Simulation of the Adhesion of Particles to Surfaces

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The removal of micrometer and submicrometer particles from dielectric and metal films represents a challenge in postchemical mechanical polishing cleaning. Proper modeling of the adhesive force between contaminant particles and these films is needed to develop optimal solutions to postchemical mechanical polishing cleaning. We have previously developed and experimentally validated a model to describe the adhesion between spherical particles and thin films. This simulation expands previous models to characterize the adhesive interaction between asymmetrical particles, characteristic of a polishing slurry, and various films. Our simulation accounts for the contact area between particles and substrates, as well as the morphology of the surfaces. Previous models fail to accurately describe the contact of asymmetrical particles interacting with surfaces. By properly accounting for nonideal and geometry and morphology, the simulation predicts a more accurate adhesive force than predictions based upon an ideal van der Waals model. The simulation is compared to experimental data taken for both semi-ideal particle–substrate systems (polystyrene latex spheres in contact with silicon films) and asymmetrical systems (alumina particles in contact with various films).

Key Words: particle adhesion; van der waals forces; postchemicals mechanical polishing cleaning; semiconductor processing; chemical mechanical polishing.

INTRODUCTION

In the semiconductor industry, micrometer and submicrometer particle surface contamination can cause device failure and lower process yield. As circuit linewidths continue to decrease, removal of these particles becomes increasingly important. In order to develop optimal methods to remove particles, models to quantify the adhesive forces that hold particles to surfaces are needed.

Adhesive forces have been classified by Krupp (1). Class I includes intermolecular forces such as van der Waals (vdW) interactions. Class II includes various chemical bonds, including hydrogen bonds. Class III includes sintering effects such as diffusion and condensation and diffusive mixing. When studying polymer systems, interdiffusion and entanglement of polymer chains across the interface are considered Class III interactions.

Class I forces, in particular vdW forces, are present in all systems and are generally considered the controlling force in particle adhesion. Therefore, theories to describe particle adhesion focus on quantifying vdW interactions. The current accepted method to predict particle adhesion is to determine the system’s Dupré work of adhesion and insert this value into the proper equilibrium model, such as the Johnson–Kendall–Roberts (JKR) (2), Maugis–Pollock (MP) (3), or Derjaguin–Mueller–Toporov (DMT) (4) models. This approach characterizes ideal systems in inert environments with a high degree of certainty. Ideal systems are systems where the geometries of the interacting surfaces are well characterized, the interacting area is smooth with uniform chemical properties, and the only force present is the vdW dispersion force. However, when the system deviates from ideal conditions, model predictions disagree with experimental data. Therefore, a more comprehensive method to describe particle adhesion is needed. Below is a description of the current accepted method to predict particle adhesion, a review of the limitations of this approach, and a detailed description of our simulation. Our simulation advances the current approaches to better account for geometry, surface morphological and chemical heterogeneities, and surface mechanical properties. It also provides statistical information about observed variations in the adhesion force. Current approaches predict a singular value for the adhesive force for a given system and do not account for observed variances in removal forces.

The surface force apparatus (SFA), the atomic force microscope (AFM), and the interfacial force microscope (IFM) have provided direct methods to measure the force to separate contacting surfaces. They have allowed the measurement of particle adhesion for both ideal and nonideal systems. Measured removal forces for ideal systems agree with predictions made using one of the equilibrium models described above (5–7). However, most systems of interest are not ideal. Instead, these systems generally exhibit surface roughness and asymmetrical geometries and are influenced by other forces in addition to dispersion forces. Measured removal forces for nonideal systems vary between one and three orders of magnitude from predictions made using one of the equilibrium models.

When experimental measurements differ drastically from predictions based upon one of the equilibrium models, the
reason most commonly given is nonideal surface morphology (8, 9). Recently, there have been a number of investigations into
the effect of surface morphology on colloidal forces inside and
outside of contact. Walz has published a literature review that
describes the work in the area (10). Several groups have focused
on modeling the effect of surface morphology on colloidal forces outside of contact (11–16) but there have been only a few
investigations modeling the effect of surface morphology on
adhesion.

Fuller and Tabor (17) modeled the adhesion of a smooth
flat surface in contact with a rough flat surface. They modeled
roughness as asperities with equal radius of curvature but with
a Gaussian distribution in heights and employed the JKR equi-
librium theory to calculate the removal force for each individual
asperity. They also quantified the effect of dispersity in asper-
ity heights on adhesion. By adjusting a parameter that repre-
sented the dispersity in asperity heights, they were able to fit
data they collected for the adhesion between optically smooth
rubber spheres and hard, flat, surfaces of Perspex with various
degrees of roughness. They found that removal force decreased
as the polydispersity in asperity heights increased. This agrees
with data obtained in our lab, where the adhesion between rough
tin spheres and atomically smooth mica and highly
polystyrene latex (PSL) spheres and rough and smooth silicon
surfaces was measured with an AFM (18). As the roughness
of the silicon surface increased, the removal force decreased,
and we attributed this result to a reduced mass interacting in
the interfacial area. Mizes (19) and Sasaki (8) obtained similar
results by measuring both the localized topography and the lo-
calized adhesive forces between various planar surfaces and an
AFM cantilever outside of contact (11–16) but there have been only a few
investigations modeling the effect of surface morphology on
adhesion.

Schaefer et al. measured the removal force between glass,
PSL, and tin spheres and atomically smooth mica and highly
oriented pyrolytic graphite surfaces with an AFM (20). The val-
ges they measured were ~50 times less than expected based on
JKR theory and they attributed the difference to surface mor-
phology of the particles. They proceeded to quantify the surface
morphology of the individual particles using AFM line scans.
This allowed them to calculate the radius of curvature of in-
dividual asperities, which they plugged into the JKR theory to
predict a removal force for each asperity. By summing the re-
moval force of all the asperities, they obtained a removal force
that still overpredicted the measured removal force by a factor
of three.

The approaches described above are a good foundation for
developing comprehensive descriptions of the effect of surface
morphology on particle adhesion. However, these studies do not
provide an accurate description of the adhesive force for nonideal
particles. First, much of this work was developed for the inter-
action between either smooth surfaces or one rough surface and
one smooth surface. In real systems both surfaces have a certain
degree of roughness. Second, the above work models asperities
as spherical particles distributed over the surfaces. Roughness
on real surfaces can have set geometric patterns, random rough-
ness patterns, or complex fractal patterns (21). Third, this work
does not account for compression and deformation of surface as-
perities resulting from either the adhesive force or the adhesive
force summed with an external applied load. By estimating the
compression of asperities on the surface of PSL particles inter-
acting with silicon surfaces using the JKR model, Schaefer (20)
concluded that compression would not significantly alter the as-
perities’ shape and therefore would not influence the removal
forces. Following a similar approach, Biggs (22) determined
that under certain conditions the load would cause substantial
compression of the asperities.

The existing models describe only the interaction of spher-
ical, elastic particles with substrates. Real particles are asym-
metrical and can consist of rigid, elastic, elastoplastic, or plastic
materials. Figure 1 is a scanning electron micrograph (SEM)
of an alumina particle on a silicon surface. Currently, alumina
slurry particles represent a contamination problem during chem-
ical mechanical polishing (CMP) in semiconductor processing.
These particles are rigid and asymmetrical, and they adhere
strongly to silicon surfaces. Current adhesion models could not
account for the geometry, morphology, or mechanical proper-
tries of these particles. The work presented here, which couples
computer simulation with a fundamental adhesion model, was
designed to predict the adhesive interactions for ideal and real
particles by accounting for particle and surface morphology, com-
pression, and asymmetry, as well as variations in deformation
behavior.

FIG. 1. Scanning electron micrograph of an alumina particle.
Model Description

Our model predicts the adhesive interactions between two surfaces of arbitrary shape, each with localized chemical and morphological heterogeneities. The basic procedure for our simulation involves constructing a mathematical description of two solid surfaces, bringing the surfaces toward each other so that vdW interactions may be important and then summing the vdW interactions calculated between individual volume elements in the two surfaces. The calculations are performed on a desktop computer using a C++ code developed at ASU. Figure 2 is a schematic outlining the procedure. The specific steps are described in more detail here.

1. Macroscopic Surface Description

The first step in our simulation is to assume both surfaces are atomically smooth and determine the area in contact between the interacting solids based only on their geometry. These contact regions, when modified to account for morphological effects, control the magnitude of the adhesion force. As a particle is withdrawn from a surface, two factors determine the contact area immediately prior to particle removal. These factors are the type of deformation the particle undergoes and the separation mechanism when the particle is pulled from the surface. Separation can either occur at the interface (“brittle” or adhesive rupture) or within the softer of the two materials (“ductile” or cohesive rupture) (3). Contact area at pull-off is not well understood during brittle rupture. AFM studies by Biggs and Spinks suggest that brittle rupture occurs at slow pull-off speeds and large applied loads (28). We have designed our model and experiments to simulate ductile rupture based on molecular dynamic simulations of instantaneous adhesive rupture interactions involving PSL spheres and various substrates (23). According to Maugis and Pollock, separation for ductile rupture occurs at the maximum contact area achieved between the colloid and the substrate (3).

Our simulation determines the contact area by one of two different approaches depending upon the characteristics of the particle being studied. Case I is for the interaction of flat surfaces with spherical particles that have been allowed to settle on the surface for an extended period of time and for which the deformation of the particle or substrate has been modeled. This case considers ideal geometries. Case II is for asymmetrical particles. This case determines the contact area of the particle by CAD volume reconstruction of the particle from SEM micrographs. In all cases the separation is assumed to be ductile.

Case I: Ideal geometries, contact area based on observation. Rimai et al. (24) designed experiments that used an SEM to measure the contact radius, ca, of spherical particles on surfaces for particles of varying radii. From their data, they were able to model the contact radius as a function of particle radius. In prior work, we used this approach to model the contact area as a function of particle radius for PSL spheres in contact with a silicon (with surface oxide) surface (25). The result is:

\[
ca(\mu m) = 0.24 * R(\mu m)^{0.5}.
\]  

This model can be used in our simulation to determine the contact area between PSL spheres and silicon surfaces that have been in contact for long times.

For spherical particles that deform, this is a convenient way to determine contact area. This is because this method does not require knowledge of material properties or initial values for simulation iterations.

Case II: Nonideal geometries. This case provides an estimate of contact area for particle–substrate interactions when particles with asymmetrical geometries, such as shown in Fig. 1, are present. It estimates the geometry of the contact region based on AFM and SEM images of the particle. Specifically, we construct a mathematical representation of the surface of the particle from the images, rotate the mathematical particle representation to simulate how it settles on the surface, and then predict the contact area between the particle and the substrate. Figure 3 displays an alumina particle that is mounted onto an AFM cantilever. The left side of Fig. 3 is a reconstructed 3D image of the surface of the alumina particle. The right image in Fig. 3 is a field emission (FESEM) of that particle.

The reconstruction shown in the left side of Fig. 3 was accomplished with an imaging software package (PhotoModeler). By reconstructing the surface in this manner we are able to obtain a mathematical representation of the surface (26). After the particle was reconstructed, it was rotated around its lowest point until three separate points on the particle could contact the substrate. This is only an approximation of how a particle settles, but it is adequate for this first simulation. Once we finished rotating the particle, the contact area was estimated by determining the area of the peaks that touched the surface. This value was then inserted into our simulation.

2. Microscopic Surface Generation

Once the geometric contact area between the particle and substrate was determined, the second step was to simulate (based

![FIG. 2. A schematic diagramming the procedure for the adhesion simulation.](image-url)
4. Allowing the Surfaces to Interact

Once mathematical representations of both surfaces were generated, the surfaces were brought into close proximity and an adhesive force was calculated. This procedure consisted of the following steps:

1. Bring the two surfaces together until a single contact point, \( c_p \), is reached. Figure 5 is a schematic depicting the interaction of two rough surfaces at this condition.
2. Compress the asperities on the softer of the surfaces if any external load is present. Any vdW effects are not considered until later.
3. Calculate the adhesive force between the surfaces based on vdW interactions.
4. Return to step 2 and recompress the surface asperities to compensate for the adhesive force.
5. Recalculate the force.

Steps 2–5 were repeated until the change in the calculated adhesive force was less than one percent.

As mentioned by Biggs (22), compression of asperities is a complex problem that involves both bulk material collapse and asperity deformation. To account for asperity compression we focused on two opposite extremes of asperity behavior. Figure 6 is a schematic of the types of compression considered. The first type of asperity compression represents the surfaces coming closer together as a result of an increase in the density of the softer material (Fig. 6A). The second type of compression represents the flattening of the surface of the softer of the two materials by the load (Fig. 6B). The actual compression is expected to be a combination of these extreme cases (Fig. 6C). Our simulation estimates the compression by averaging predictions based on the two extremes.

The interaction force was calculated from a macroscopic, or pairwise additive, approach. This approach divided the particle into individual volume elements, each a different distance $D$ from the surface. The vdW force for each element was then calculated. The total adhesive force was the sum of the forces from the individual volume elements. Cylindrical elements were used, as depicted in Fig. 7.

The force between a cylindrical volume element and a substrate was calculated from

$$F_{\text{attr}} = -\frac{A \cdot (\text{Area cylinder})}{6 \cdot \pi \cdot D^3},$$

where $F_{\text{attr}}$ is the adhesive force (N) and $A$ is the system’s Hamaker constant. Cylindrical volume elements of 1 nm diameter were used.

The models just described use a vdW formulation to account for the interfacial interactions between a particle and a substrate. The key parameters in the calculation are the Hamaker constant of the system and the compressibility, geometry, morphology, and deformation behavior of the interacting surfaces.

To validate our simulation, we conducted two separate sets of experiments. In the first set of experiments we measured the interaction force between PSL spheres and silicon substrates in aqueous solution (18, 25). These experiments can be described by the contact area model in Case I. In the second set of experiments we measured the interaction force between an asymmetrical alumina particle and both a SiO$_2$ and a Cu substrate. These experiments can be described by the contact area model in Case II.

**EXPERIMENTAL PROCEDURE**

The results presented here and the complete experimental procedure employed to obtain these results have been previously published (18, 25). Below is a review of the experimental procedure.

An AFM was used to measure the removal force for these systems. The PSL and alumina particles were mounted on an AFM cantilever by a modified version of the technique developed by Ducker (27, 28). The spring constants of the cantilevers were determined by a method developed by Cleveland et al. (29). Once the particles were mounted on the cantilevers and the spring constants of the cantilevers were determined, each cantilever with mounted particle was inserted into the AFM. Next the AFM was employed to bring the particles into contact with the substrate and to measure the removal force. During these measurements both the applied load and the contact time were carefully controlled. SEM micrographs of the particles were obtained to determine the size, the contact area, and the mass of the particles. The AFM was employed in topographic mode to measure the roughness of the colloids and surfaces.

**RESULTS AND DISCUSSION**

Case I of our simulation is compared against two different sets of experimental data. The first set of data documents the adhesion interaction between PSL spheres and silicon substrates in deionized water. This system represents the interaction of one rough, deformable surface (PSL) with a second smooth rigid surface (silicon). The second set of data documents the adhesion interaction between PSL spheres and silicon substrates in...
an aqueous KNO₃ solution at pH values from 2 to 10. The solutions were prepared by combining HNO₃ and KOH at a constant ionic strength of 0.03 M. Since the KNO₃ etches the silicon at elevated pH values, this system represents the interaction of two rough surfaces. In both cases, the silicon was covered with a surface oxide film, as described elsewhere (18). Case II is compared against experimental data for the interaction between an Al₂O₃ particle and polished SiO₂ and Cu substrates in dry N₂ and aqueous environments.

Case I assumed that the PSL spheres deformed to their equilibrium level on the surface before they were removed. This allowed the contact area established between the spheres and surface to be predetermined based on the model of SEM contact area data, as previously described (25) and shown in Eq. [2]. By studying the shape of AFM force curves when particles are withdrawn from surfaces, Biggs and Spinks were able to predict what type of deformation particles underwent (22). However, the amount a particle deforms when in contact with a surface in different media has not been comprehensively modeled as a function of applied load and contact time. Therefore, although our assumption that the particle completely deforms under minimal contact time and applied load may not be entirely accurate, it represents one limiting case of behavior.

The following parameters were used in the simulation: $A = 3.2 \times 10^{-20}$ J (25), Lennard-Jones separation $D = 4$ nm (30), $E$ (PSL) $= 3 \times 10^{9}$ N/m² (24), and applied load $= 50$ nN. The topography of the PSL also was included (fractional coverage, $fc = 30\%$; mean asperity size, $\varepsilon = 5.56$ nm; standard deviation in asperity size, $std = 4.38$ nm).

Figure 8 displays a histogram of 10,000 model predictions for the adhesive force for a 5-μm radius PSL sphere interacting with a smooth silicon substrate in DI water. Each of these predictions is for a $R = 5$-μm particle, but with a random distribution of asperities constrained by the experimentally determined parameters $fc = 30\%$, $\varepsilon = 5.56$ nm, and $std = 4.38$. Figure 8 shows a peak around 124 nN which tails off quickly. The simulation predicts an average removal force of 120 nN, with a standard deviation of 24.4 nN. Our measured removal force for this system was $127 \pm 20.7$ nN (25). This represents excellent agreement in both average value and variance. Other studies reviewed exhibit similar distributions in removal force measurements (31, 32).

Figure 9 is a comparison of the measured and predicted removal forces for PSL spheres in contact with silicon in DI water as a function of particle radius (25). Each data point is the average of 50 removal force measurements. The solid black line in Fig. 9 is the average value predicted by our simulation employing Eq. [3]. The upper and lower dashed lines in Fig. 9 are one standard deviation from the average prediction. Three important points can be drawn from Fig. 9. First, Fig. 9 shows our simulation’s ability to predict the removal force for the interaction of a rough particle with a smooth surface. Second, it displays our simulation’s ability to predict the variance in the measured removal force. Third, the agreement between experiment and prediction is accomplished with only measured parameters, and no adjustable parameters, in our equations.

In our previous work, we measured the removal force between 5 μm radius PSL spheres and a silicon surface (with surface oxide) as a function of pH in a 0.03 M KNO₃ solution (18). At low pH values the surface remained atomically smooth and the adhesive force was similar to the values shown above in Fig. 9 ($127 \pm 20.7$ nN). However, at pH values greater than 5, the silicon surface was etched by the KOH leaving behind a
FIG. 9. Predicted and observed removal force as a function particle radius for PSL spheres interacting with smooth silicon surfaces in DI water. The black squares are the average of 50 measured values. The solid black line is the average of 5000 simulated particle surface interactions. The upper and lower dashed lines are one standard deviation from the predictions.

rough surface. The adhesion force at these pH values was barely measurable (∼10 nN). The topography of the silicon surface at pH values greater than 5 was measured as having a fractional asperity coverage, fc, of 20%, a mean asperity size, μ, of 25 nm, and a standard deviation in asperity size, std, of 20 nm. The outermost surface of the silicon was an oxide throughout the pH range (18). Figure 10 compares the observed adhesive force to predictions, based on our simulation, for both the case where the silicon surface is atomically smooth (F = 127 nN) and the case where the silicon is rough, with topography characterized by the above measured values (F ∼ 10 nN). As can be seen, the substrate roughness dramatically influenced the observed and predicted adhesive interaction between the particle and the substrate.

In the second group of experiments, an AFM was employed to measure the removal force between an alumina particle (as shown in Fig. 3) and polished SiO2 and Cu substrates in dry N2 and deionized water. The morphologies of the SiO2 and Cu substrates and the alumina particle were measured with an AFM operated in topographic mode and are provided in Table 1. Figure 11 displays topographic AFM images of the polished SiO2 and polished Cu substrates. As can be seen, there is a significant difference in the roughness on these two surfaces. The SiO2 is approximately atomically smooth, while the Cu has a substantial amount of surface roughness.

In addition to the parameters in Table 1, the following parameters were used to simulate the adhesion between alumina

<table>
<thead>
<tr>
<th>Material</th>
<th>r (nm)</th>
<th>Std (nm)</th>
<th>Frac. coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>1.7</td>
<td>0.7</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>53.8</td>
<td>25.2</td>
<td>0.33</td>
</tr>
<tr>
<td>Al2O3 particle</td>
<td>1.6</td>
<td>0.7</td>
<td>0.03</td>
</tr>
</tbody>
</table>

TABLE 1 Surface Roughness of Materials in Our Study

FIG. 10. Predicted and observed frequency of occurrence of removal force (nN). The peaks from 0 to 30 nN are for the interaction between a rough R = 5-μm PSL sphere (fc 30%, μ = 5.56 nm, σ = 4.38 nm) and a rough silicon surface (fc 20%, μ = 25 nm, σ = 20 nm). The peaks from 50 to 200 nN are for the interaction between a rough R = 5-μm PSL sphere (fc 30%, μ = 5.56 nm, σ = 4.38 nm) and a smooth silicon surface.
particles and SiO$_2$ and Cu substrates: $A = 21.7 \times 10^{-20}$ J (Cu/N$_2$/Al$_2$O$_3$), $9.7 \times 10^{-20}$ J (SiO$_2$/N$_2$/Al$_2$O$_3$), $6.2 \times 10^{-20}$ J (Cu/H$_2$O/Al$_2$O$_3$), $1.3 \times 10^{-20}$ J (SiO$_2$/H$_2$O/Al$_2$O$_3$) [33–37]), Lennard-Jones separation $= 0.4$ nm, $E_D = 5 \times 10^{11}$ N/m$^2$ for the Al$_2$O$_3$ and SiO$_2$ and $1.2 \times 10^{11}$ N/m$^2$ for the Cu [38; 39], and applied load $= 1500$ nN. The contact areas between the particle and the substrates were estimated using the 3D-reconstruction method outlined above. In both cases, the area of contact was 600 nm. The particle was estimated to have a volume of $25.2 \, \mu$m$^3$, which corresponds to a spherical particle of radius $R = 1.8 \, \mu$m. Each simulation is the average 1000 model predictions.

Figure 12 compares experimental measurements with predictions from our simulation and an ideal vdW model ($F = AR/6D^2$). The dashed lines in Fig. 12 are the predictions from the ideal vdW model for a spherical alumina particle of radius $1.8 \, \mu$m. The solid lines are the average predictions based on our simulation and the box represents 1 standard deviation in our simulation prediction.

Figure 12 shows that our simulation is in better agreement with experimental data than predictions based on an ideal vdW model for the alumina/SiO$_2$ system. For the alumina/Cu system, although the average prediction for our simulation and an ideal vdW model show reasonable agreement with the average measured force, our simulation accurately describes the observed variance in removal force. Traditional models (vdW and equilibrium models) provide a singular prediction for removal force. Figure 12 also displays the enormous effect surface roughness can have on both the removal force and the variance in the removal force. For smooth systems (SiO$_2$ substrate), a narrow range of removal forces is both predicted and observed. However, as the roughness increases, the range of observed and predicted removal forces increases (Cu substrate). This results from the fact that the two interacting surfaces have an increased number of potential configurations when in contact.

**CONCLUSION**

We have developed and experimentally validated a simulation that predicts particle adhesion in aqueous and dry environments. This simulation is an extension of vdW analysis that better accounts for the effects of particle and substrate surface morphology and mechanical properties. The predictions generated in our work can be incorporated into comprehensive models to describe particle removal processes. The simulation is not limited to describing the adhesive interaction between spherical elastic particles and rigid surfaces but has been shown to predict the interaction for other particle–surface combinations whose physical characteristics can be assessed.

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REFERENCES