The effects of hydrogen bonds on the adhesion of inorganic oxide particles on hydrophilic silicon surfaces

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Hydrogen bonds have a dominant effect on the adhesion of inorganic oxide particles, such as SiO₂ and Al₂O₃, to hydrophilic silicon surfaces. An analysis of adhesion forces due to hydrogen bonds between particle and substrate surfaces has been carried out, and is used to interpret the efficiencies of removing polystyrene latex, SiO₂, and Al₂O₃ particles from a hydrophilic silicon surface by laser cleaning. Evidence of the dominant effect of hydrogen bonding was confirmed by using alcohol instead of water during particle deposition. © 1999 American Institute of Physics.

I. INTRODUCTION

Contamination on wafer surfaces remains a serious problem in semiconductor manufacturing.¹ It is well known that particle contamination decreases device yield drastically.² To remove particles from a wafer surface requires a knowledge of those adhesion forces which hold the particles to that surface.

The attractive interaction forces between different media are classified as long and short range. Long-range forces act to bring the particle to the surface and establish the adhesion contact area; they include van der Waals and electrostatic forces. Short-range forces can add to adhesion only after the establishment of an adhesive contact area; they include the various types of chemical bonds: metallic, covalent, and ionic, as well as hydrogen bonds.³ Much work has been done to describe adhesion forces between particle and substrate surface.⁴⁻⁷ This work has led to the conclusion that van der Waals, capillary, and electrostatic adhesion forces are the major contributors. Chemical bonds at the contact area between the adherents are so far accounted for only qualitatively,⁴⁻⁷ although they may play an important role on the silicon surface, because a quantitative treatment of chemical bonds between particle and substrate surface is very difficult.

It is well known in surface chemistry that many solid surfaces contain potential hydrogen bond donors and acceptors. Because hydrogen bond formation has a low activation energy, it occurs at room temperature; therefore, particle–substrate surface interactions via hydrogen bonding are possible.¹⁰ Water viscosity experiments have demonstrated the existence of hydrogen bonds between spherical and flat fused silica surfaces.¹¹ Although the hydrogen bond is not a strong chemical bond (its bond energy is generally about 5 kcal/mole or 0.22 eV/bond),³ it is, nonetheless, much stronger than the energy of van der Waals adhesion, typically a 1 kcal/mole or 0.043 eV/bond.¹² Thus, hydrogen bonding may play a very important role in the adhesion of particles to substrate surfaces.

This article discusses the adhesion forces due to hydrogen bonds between both SiO₂ and Al₂O₃ particles and a hydrophilic silicon surface, then uses the chemical adhesion model to explain the experimental laser cleaning results.

II. EXPERIMENTS

Although the details of particle removal by laser cleaning have been given previously,¹³ a brief description will be given here. We irradiated the contaminated wafer surface in ambient air with KrF excimer laser pulses (MPB Technologies, Inc. AQX-150, at 248 nm wavelength, with a 22 ns pulse width at half maximum), using both dry and steam laser cleaning techniques. Steam laser cleaning has a high cleaning efficiency, made possible by the use of a thin film of deposited water as an energy transfer medium and adhesion force reduction agent. Dry laser cleaning is simpler, in that no liquid is involved; and is compatible with cluster tools.

Three kinds of particles were deposited onto a silicon wafer surface using a particle generator (Particle Measuring System, Inc.). The particles were: 0.1 μm polystyrene latex (PSL) from Particle Measuring System, Inc., and 0.1⁻⁻⁻₀.2 μm agglomerated SiO₂ and 0.2 μm Al₂O₃ from Beta Diamond Corp. The particle generator used a diaphragm pump to force air through a filter. Filtered air then moved through a nebulizer having about 0.007% monodisperse particles suspended in de-ionized (DI) water. The flow then passed through a drying chamber where the water droplets evaporated. Finally, the particle-laden air was sprayed onto the wafer surface through a long tube with a movable nozzle.

III. RESULTS

Figure 1 shows the particle densities for each kind of particle, before and after laser cleaning. We found that, for dry cleaning, KrF excimer laser radiation effectively removed all the PSL particles from the silicon surface but, for SiO₂ and Al₂O₃ particles, the particle densities were not
much reduced. For steam laser cleaning, both SiO$_2$ and Al$_2$O$_3$ particles were removed with high efficiencies.

A second set of experiments was used to verify the effect of hydrogen bonds on the adhesion of particles to hydrophilic silicon surfaces. This was achieved by using two different alcohols (methanol and ethanol) instead of DI water during particle deposition. On alcoholic steam cleaning, which immediately followed particle deposition and had experimental conditions identical to those of steam cleaning except for a larger laser flux, the cleaning efficiencies of SiO$_2$ and Al$_2$O$_3$ particles were drastically reduced, as shown in Fig. 2.

### IV. CHEMICAL BONDS AND ADHESION FORCES

A summary of our previous discussion of adhesion forces between PSL and SiO$_2$ particles and a hydrophilic silicon surface,\textsuperscript{15} is given in Table I. There, the van der Waals force was shown to dominate capillary and electrostatic forces for submicron sized particles attached to the silicon surface. It can be expressed as\textsuperscript{5}

\[
F^V = F^V_0 + F^V_{\text{Deformation}} = \frac{\hbar \omega_{132} r_p}{8 \pi \varepsilon_0} a^2 + \frac{\hbar \omega_{132} a^2}{8 \pi \varepsilon_0}.
\]

The first term of Eq. (1) is the van der Waals forces between a sphere and a plane, and the second term is due to elastic or plastic deformation. $\hbar \omega_{132}$ is the Lifshitz–van der Waals constant, $r_p$ is the particle radius, $\varepsilon_0$ is the separation distance between particle and substrate, which is not measurable but assumed to range from 4 to 10 Å\textsuperscript{4} (we used $\varepsilon_0 = 4$ Å), $a$ is the deformation contact radius of particle on the surface, which can be calculated using the JKR model\textsuperscript{14} for rigid particles (SiO$_2$ and Al$_2$O$_3$):

\[
a^3 = \frac{9}{2} W \pi r_p^2 \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right),
\]

where $W$ is the work of adhesion of the particle on the substrate surface which approaches the value of $2(\gamma_1 \gamma_2)^{1/2}$, $\gamma_1$ and $\gamma_2$ being the surface free energies of particle and substrate, respectively; $\nu$ and $E$ are Poisson’s ratio and Young’s modulus for particle and substrate. For PSL particles, the contact radius is not a function of the particle radius to the 2/3 power but, rather, to the 1/2 power.\textsuperscript{15} The softer the particle, the larger both the contact radius and the adhesion force. Based on these calculations, PSL particles should be more difficult to remove than the two inorganic particles, but the laser cleaning experiments give the opposite results.

To explain this contradiction, we consider the short-range adhesion forces from hydrogen bonds between hydroxyl groups on the inorganic oxide particle surfaces and on the hydrophilic silicon surface. PSL particles, having no surface oxide, do not produce such hydroxyl groups.

A key characteristic of the SiO$_2$ surface is that it becomes covered with silanol (SiOH) groups at room temperature.\textsuperscript{16} The concentration of SiOH groups on the silica surface is about the same for different type of silica;\textsuperscript{17} the results of several methods agree very well and give an average value of 4.6±0.2 OH/nm$^2$ for a fully hydroxylated silica surface.\textsuperscript{10,16} This average number of silanol groups very nearly corresponds to the number of silicon atoms on a silica surface. The metal–oxygen bond of many metal oxides is more ionic in character than that of silica. The oxygen ions of an alumina surface seem to be effective hydrogen bond acceptor sites; furthermore, alumina surfaces which were previously exposed to water vapor or moist air are terminated by a monolayer of hydroxyl groups, each occupying

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<th>Table I. The adhesion forces of 0.2 μm PSL and SiO$_2$ particles on the silicon surface.</th>
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about 0.08 nm$^2$ on the surface, corresponding to 12.5 OH/nm$^2$.

Our hydrophilic silicon surface was hydroxylated during SC$_1$ pretreatment. SiO$_2$ and Al$_2$O$_3$ particles were kept in air and immersed in water for deposition, so their surfaces were also hydroxylated. Water, which has both hydrogen bond donor and acceptor properties, has a pronounced tendency to interact with the OH groups on hydroxylated surfaces through hydrogen bonding. Figure 3 shows several examples of a water molecule may be bound to a hydroxylated surface.

An operational definition commonly used states that a hydrogen bond between two groups X–H and Y exists when there is evidence of interaction between X–H and Y. The distance between atoms X and Y (in our case, the hydrogen bond is O–H–O) is comparable with the van der Waals contact distance (~3.4 Å) so, when the particles are deposited on the substrate surface, they may be bonded to the surface either (a) indirectly, through hydrogen bonding with water molecules adjacent to the contact area, or (b) directly, through hydrogen bonding of the hydroxyl groups of particle and substrate in the deformation area, as shown in Fig. 4. Absorbed water molecules can be retained around the contact area up to a temperature of 180 °C.

In order to calculate the adhesion force due to hydrogen bonding, we must know the total bond energy $E_{\text{total}}$ which is calculated as

$$E_{\text{total}} = DSE_{\text{bond}},$$

where $D$ is the OH group density, $S$ and $E_{\text{bond}}$ are the total interaction area and the hydrogen bonding interaction energy between particle and substrate. $E_{\text{bond}}$ depends on the natures of the surfaces, in particular on their degrees of hydroxyl and on the electronic structure of the materials. The average bonding energy of the O–H–O hydrogen bond is about 5 kcal/mole ($\sim$0.22 eV/bond). In the case of dry cleaning, the interaction area is

$$S = \pi a^2 + 2\pi r_d \Delta z b,$$

where the first term is the deformation area of the particles and the second term is the ring area cut at a height $\Delta z$ near the contact point with the probability $b$ that particle and surface form a hydrogen bond.

In general, the total O–H–O bond length is 2.72 Å and the length of a hydrogen bond H–O is 1.7 Å. The X–H–O bond angle was set at 120°. The length of the O–Si bond is 1.66 Å and we used 0.96 Å as the length of the O–H bond in a water molecule and a surface silanol group. According to the hydrogen bond structure in Fig. 4, $\Delta z$ is approximately equal to the total length of the hydrogen bond chain. If there is only one water molecule involved, the chance of this water molecule connecting particle and surface is 50%; if two water molecules participate, the possibility reduced to 25% etc. For SiO$_2$ particles, $\Delta z b$ is $\sim$7.21 Å and, for Al$_2$O$_3$, it is $\sim$7.05 Å. During steam cleaning, a water film covers the particle surface, the hydrogen bond has a 50% probability of connecting the particle to the surface or connecting the free water molecules in the film, so the second term in Eq. (4) is reduced by half. To break the hydrogen bonds between particle and substrate, the work done by the cleaning force must be larger than the total adhesion energy of hydrogen bonding. To simplify the problem, we assume the adhesion force of a hydrogen bond as being uniform and existing in the range from its potential minimum to the dissociation distance $d_{\text{bond}}$. Finally, we obtain the adhesion force due to hydrogen bonding:

$$F_{\text{H bond}} = E_{\text{total}}/d_{\text{bond}}.$$
energy, the dissociation distance should be near 1 Å. We arbitrarily selected this value as the dissociation distance in our calculation.

Using Eqs. (3)–(5), we calculated the adhesion forces due to hydrogen bonding between particle and substrate for both dry and steam cleaning, as shown in Fig. 5; the van der Waals forces, calculated from Eqs. (1) and (2), are also shown in Fig. 5, for comparison with the hydrogen bonding forces. It appears that the adhesion force due to hydrogen bonding is much larger than that due to van der Waals interaction. For PSL particles, there are no surface groups capable of participating in hydrogen bonding, so only van der Waals forces play a role. Hydrogen bonding is the reason why SiO₂ and Al₂O₃ particles have lower dry cleaning efficiencies than PSL particles.

The dissociation distance can have a substantial effect on the calculated results of the adhesion force due to hydrogen bonds. For example, bond lengths 30% shorter in dissociation distance will cause a 40% increase in the calculated adhesion force. There are other parameters which can induce calculation errors, such as the degrees of hydroxylation on particle and substrate surfaces and the presence of asperities on the surfaces. Here we use 100% hydroxylation although, in practice, it may be less. The presence of asperities on particle and substrate surfaces can greatly reduce the adhesion forces, a subject which will be considered in a subsequent article.

When we used methanol and ethanol instead of water during particle deposition, we expected similar adhesion behavior for the hydroxylated particle surfaces because their OH groups can also act as hydrogen bond participants. Examples of alcohol molecules on SiO₂ and Al₂O₃ surfaces are shown in Fig. 6. When the particles deposit on the hydrophilic silicon surface, alcoholic hydroxyl groups adsorbed on the particle surfaces bond with hydroxyl groups on the substrate surface. The interaction energy of H–O–R is about 7 kcal/mole for silica and about 14 kcal/mole for alumina, so that the order of the interaction energies between particle and surface with the different deposition liquids is: Al₂O₃/ROH > SiO₂/ROH > Al₂O₃/H₂O > SiO₂/H₂O. During steam cleaning, free water molecules have difficulty replacing the alcohol molecules involved in indirect hydrogen bonds because the alcohols have larger interaction energies than water. Therefore, the order of laser cleaning efficiencies is expected to be Al₂O₃/ROH > SiO₂/ROH > Al₂O₃/H₂O > SiO₂/H₂O, as found experimentally.

V. CONCLUSIONS

The hydroxilated surfaces of inorganic oxide particles and hydrophilic silicon wafers can interact to form hydrogen bonds. A simple model has been developed to calculate the adhesion forces due to such hydrogen bonds. The values of the adhesion forces calculated according to our model can rationalize the experimental results of laser cleaning, in which PSL particles were easily removed by dry cleaning but SiO₂ and Al₂O₃ particles were not. When we used alcohol as a dispersal agent instead of water during particle deposition, the cleaning efficiencies of SiO₂ and Al₂O₃ particles were greatly reduced during the steam cleaning which followed because the hydrogen bonds formed with alcohol molecules have stronger interaction energies and are more difficult to replace by free water molecules during steam cleaning.

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