Table III since it appears that cerium oxide has a hardness equal to that of MgO.

A more satisfactory explanation may be arrived at by considering the isoelectric points of the materials used. Table II indicates that the isoelectric point of MgO is by far the highest of all the materials used. Because the zeta potential decreases as the pH increases,[26] MgO is the only material for which the zeta potential is strongly positive in DI water. Since Si has a negative zeta potential in water,[26] the double-layer electrostatic attraction mechanism described by Donovan and Menon[26] may play a major role for MgO. While for all the other particles used, electrostatic repulsion may result in a reduction of the adhesion forces and, therefore, in a cleaning efficiency improvement, for MgO particles the adhesion forces are reinforced by the electrostatic attraction due to the opposite signs and strong difference of the zeta potentials between the particles and the Si surface.

IV. CONCLUSION

A CO_2 laser-induced, vapor-assisted particle removal system, capable of raster cleaning, was constructed and evaluated. A water film was used to absorb the 10.6 μm radiation. Its explosive evaporation resulted in the ejection of the contaminating particles. It was demonstrated that this system is efficient in removing 0.1 μm Al_2O_3 particles from Si surfaces down to a concentration of 25 particles/cm^2 for initial concentrations several orders of magnitude greater.

Cleaning efficiency exhibited a threshold at a fluence of 0.65 J/cm^2 and was optimal for a fluence varying from 2.9 to 3.2 J/cm^2 for Si surfaces, from 3.2 to 6.2 J/cm^2 for gold and oxide surfaces and a fluence greater than 6.2 J/cm^2 for aluminum. The minimum thickness of the water film necessary for efficient cleaning was calculated to be about 6 μm. The particle removal process was independent of the optical and thermal properties of both surface and particles. However, zeta potentials of opposite sign for particles and surface greatly reduced the cleaning efficiency.

ACKNOWLEDGMENTS

The authors thank J. P. Levesque for his technical assistance and Dr. B. Oliver from Nortel (Ottawa, Canada) for instructive discussions concerning cleaning strategies and contamination problems in a cleanroom environment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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