A Theoretical and Experimental Study of Surface Forces in Adhesion of Particles to Thin Films

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Applications

- Surface forces play a decisive role in many surface-/interfacial processes
  - Colloidal/emulsion stability
    - Relevant to pharmaceutical, food and coating industries
  - Surface modification of thin films or substrates **to promote or reduce adhesion**
    - Biosensors, oil recovery, cleaning of micron-/nano-scale contaminants

- Our focus: Microelectronic manufacturing

Wafer cleaning

Integrated circuits (IC) chip- or Photomask- cleaning
Motivation/Objective

- **Contaminants**
  - Rough
  - Irregular
- **Substrate**
  - Rough
  - Inhomogeneous
  - Fragile

- **Challenge**
  - 99.99% cleaning efficiency **without surface damage or film-loss**
    ✓ Contaminants as small as 7nm
- **Need**
  - Detail understanding of particle (μm- to nm- sized) adhesion in these systems
  - Estimation of **required removal force** window
  - Optimal cleaning process parameters
Particle Adhesion: Theory, Experiments and Modeling Approach
Fundamental Forces in Particle Adhesion

- **van der Waals (vdW)**
  - Interactions between dipoles (and/or induced dipoles)
- **Electrostatic (ES)**
  - Columbic or double layer
- Steric Force
- Hydrophobic Force
- Chemical Bonds

van der Waals (vdW) and ES forces are the major contributors in adhesion

In fact, vdW force is the most dominating force in close-contact
van der Waals (vdW) Force

- $\mu = ql$ (instantaneous dipole moment)

- Electric field lines

- Induced dipole moment

- $F_{vdW} = F_{Keesom} + F_{Debye} + F_{London}$
  - induced-permanent
  - permanent-permanent
  - induced-induced

- vDW forces are always present

- Interactions between dipoles in particle, solution (if present) and surface
Electrostatic (ES) Force

- **In air**, a particle and surface out of contact have fixed potentials
- **In solution**, a particle and surface attract counter-ion clouds and form double layers

Ion cloud that remains with surface gives surface an effective potential, the zeta potential

The thickness of EDL depends on the solution and the surface of interest, typically 10s to 100s of nm
Approach: Experimental

Sample preparation
FESEM micrographs
Micron-scale SiO₂ and Al₂O₃ particle
Nano- scale Si₃N₄ AFM-probe

Distribution of forces

Frequency
Adhesion Force

Typical AFM force curve

✓ Surface heterogeneity leads to a distribution of adhesion forces
Model Inputs
Identify key parameters that control adhesion force and quantify their effects

Model Prediction
Distribution of forces

Model Validation
Compare model prediction with experimental measurement

Approach: Theoretical

- Unusual geometry
- Random surface morphology
- Chemical heterogeneity

Net predicted force:
\[ F_{\text{Adhesion}} = F_{\text{vdW}} + F_{\text{ES}} \]

Needs:
- Geometry
- Surface morphology
- Surface composition

Needs:
- Computational approach
Modeling Approach

• **Surface Characterization - Geometry**

  - **Geometry**
    - **Irregular**
    
  - **Geometry**
    - **Regular**

  PhotoModeler wire-mesh (Top-projection)
  
  Top-view of the constructed surface
  
  (Height data are in nanometer)

  FESEM micrographs of Al₂O₃

  Si₃N₄ Nanosize pyramidal tip  Zoomed-In view: ROC ~ 75nm

  Modeled tip
Modeling Approach

**Surface Characterization - Roughness**

- FFT
- Extract Fourier coefficients
- Addition of random phase angle
- Inverse Fourier
- Multiple roughnesses, same spectrum density

Mathematical Expression:

\[ z_{x, y} = \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} Z_{k, l} e^{i 2 \pi \left[ \varphi_{k, l} + \frac{k x}{m} + \frac{l y}{n} \right]} \]

- Nanoscale system

AFM scan of Chrome surface

FFT generated Chrome roughness (With random phase shift)

AFM scan at small area

Region of interaction

Order of 10’s nm

Fourier Interpolation

Highly resolved surface roughness
Modeling Approach

Geometry

+ Surface morphology

Contact Surfaces

Generate mathematical surface representations

Force Calculation

(Contactual Approach)

vdW Force Model

F_{vdW}

ES Force Model

F_{ES}

Removal Force Statistics

AFM Measurements

vdW Force Model

Surface morphology
van der Waals (vdW) and Electrostatic (ES) Force
Model Description

\[ F_{ij} = C \frac{\partial}{\partial D} \int d\psi_j \int d\psi_i \frac{d}{\rho_i} \]

\[ F = \sum_i \sum_j F_{ij} \]

Point-by-point additivity

F_{Adhesion} = F_{vdW} + F_{ES}

\[ \nabla^2 \psi = k^2 \psi \quad \text{Poisson-Boltzmann Eq.} \]

Reciprocal Debye length

\[ k = \sqrt{\frac{e^2 \sum z_i^2 n_i}{\varepsilon_0 \varepsilon_r K_B T}} \]

Constant potential boundary conditions

Coulombic

\[ F_{el} = \left( \frac{1}{4\pi \varepsilon} \right) \left( \frac{q^2}{(D^2 + 2RD)^2} \right) \]
Adhesion in Micron-Scale Particulate-Substrate System

- Particle geometry and particle and substrate roughness were measured and modeled

**Regular geometry**
Silica particle (~3μm) on TaON in air

- \( F_{av, Measured} = 18.2 \text{ nN} \)
- \( F_{av, Predicted} = 19.1 \text{ nN} \)

**Irregular geometry**
Silicon nitride particle (~4μm) on TaON in DI water

- \( F_{av, Measured} = 2.1 \text{ nN} \)
- \( F_{av, Predicted} = 2.2 \text{ nN} \)

- Range of predicted force is wider than measured
  - Measured forces are in the range of model predictions
Adhesion in Nano-Scale Body-Substrate System

- Silicon nitride AFM probe on silicon dioxide surface in air and DI water
  - Tip ROC ~ 50nm

\[ \text{Si}_3\text{N}_4/\text{Air}/\text{SiO}_2 \]

\[ \text{Si}_3\text{N}_4/\text{DI}/\text{SiO}_2 \]

- Adhesion model is capable of predicting the adhesion forces for systems as small as few 10’s of nm
- DI water screens the net adhesion force (vdW force)
Conclusions

- Adhesion forces for most of the microelectronic systems can be described by considering only vdW and ES interactions.

- Continuum approximation based adhesion model can describe the adhesion force for systems of sizes down to few 10’s of nm.
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