Excimer laser cleaning for microelectronics:

Modeling, applications and challenges

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ABSTRACT

Chlorofluorocarbon-free laser cleaning techniques, compatible with cluster tool processing, have been developed for application to microelectronics processing. A KrF excimer laser (248 nm) is directed toward the wafer to be cleaned and rastered over the surface which might be intentionally covered by a thin liquid layer. It is demonstrated that various types of submicrometer-sized particles including polystyrene latex (PSL), silica and alumina, can be efficiently removed, by laser cleaning, from the front sides of silicon wafers. These results are explained by a particle adhesion model, including van der Waals forces and hydrogen bonding, and a particle removal model involving rapid thermal expansion of the substrate due to the thermoelastic effect and the pressure shock due to bubble generation in the condensed water film. The results of the calculations of the adhesion and removal models are consistent with the experimental observations. In addition, the excimer laser technique was successfully used to remove micrometer-sized metallic particles (iron oxide) from the backsides of silicon wafers; such a removal represents a challenging task in today's integrated circuit technology.

Keywords: excimer laser, laser cleaning, microelectronics, metallic contamination

1. INTRODUCTION

Surface microcontamination is recognized as the main source of yield loss in integrated circuit (IC) manufacture [1-4]. It also affects device performance and reliability [3-6]. Contaminants may be particles, metallic impurities, organic materials, native oxides and adsorbed gases [2,3]. Because the total elimination of contamination sources during IC processing operations is presently not achievable [5], surface cleaning is a frequently applied after each step during circuit fabrication. The most widespread cleaning techniques in the industry are wet-chemical processes [7], which are usually based on dilute mixtures of H_2O_2 and NH_4OH, HCl or H_2SO_4 [3]. Since these liquids are, themselves, potential sources of contamination, costly ultrapure, low particulate grade chemicals and water must be used. The processing of liquids and hazardous waste disposal further increases operating costs [8], especially now that environmental issues impose more and more stringent constraints. Moreover, wet cleaning methods are not compatible with the in-situ processing trend in which cluster tools play a major role. Another important limitation of these techniques is their inability to efficiently remove particles 0.1 μm and smaller. The removal of such particles is one of the most challenging tasks the microelectronics industry has to meet in today's sub-half-micrometer IC technology.

Over the last few years, several liquid-chemical-free cleaning techniques have been developed[9]. Among these vapor- or vacuum-based methods, laser cleaning has demonstrated promising potential[10-26]. Its high efficiency in the removal of 0.1 μm particles has attracted great interest because of the simplicity of the technique, both conceptually and experimentally. It must be emphasized that this lower limit in particle size corresponds to the detection limit of currently available laser particle counters; laser cleaning might still be efficient at even lower particle dimensions.

In the present article, we give a short overview of the different approaches to the laser-cleaning of surfaces and we present a review of our work on the removal of various types of particles from silicon wafer front surfaces using an

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excimer laser. Modeling of the excimer laser particle removal will be discussed in terms of the various forces involved. An application of the laser cleaning technique to the removal of metallic contamination from silicon wafer back surfaces will also be presented.

2. PRINCIPLES OF LASER CLEANING

Two laser cleaning techniques have been investigated, to date. The first, called "steam" laser cleaning, makes use of either a CO_2 (10.6μm) [10-12, 26] or a pulsed excimer (248 nm) [13-16] laser, coupled to a liquid energy transfer medium, which is condensed on the surface. The transfer medium consists of water or a mixture of water and alcohol. The laser beam serves as a fast, localized heating source to bring the liquid film to its critical point, provoking its explosive vaporization. The forces generated are sufficient to remove the contaminant particles. The main difference between the use of a CO_2 or an excimer laser lies in the heating mechanism of the liquid film. In the former, the laser beam is partially, but directly absorbed by the liquid layer. Using an excimer laser, the medium is transparent to the radiation and the beam is strongly absorbed by the substrate surface; the latter is heated and transfers energy to the liquid film. In the work of Zapka and co-workers [13-16], it was demonstrated that the energy density required for efficient cleaning was far smaller using an excimer laser than a CO_2 laser. This was attributed to the fact that, when using UV radiation, explosive evaporation occurs at the interface and is, thus, more effective.

The second approach is dry laser cleaning, where no intermediate medium is used. A short-pulse (a few tens of nanoseconds) laser beam is either strongly absorbed by the substrate surface or the contaminant particles; fast thermal expansion of either the surface or the particles results in a strong acceleration of the particles outward from the surface [15, 24]. The beam radiation could be in either the UV (e.g., KrF excimer at 248 nm [25]) or the IR (e.g., Nd:YAG at 1.06 μm [24]) range. However, at the shortest wavelengths permitted by excimer lasers (ArF at 193 nm, KrF at 248 nm), the photons are strongly absorbed by the surface, leading to a very efficient thermoelastic removal force. This permits the removal of a wide variety of contaminants, not only particles but organic and inorganic films [17-19], by direct bond breaking.

Both "steam" and "dry" approaches are presently being investigated as potential cleaning alternatives to the conventional liquid chemicals methods. As explained above, the excimer laser is the most appropriate laser for high efficiency cleaning. It must be emphasized that microelectronics is not the only field in which laser cleaning can assert itself. The cleaning of optical components and air bearing surfaces of magnetic head sliders was successfully achieved [25, 27]. Art restoration is another field where laser cleaning has demonstrated strong capabilities [28].

3. EXPERIMENTAL

The experimental set-up has already been described elsewhere and is schematically presented in Figure 1 [29-30]. Very briefly, a KrF excimer laser (248 nm, with a pulse energy of 200 mJ and a duration of 22 ns) was focused onto the substrate surface. The substrate was mounted facing down on the underside of 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 of 0.05 - 1 J/cm^2 with an estimated error of 10 %. In the case of steam cleaning, a pulsed vapor generator was used to controllably deposit a liquid film at the spot to be irradiated, immediately before the laser pulse is triggered. The generator consisted in a heated (37-40 °C) nozzle and stainless steel container half-filled with deionized (DI) water. A nitrogen gas input of 4700 ml/min, connected to a flowmeter and valves, was used to generate a controlled volume of water vapor near the surface to be cleaned. Upon reaching the colder surface, the vapor condensed to a liquid film. A pulse-timing unit controlled the open time of the valves in the range between 0.1 and 3.5 s. After a vapor burst, several laser pulses were triggered at intervals to assure that all the water had been evaporated. In order to perform a cleaning over a sufficiently large area, the wafer was linearly stepped between 0.4 and 3 mm after each vapor burst sequence. The area cleaned was a square 50 X 50 mm^2, whose center corresponded to that of the wafer.
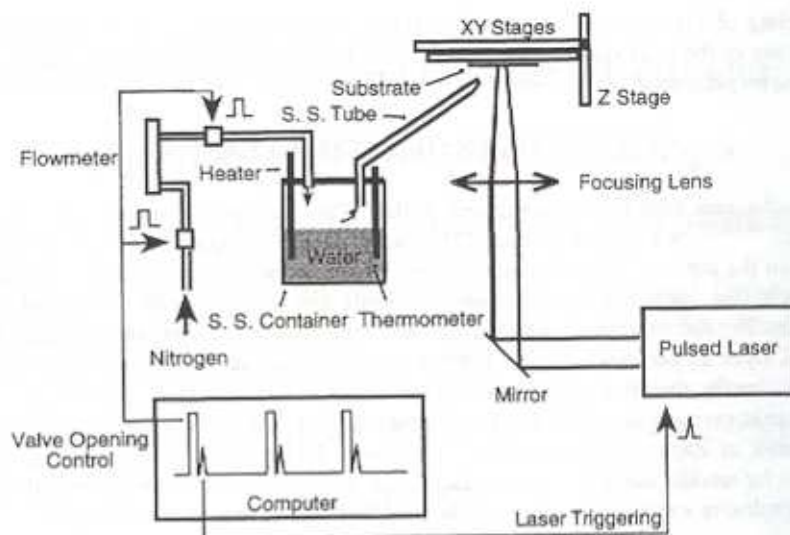
Figure 1 Schematic of the experimental set-up; S.S.: stainless steel.

The substrates were 100-mm-diameter <100> silicon wafers. Some were used as received, while others were first cleaned and made hydrophilic, using a modified RCA recipe [2, 22, 23]. Front side surfaces were artificially contaminated by various types of particles (polystyrene latex or PSL, Al_2O_3 and SiO_2) using a particle generator (Particle Measuring Systems, Inc.) [22, 23]. Similarly, back surfaces were contaminated by Fe_2O_3 particles. A dedicated particle generator, composed of a nebulizer, drying tube, chamber, and output nozzle, was used for each type of contaminant particle. To evaluate the cleaning efficiency, a laser scanning surface inspection system (Particle Measuring Systems Inc., SAS 3600) was used to classify particles according to their spherical PSL equivalents, from 0.1 to 10 μm. Inside the cleaned square area, the surface inspected was a circle of 30 mm diameter. It must be emphasized that this scanning system can only be used for the polished front surface. However, since the roughness of the wafer back side is very important, the surface photovoltage (SPV) technique was used as a cleaning evaluation tool of metallic contaminants [31-38]. Rapid thermal annealing (RTA), at 1050 °C for 4 min., was first performed to allow metallic contaminants to diffuse into the silicon wafers. SPV was then used to evaluate the iron bulk concentrations.

4. EXCIMER LASER CLEANING EFFICIENCIES

The particle densities (the number of particles divided by the area of the 30 mm diameter analyzed circle) as a function of size are shown in Figure 2. Dry excimer laser cleaning was very efficient in removing 0.1μm PSL particles from silicon. However, for Al_2O_3 (0.2μm) particles, only those with diameters >0.5μm were removed with some efficiency. By using steam excimer laser cleaning, most of Al_2O_3 particles are removed. Fig. 3 summarizes the overall particle densities for various types of particles, before and after laser irradiation, for both dry cleaning and steam cleaning.
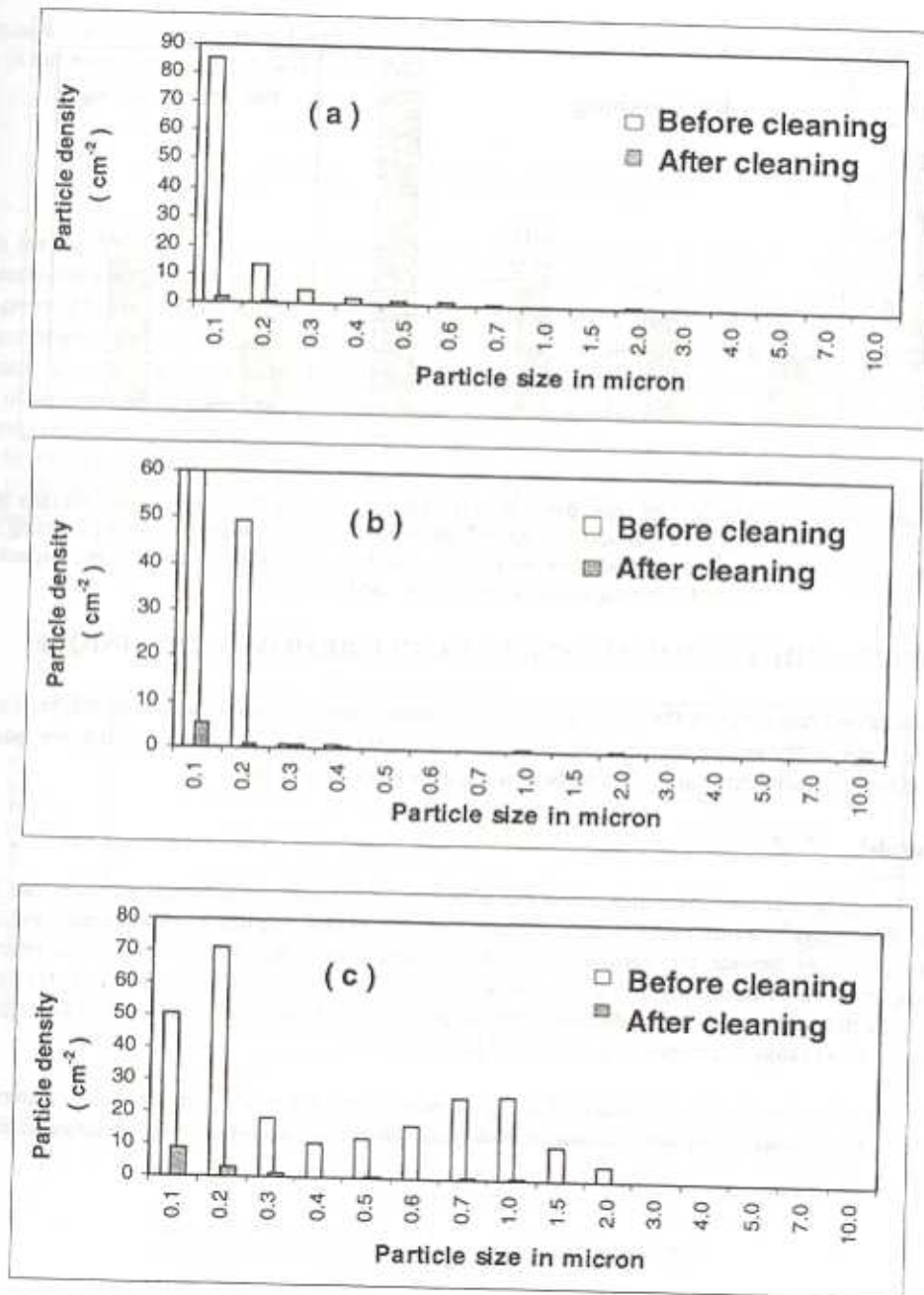
Figure 2(a) Size distribution of PSL before and after a dry excimer laser cleaning with a laser fluence of 326 mJ/cm^2 ; (b) and (c) Size distribution of silica and alumina particles before and after steam excimer laser cleaning with an energy beam density of 154 mJ/cm^2 and a water vapor burst duration of 0.2 s. The analyzed surface is a circle of 30 mm in diameter.
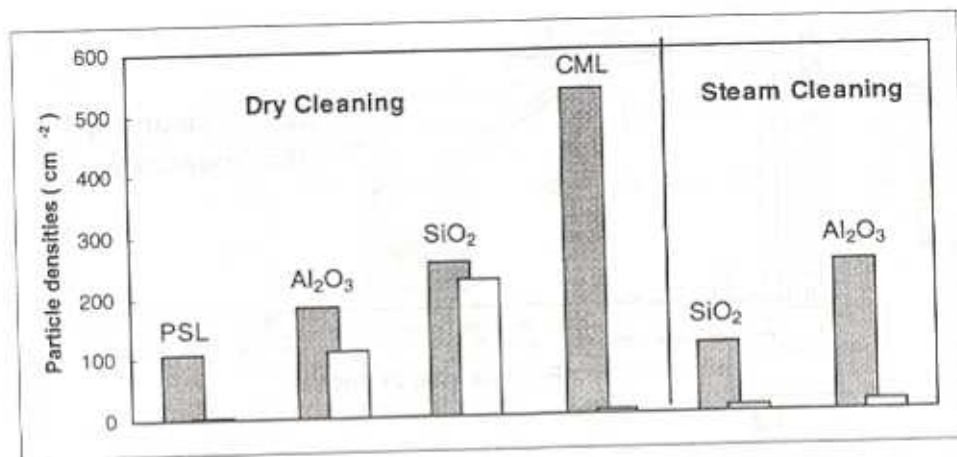
Fig. 3. Particle densities before (gray bar) and after (white bar) laser cleaning. During dry laser cleaning, the laser fluences for PSL, SiO_2, Al_2O_3 and CML were 326, 314, 326 and 353 mJ/cm², respectively, and 2, 4, 4 and 2 cleaning scanning cycles were used, respectively. During steam cleaning, the laser fluences for SiO_2 and Al_2O_3 were 180 and 154 mJ/cm², respectively, and 5 and 4 cleaning scanning cycles were used, respectively.

5. MODELING THE EXCIMER LASER PARTICLE REMOVAL TECHNIQUE

High efficiency cleaning requires that the removal forces be greater than the particle adhesion forces. To explain the large differences between dry and steam cleaning, and between organic with inorganic particles, we quantitatively analyzed the adhesion and removal forces between particles and surfaces.

5.1 Adhesion model

The interaction forces between solids which cause the adhesion of particles to substrate surfaces can be classified into long- and short-range[39]. Long-range forces include van der Waals, capillary, electrostatic and double-layer forces. Short-range forces include the various types of chemical bonds: metallic, covalent and ionic, as well as hydrogen bonds. In our previous study[29-30], it was demonstrated that, for submicron-sized particles on hydrophilic silicon surfaces, the dominant long-range adhesion force is the van der Waals interaction, while hydrogen bonding is the most important short-range contribution to inorganic particles.

Van der Waals attractive forces can be calculated using a macroscopic approach[40], in which the material properties are related to the Lifshitz-van der Waals constant. For a spherical particle and a smooth substrate surface, it can be expressed as[41]:

$$F^V = F_0^V + F_{Deformation}^V = \frac{h\varpi_{132}r_p}{8\pi z_o^2} + \frac{h\varpi_{132}a^2}{8\pi z_o^3} \tag{1}$$

The first term of equation (1) is the van der Waals forces between a sphere and a plane before deformation, and the second term is the force acting on the contact area due to elastic or plastic deformation. $h\varpi_{132}$ is the Lifshitz-van der Waals constant, r_p is the particle radius, z_0 is the atomic separation distance between particle and substrate, which is not measurable but assumed to range from 0.4 to 1 nm [8] (we used $z_0 = 0.4$ nm), a is the radius of the deformation area on the particle which can be calculated using the JKR model[42] for rigid particles (SiO_2 and Al_2O_3). For PSL particles, a is given by Rimai and Demejo[43]. During steam cleaning, particles were covered with a condensed water film. The shielding effect of the liquid greatly reduces the van der Waals forces[39]; for example, the Lifshitz-van der Waals constant of Al_2O_3 particles on silicon surfaces is reduced from 5.62 eV to 2.23 eV[44].

The adhesion force due to hydrogen bonding between inorganic particles and the hydrophilic silicon surface was discussed in our previous study[30]. It was given by:

$$F_{H-bond} = DE_{bond}(\pi a^2 + 2\pi r_p \Delta z b)/d_{bond} \qquad (2)$$

where D is the OH group density on the particle surface (12.5 OH/nm^2 for Al_2O_3[45]) and E_{bond} is the hydrogen bonding interaction energy between particle and substrate. E_{bond} depends on the natures of the surfaces, in particular on their degrees of hydroxylation and on the electronic structures of the materials[46]. The average energy of the O–H--O hydrogen bond is about 5 kcal/mole (~ 0.48 eV/bond)[46], πa^2 is the deformation area of the particles and $2\pi r_p \Delta z$ is the ring area taken to a height Δz near the contact point with the probability b that particle and surface are bonded by a chain of water molecules. For Al_2O_3 on dry cleaning, Δz b is ~ 0.38 nm[30,47,48]. During steam cleaning, free water molecules may replace and break the hydrogen bond chain connecting the particle to the surface, so the probability b is reduced by that probability. d_{bond} is the hydrogen bond dissociation distance, which is assumed to be half the length of a hydrogen bond, ~ 0.1 nm[49]. For PSL particles, there are no surface groups capable of participating in hydrogen bonding, so only van der Waals forces play a role.

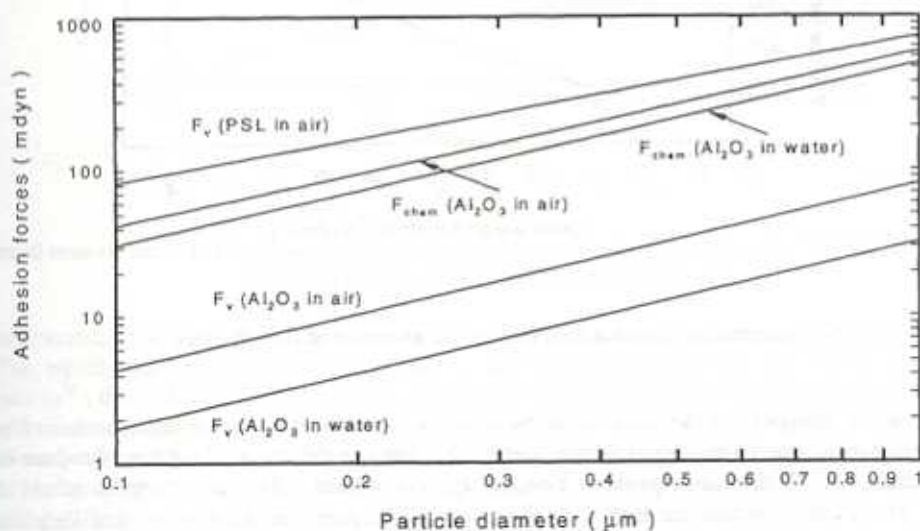Figure 4 Adhesion forces of PSL and Al_2O_3 particles on hydrophilic silicon surface during dry and steam cleaning, as a function of particle diameter.

Using equations (1) and (2), we calculated the adhesion forces versus particle diameters for a typical organic particle, PSL, and for a typical inorganic particle, Al_2O_3, contacting a hydrophilic silicon surface ; this was done for both dry and steam cleaning, as shown in Fig. 4. It appears that the adhesion forces are almost a linear function of particle diameter ; they are greatly reduced during steam cleaning, and hydrogen bonding between Al_2O_3 particles and hydrophilic silicon surfaces becomes much stronger than van der Waals interactions. The van der Waals forces of Al_2O_3 particles are already much less than those of PSL particles due to their smaller deformation.

5.2 Laser cleaning model

During laser pulse irradiation, the particle and silicon substrate absorb laser energy and are heated rapidly. Due to the thermoelastic effect[50], an extremely rapid thermal expansion of the substrate ejects the particles from the surface. In order to calculate the removal forces, we must first know the temperature increase of both particles and silicon substrate due to the laser irradiation.

Since the dimension of the 248 nm excimer laser beam (0.8 mm × 18 mm) on silicon, is much larger than the light absorption length α^{-1} of 5.5 nm[51] and the heat diffusion length of 4.3 μm[52,53], the semi-infinite, one-dimensional heat equation is a good approximation[52]. Heat losses at the substrate surface may be neglected, because heat conduction from the substrate surface to the ambient air is very slow, and the radiation losses are much smaller than the laser energy. The one-dimensional conductive heat transfer equation was solved numerically by an implicit finite difference algorithm. The peak surface temperature of the silicon substrate as a function of laser fluences is shown in Fig. 5.
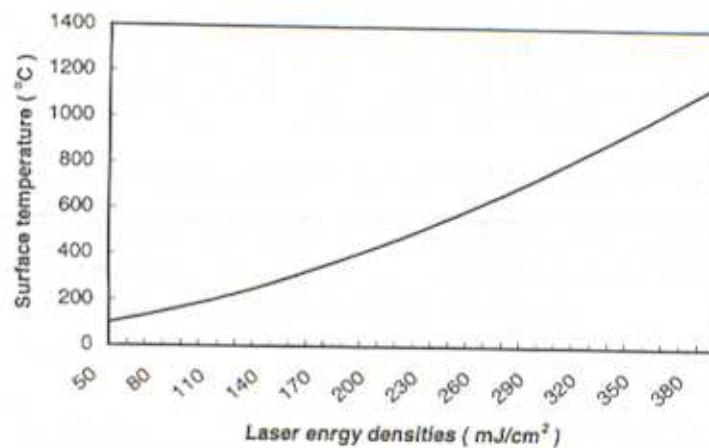

Fig. 5 Surface temperature of silicon substrate as a function of laser fluences.

The calculation of the temperature distribution in particles is a very complex problem because of non-uniform surface absorption due to small particle Mie-type scattering[54] and the difficulty of solving the three-dimensional, spherical coordinate, heat diffusion equation. Fortunately, the optical absorption lengths α^{-1} of the particle considered are $10-10^2$ μm, much larger than the dimensions of the particles. This means that the particles absorb laser energy weakly, the temperature increase in the particle during laser irradiation is not large, and we can assume that the submicron-sized particles maintain a constant temperature during laser irradiation.

The rapid temperature rise in the substrate, induced by the laser pulse, generates stresses and strains in the irradiated area. These strains cause some particle displacement. From the point of view of the particles, their resistance of these strains subjects them to ejection forces from the substrate surface, equal to the stresses in the substrate[55]. If the particles are to be detached from the surface, they must experience a real displacement. Based on the relationship between stresses and strains[52], an expression for the thermal removal force on the particles produced by the thermal expansion of the substrate can be obtained:

$$F_{thermal} = \gamma E \pi a^2 \Delta T \tag{3}$$

where γ, E, ΔT are the linear thermal expansion coefficient, the elastic modulus and the temperature increase at the substrate surface. πa^2 is the deformation area of the particle. The equation shows that the thermal removal forces

depend on the deformation area of the particle. Soft particles such as PSL should suffer much stronger removal forces from the substrate than hard particles, such as SiO_2 and Al_2O_3. Fig. 6 shows the removal forces on PSL and Al_2O_3 particles due to the thermoelastic effect during dry cleaning (the incident laser energy density is about 320 mJ/cm^2) as a function of the particle diameter. The dominant adhesion forces are also included in Fig. 6 for comparison purposes. It is apparent, in Fig. 6, that the thermal removal force is large enough to overcome the adhesion forces for PSL particles, but is much less than hydrogen bonding forces in the case of the Al_2O_3 particles. These predictions are consistence with the laser cleaning experiments.

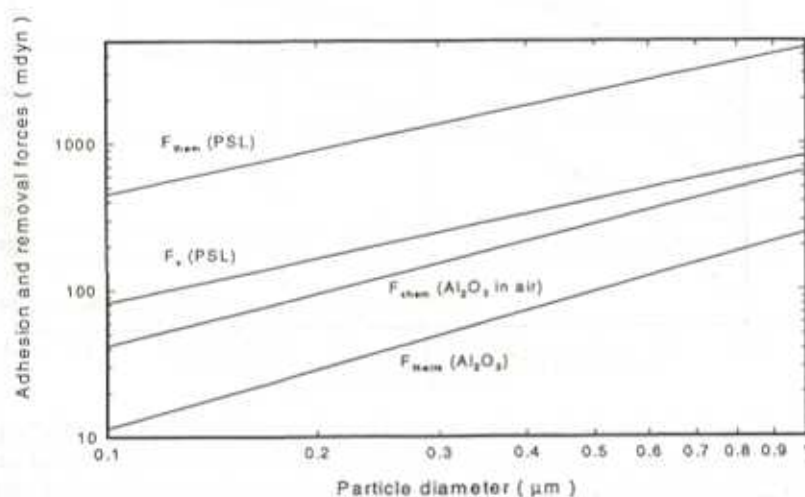Fig. 6 Thermal removal forces and dominant adhesion forces, as a function of particles diameter, for PSL and Al_2O_3 particles during dry cleaning with a laser flux of 320 mJ/cm^2.

During steam cleaning, the water film is transparent to the excimer laser. The laser energy is absorbed only by the substrate. The rapidly heated substrate surface induces the water layer adjacent to it to be superheated before nucleation sets in[56] ; this is followed by the creation of a layer of bubbles at the water/substrate interface, called film boiling. A detailed description of the explosive evaporation of the water film is extremely difficult, due to the formation of a superheated liquid, the thermal instability of the bubble and the development of nucleation centers[57]. The incident laser energy density (10^2 J/cm^2) is much larger than the heat energy density needed to heat liquid water to boiling (10^3 J/cm^2) or to vaporization (10^{-2} J/cm^2)[58]. The heat isolated by the vapor layer continues to transfer from substrate to liquid water, so that the temperature distribution in the substrate is approximately the same as during dry cleaning. The rapid bubble layer formation creates a pressure shock on the particles attached to the surface, with the removal force acting on the particles given by:

$$F_{bubble} = \pi r_p^2 \left[P_v(T) - P_v(T_0) \right] \qquad (4)$$

where r_p is the radius of the particle, $P_v(T)$ is the vapor pressure at temperature T, and $P_v(T_0)$ is the ambient liquid pressure[58]. The removal forces due to bubble generation and the thermoelastic effect, and the dominant adhesion forces due to hydrogen bonding, as functions of the particle diameter, are shown in Fig. 7 under steam cleaning conditions (the incident laser energy density is about 150 mJ/cm^2). During steam cleaning, as shown in Fig. 7, the explosive evaporation of the water film generates a strong removal force, much higher than the thermal expansion

force, which is also much greater than the adhesion force due to hydrogen bonding. This model appears to interpret the high cleaning efficiencies of steam cleaning for Al_2O_3 particles.
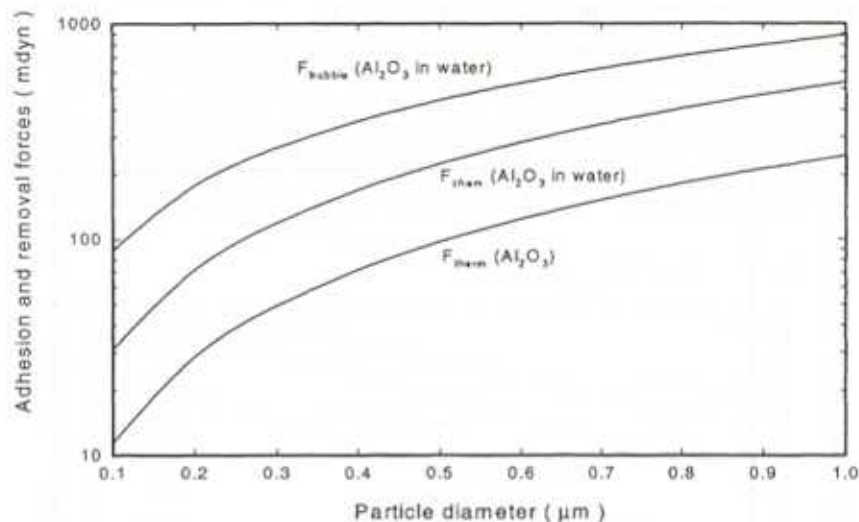

Fig. 7 Thermal removal forces, bubble removal forces and dominant adhesion forces, as a function of the particle diameter, for Al_2O_3 particles during steam cleaning with a laser flux of 150 mJ/cm².

6. APPLICATION OF EXCIMER LASER CLEANING TO THE REMOVAL OF BACK SIDE METALLIC CONTAMINATION

Metallic contaminants that are present during semiconductor processing introduce deep recombination levels in the bandgap. Such contamination affects the device reliability and performance by reducing the lifetime of minority carriers and by increasing the leakage current at p-n junctions [31-38]. For example, the presence of 10^{12} cm⁻³ of iron, as measured by surface photovoltage (SPV)[38], reduces the electronic diffusion length to a value as low as 60 μm. This problem of metallic contamination will become more important as critical device dimensions are reduced. The SIA Roadmap has determined that metallic contamination must decrease from 10^{12} cm⁻³ for 0.8 μm technology to 10^{10} cm⁻³ for 0.35 μm technology. Among the various metallic contaminant sources, equipment and vacuum systems fabricated from stainless steel appear to be the primary sources: handling the wafers in these systems may generate particulates which deposit on either side of the wafer. Much care is presently taken to prevent the particles from interfering with the lithographic processes performed on the front side. Unfortunately, particles on the back side are generally ignored[38]. These particles come from the different chucks and holders which the wafers contact during the various steps of integrated circuit fabrication. The most critical steps are those carried out at the front-end of the fabrication, before the high-temperature annealing processes. Such thermal processes permit the metallic contaminants at the back side to diffuse through the wafer and reach the sensitive front side, reducing device performance. To avoid these adverse effects, the particles deposited on the back side during handling must be removed before any important thermal budget step at the front-end of the line, such as thermal oxidation or RTA.

Due to the fact that iron has a relatively high diffusivity and is the most troublesome contaminant, we have investigated the use of an excimer laser-based cleaning technique to eliminate it. Our preliminary results on the removal of Fe_2O_3 particles (0.2 - 2 μm) from both sides of the wafer[59] are shown in Table 1. In these experiments, it is clear that deliberate contamination by iron oxide led to a significant Fe bulk contamination level after RTA at

1050 °C for 4 min.. However, when the surface was first laser-cleaned, the Fe concentration was reduced by more than an order of magnitude. Note that the cleaning efficiency is independent of the roughness. Improvements are being performed on our laser cleaning system to increase its efficiency in the removal of such metallic contamination.

TABLE 1: Steam excimer laser cleaning of Fe_2O_3 particles (at a fluence of 200 mJ/cm²) from the front- and back sides of a silicon wafer. Diffusion lengths and iron concentrations were obtained from SPV measurements at the center of the wafer.

	Fe_2O_3 particle density (>0.3μm) (cm⁻²)	Diffusion length (center point) (μm)	Iron concentration (center point) ($X\ 10^{12}\ cm^{-3}$)
Front side			
Before laser cleaning	243	63	16
After laser cleaning	17	171	1.1
Back side			
Before laser cleaning	NA	82	7.3
After laser cleaning	NA	138	1.3
Not contaminated	no contamination	136	1.6

NA : impossible to measure due to extensive surface roughness

7. CONCLUSIONS AND CHALLENGES

The removal of particles as small as 0.1 μm from silicon surfaces can be achieved using the excimer laser-based cleaning technique. Cleaning efficiency may be optimized by controlling various parameters such as the beam energy density and the use (or not) of an energy transfer liquid. The application of this cleaning technique to the removal of back side metallic contamination has also been demonstrated.

Theoretical models of particle adhesion and removal were used for the purpose of explaining our excimer laser cleaning results. The dominant adhesion force holding organic particles, such as PSL, to the surface is the van der Waals force with deformation. Hydrogen bonding between inorganic particles, such as Al_2O_3, and the substrate is the dominant contribution to adhesion forces. A deposited water film greatly reduces the adhesion forces, due to the shielding effect of the van der Waals force and the breaking of the hydrogen bond chain between particle and surface. The laser pulse-generated thermoelastic effect of the heated substrate gives rise to the removal force on the particles attached on the surface during dry and steam cleaning. An additional removal force, due to bubble pressure during steam cleaning, is larger than that due to the thermoelectric effect.

Development of the excimer laser cleaning technique involves many challenges. A real integration of this technique into a cluster tool will probably require *dry* excimer laser cleaning. While the transfer medium, such as water, seems to be necessary for the removal of inorganic particles, research should be done to improve the cleaning efficiency of the dry approach. Most of the development so far was done on bare silicon substrates for which this technique is very appropriate. However, cleaning real circuits with this technique sometimes causes the breaking metallic lines, probably because these lines have poor adhesion to the substrate. The scaling up of this technique will involve the use of a larger and uniform excimer laser beam. Investigations should be made to develop a "find and clean" system in which an appropriate system will find a particle and the excimer laser will be use to remove it. This cleaning approach will probably be simpler and faster that the approach presently used.

ACKNOWLEDGMENTS

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