



CHEMICAL ENGINEERING

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

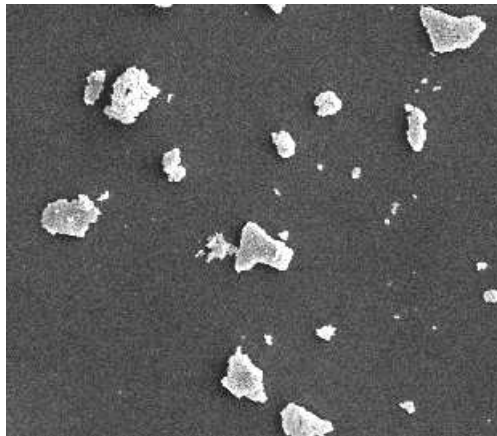
Ravi Jaiswal, Caitlin Kilroy, Gautam Kumar

Prof. Stephen Beaudoin

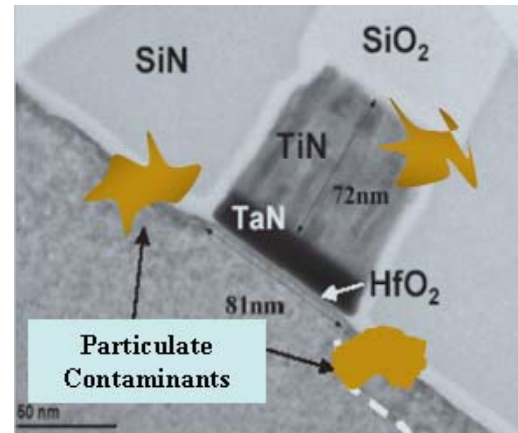
Purdue University

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



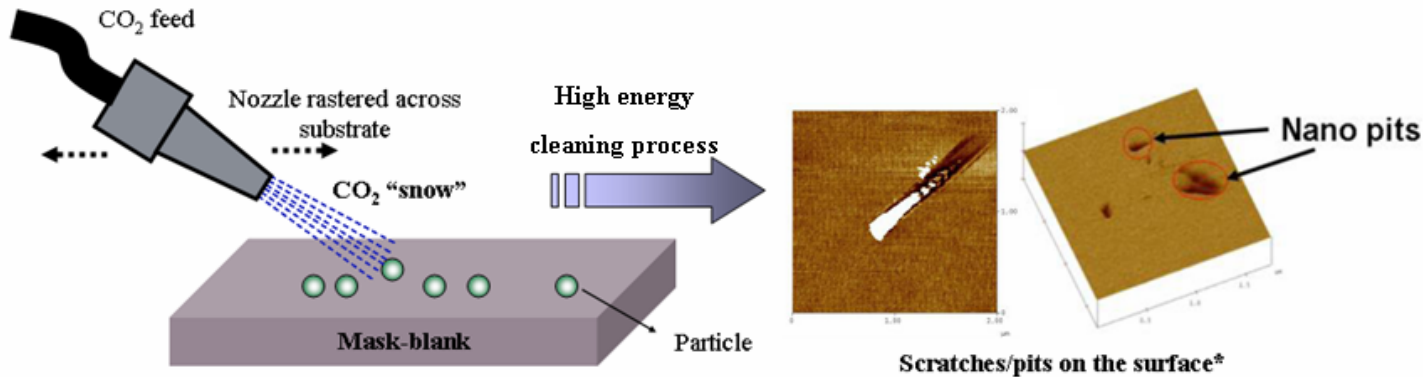
Integrated circuits (IC) chip- or
Photomask- cleaning



Motivation/Objective



Contaminants adhered to IC chip/photomask surfaces



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

- High energy cleaning processes cause surface damage

- **Challenge**

- 99.99% cleaning efficiency **without surface damage or film-loss**
 - ✓ Contaminants as small as 7nm

- **Need**

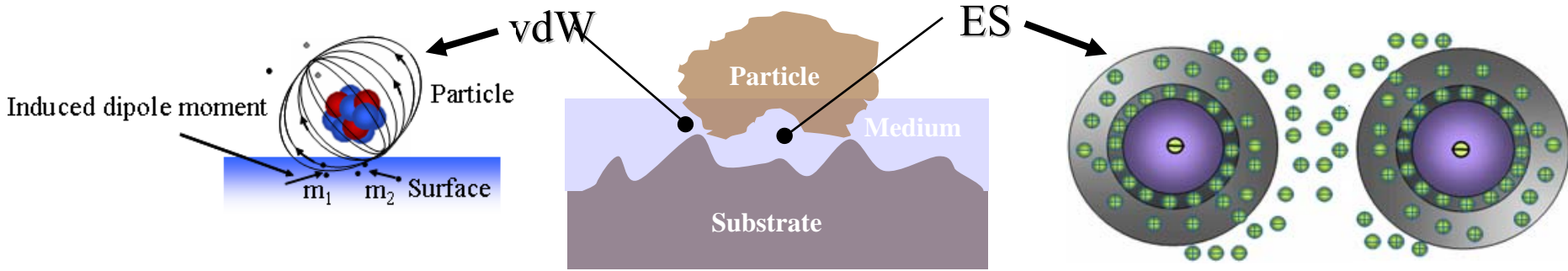
- Detail understanding of particle (μm - to nm - sized) adhesion in these systems
- Estimation of **required removal force** window
- Optimal cleaning process parameters



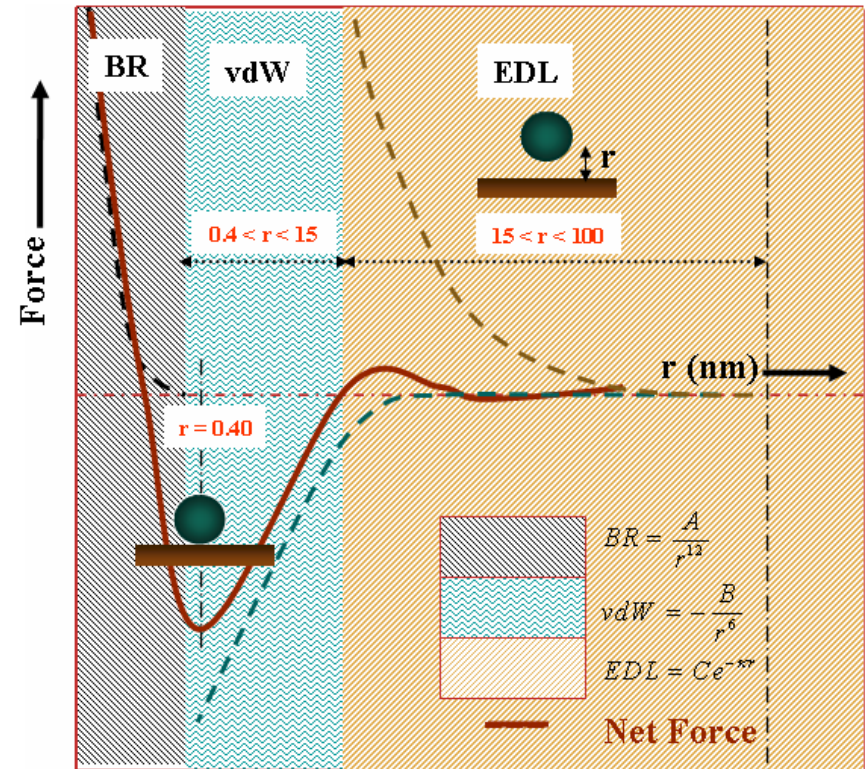
Particle Adhesion: Theory, Experiments and Modeling Approach



Fundamental Forces in Particle Adhesion



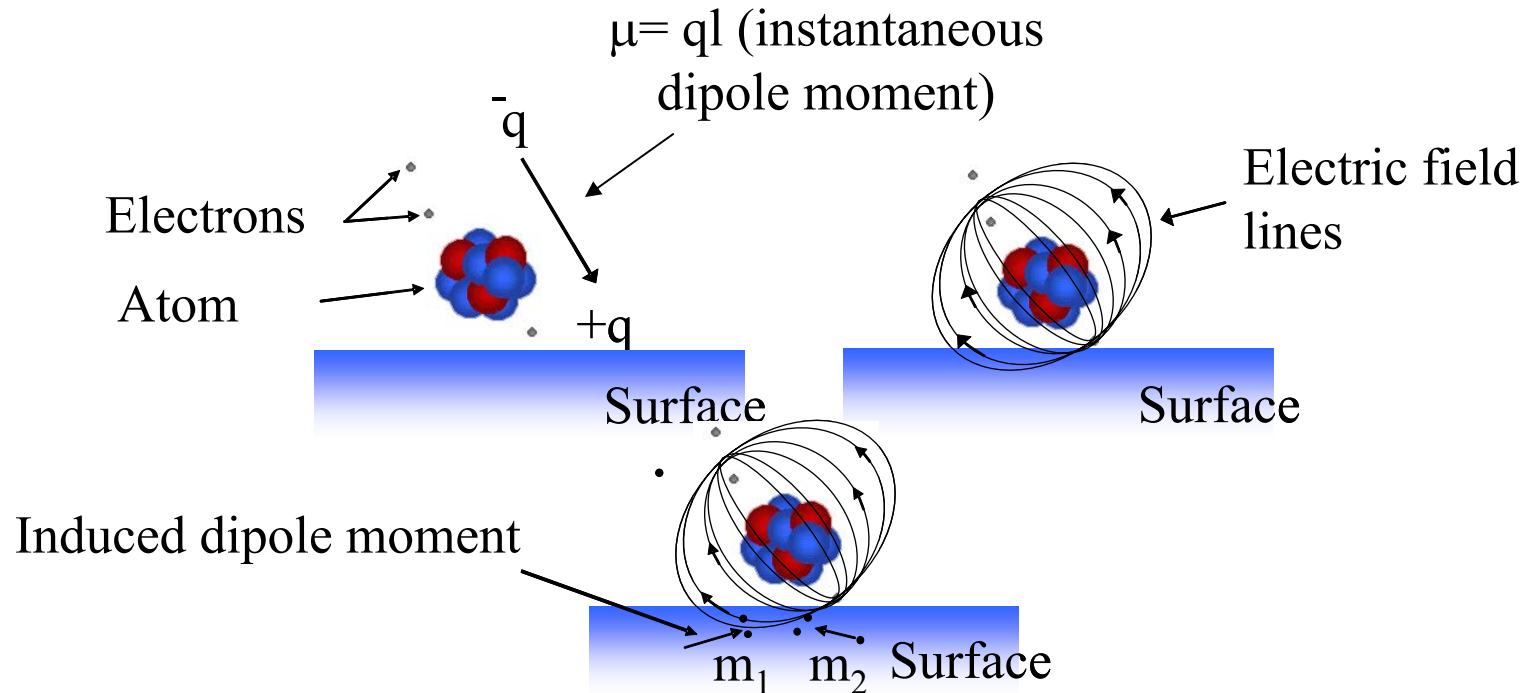
- **van der Waals (vdW)**
 - Interactions between dipoles (and/or induced dipoles)
- **Electrostatic (ES)**
 - Columbic or double layer
- Steric Force
- Hydrophobic Force
- Chemical Bonds



✓ 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



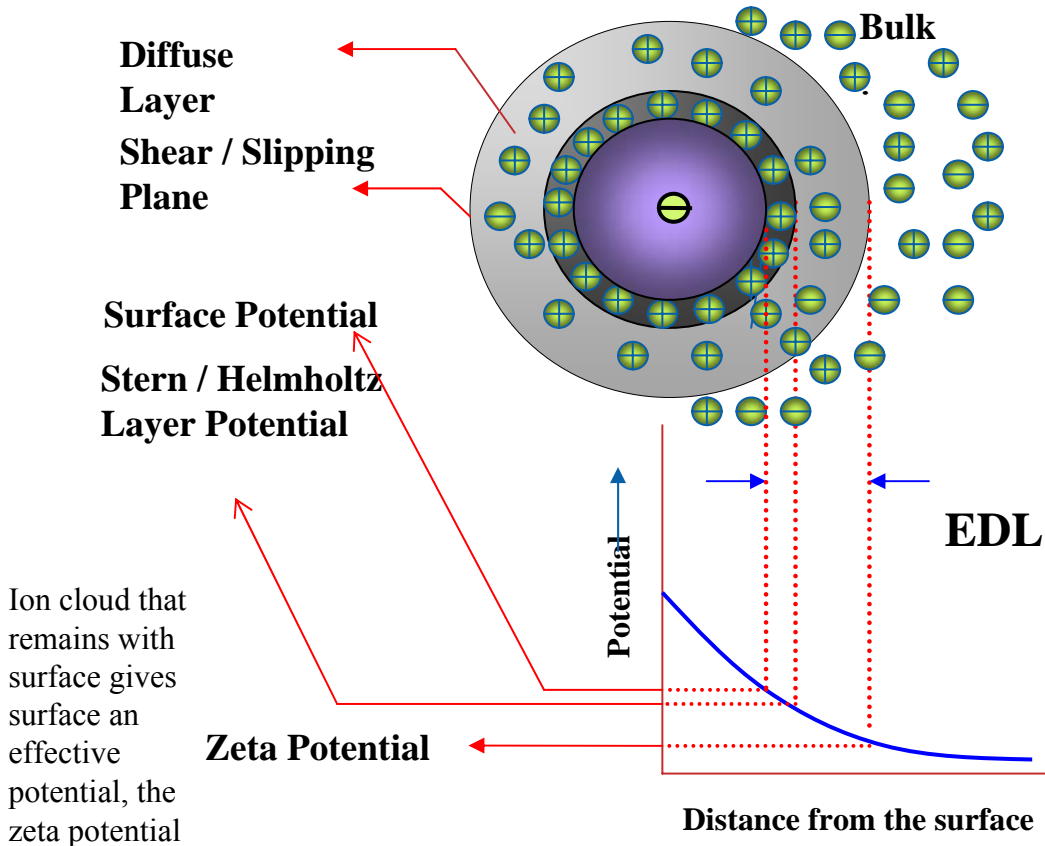
- vdW forces are always present
- Interactions between dipoles in particle, solution (if present) and surface

$$F_{\text{vdW}} = F_{\text{Keesom}} + F_{\text{Debye}} + F_{\text{London}}$$

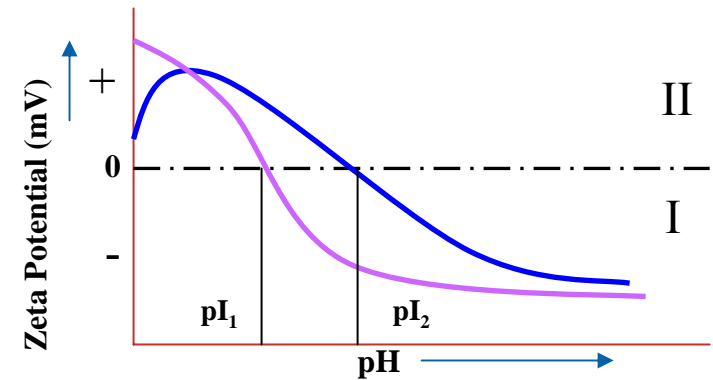
induced-permanent
permanent-permanent
induced-induced



Electrostatic (ES) Force



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

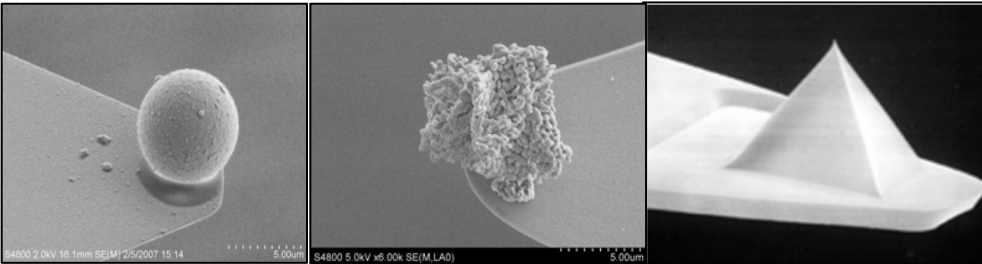
- In air, a particle and surface out of contact have fixed potentials
- In solution, a particle and surface attract counter-ion clouds and form double layers



Approach: Experimental

Sample preparation

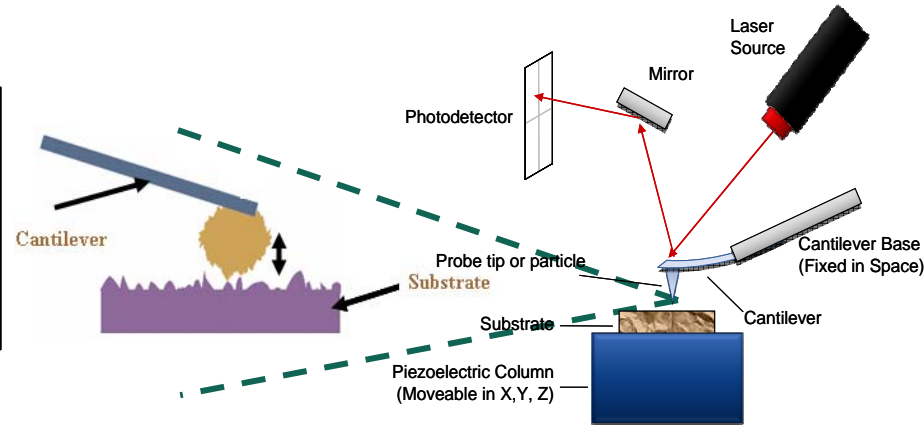
FESEM micrographs



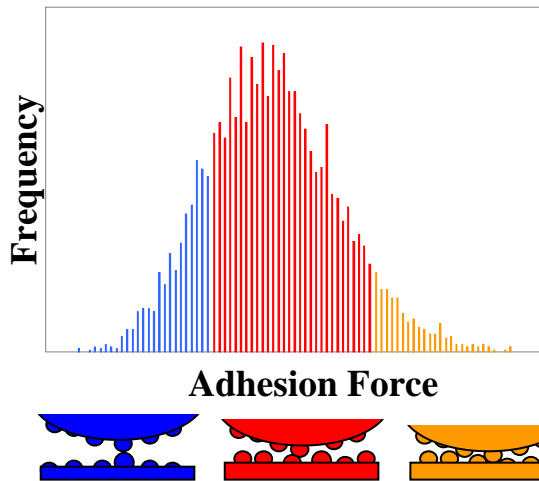
Micron-scale SiO_2 and Al_2O_3 particle

Nano-scale Si_3N_4 AFM-probe

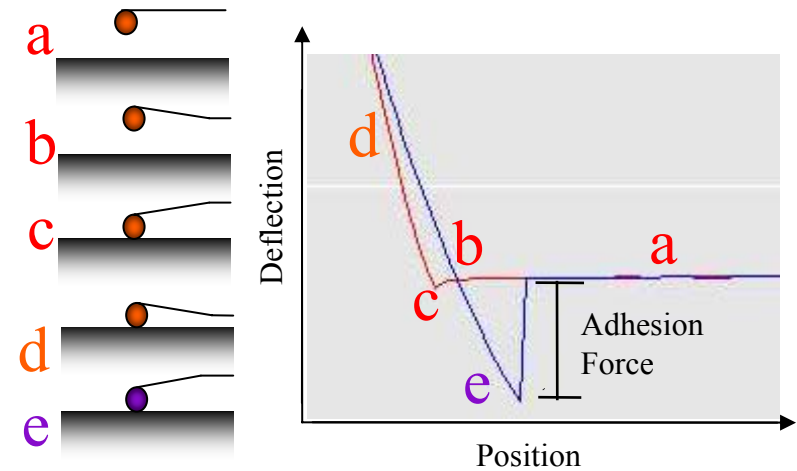
AFM force measurement



Distribution of forces



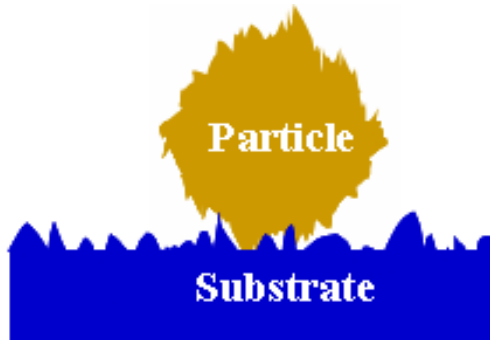
Typical AFM force curve



✓ Surface heterogeneity leads to a distribution of adhesion forces



Approach: Theoretical



- Unusual geometry
- Random surface morphology
- Chemical heterogeneity

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

Needs:

- Geometry
- Surface morphology
- Surface composition

Needs:

- Computational approach

Net predicted force:

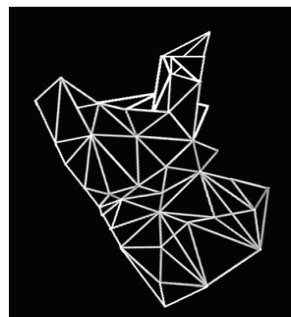
$$F_{\text{Adhesion}} = F_{\text{vdW}} + F_{\text{ES}}$$



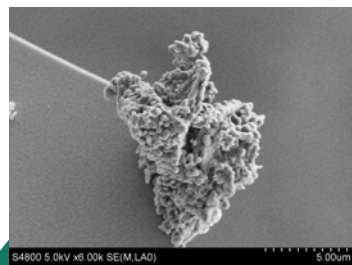
Modeling Approach

- **Surface Characterization- Geometry**

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

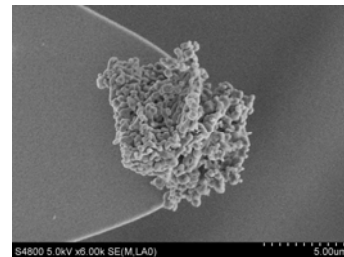
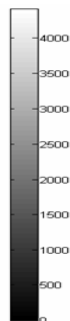


PhotoModeler wire-mesh
(Top-projection)

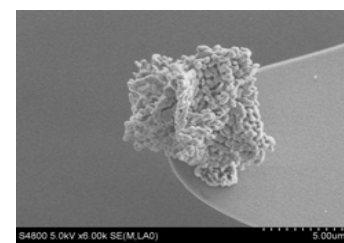
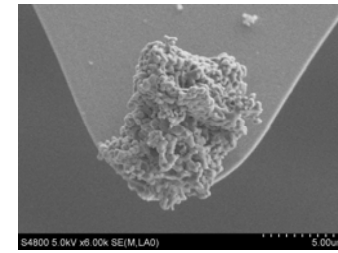


Top-view of the
constructed surface

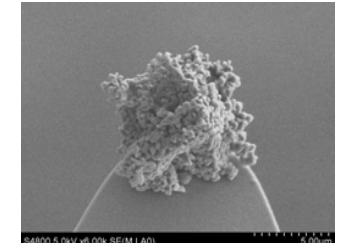
(Height data are in nanometer)



+

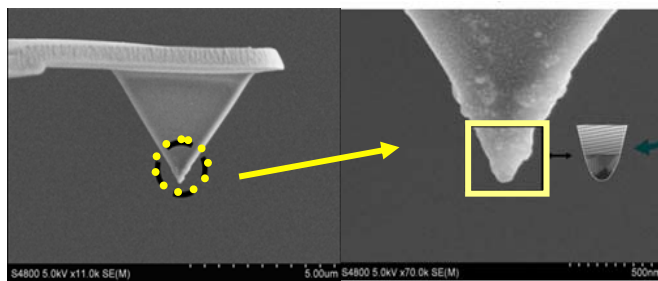


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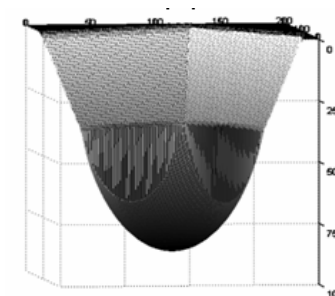


FESEM micrographs of Al_2O_3

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



Si_3N_4 Nanosize pyramidal tip Zoomed-In view: ROC ~ 75nm

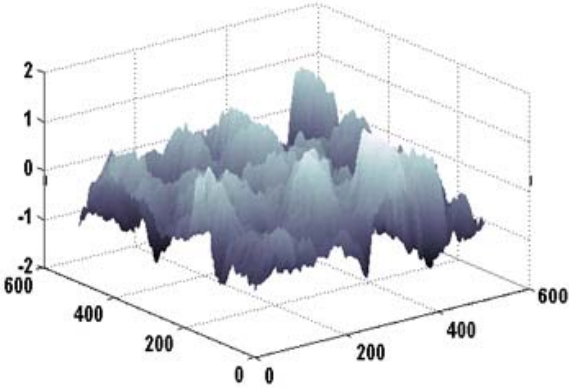


Modeled tip



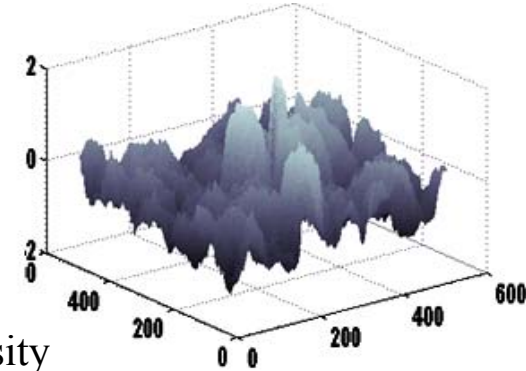
Modeling Approach

• Surface Characterization- Roughness



AFM scan of Chrome surface

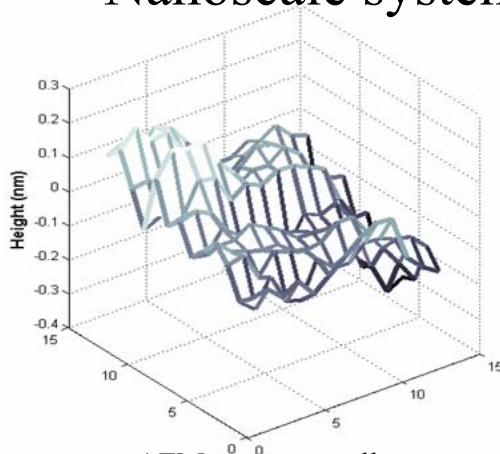
- FFT
 - Extract Fourier coefficients
-
- Addition of random phase angle
 - Inverse Fourier
 - Multiple roughnesses, same spectrum density



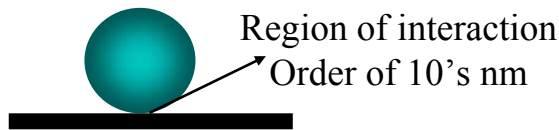
FFT generated Chrome roughness
(With random phase shift)

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

• Nanoscale system

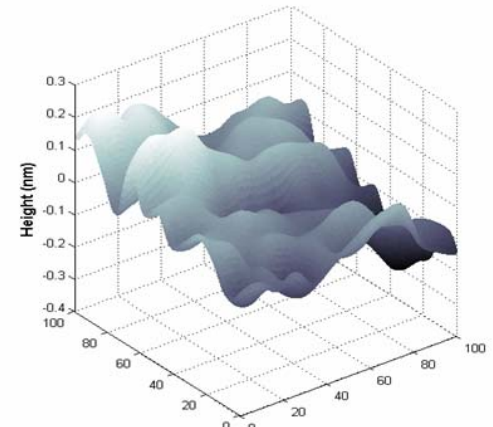


AFM scan at small area



Fourier Interpolation

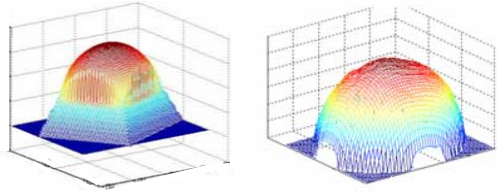
→



Highly resolved surface roughness

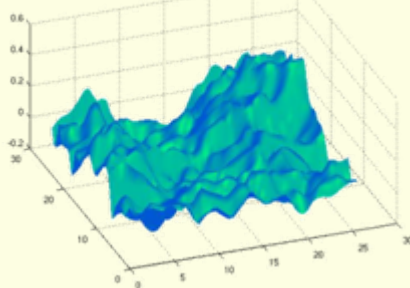
Modeling Approach

Geometry



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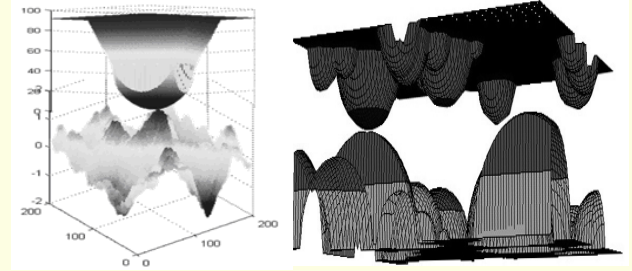
Surface morphology



Contact Surfaces

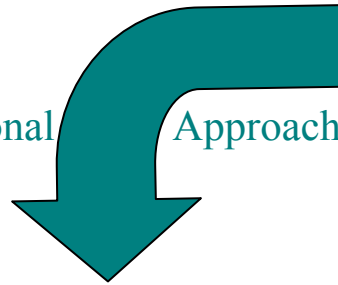


Generate mathematical surface representations



Force Calculation

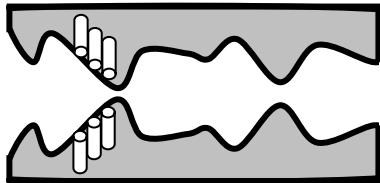
(Computational Approach)



Contact area determination



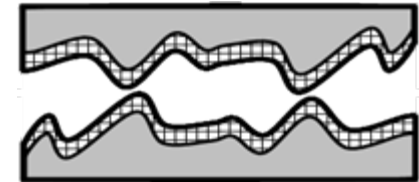
vdW Force Model



F_{vdW}

F_{ES}

ES Force Model



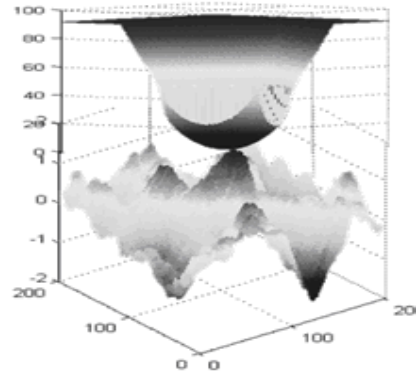
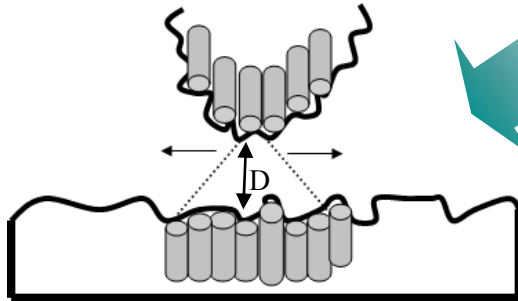
Removal Force Statistics

AFM Measurements

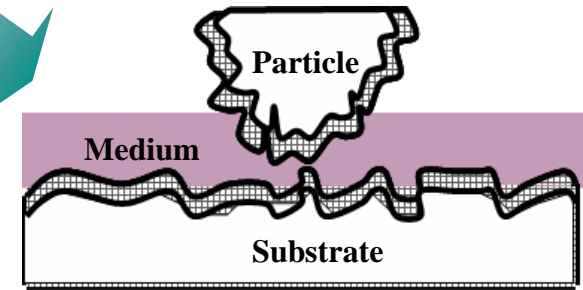


van der Waals (vdW) and Electrostatic (ES) Force Model Description

vdW



ES



+

Double Layer

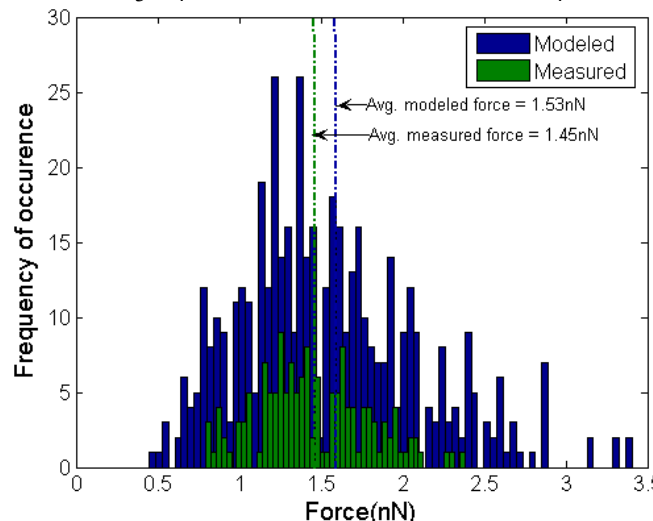
$$F_{1j} = C \frac{\partial}{\partial D} \iiint dV_j \iiint \frac{dV_1}{r^{16}}$$



$$F = \sum_i \sum_j F_{ij}$$

Point-by-point additivity

Si₃N₄ on TaN in Aqueous NH₄OH



$$\nabla^2 \psi = k^2 \psi \quad \text{Poisson-Boltzmann Eq}$$

$$k = \sqrt{\frac{e^2 \sum_i z_i^2 n_{i0}}{\epsilon_0 \epsilon_r K_B T}} \quad \text{Reciprocal Debye length}$$

Constant potential boundary conditions

Columbic

$$F_{el} = \left(\frac{1}{4 \pi \epsilon} \right) \left(\frac{q^2 R (D + R)}{((D^2 + 2 R D)^2)^2} \right)$$

$$F_{\text{Adhesion}} = F_{\text{vdW}} + F_{\text{ES}}$$

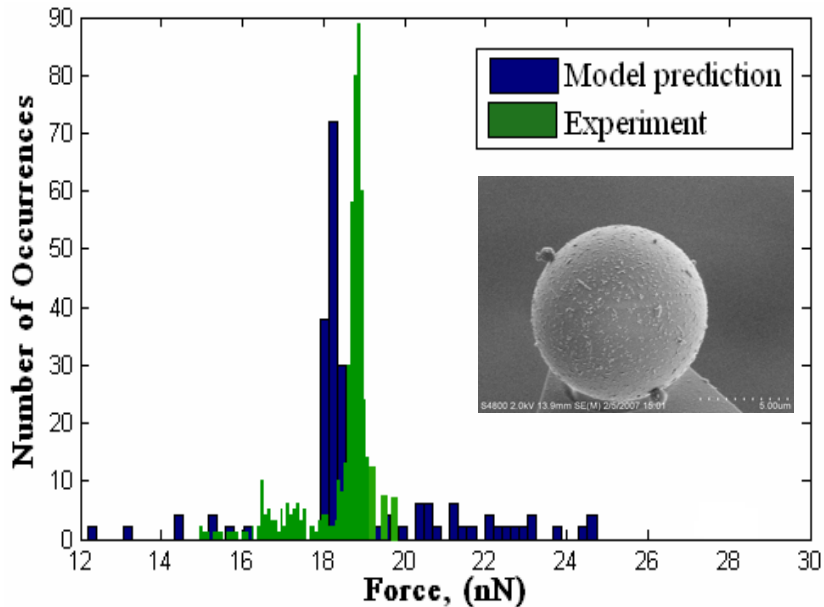


Adhesion in Micron-Scale Particulate-Substrate System

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

Regular geometry

Silica particle ($\sim 3\mu\text{m}$) on TaON in air

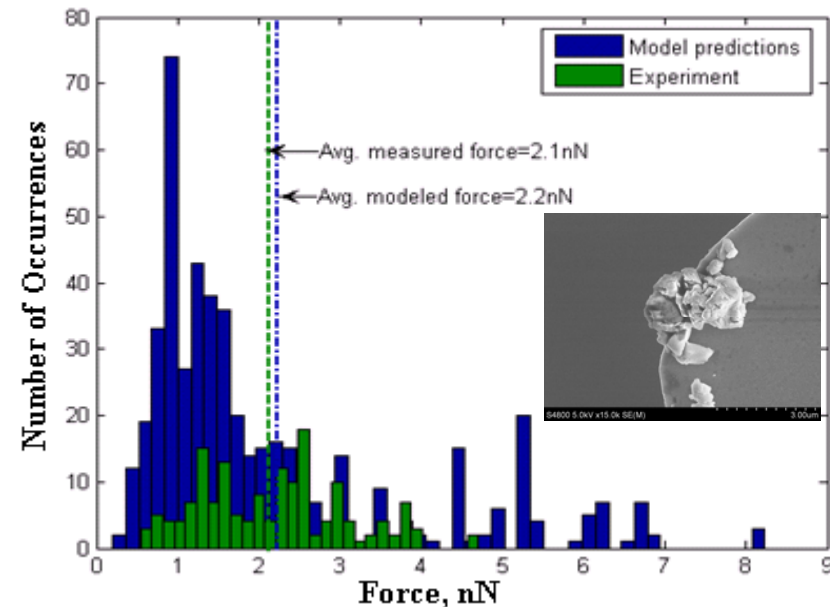


$F_{,av\text{-Measured}}$: 18.2 nN

$F_{,av\text{-Predicted}}$: 19.1 nN

Irregular geometry

Silicon nitride particle ($\sim 4\mu\text{m}$) on TaON in DI water



$F_{,av\text{-Measured}}$: 2.1 nN

$F_{,av\text{-Predicted}}$: 2.2 nN

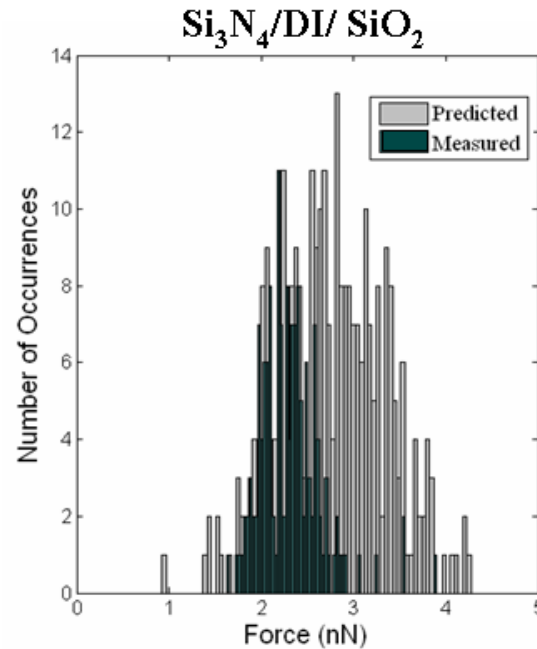
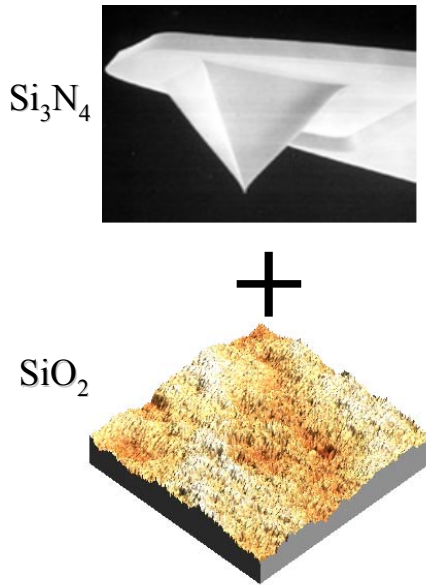
- Range of predicted force is wider than measured

✓ Measured forces are in the range of model predictions



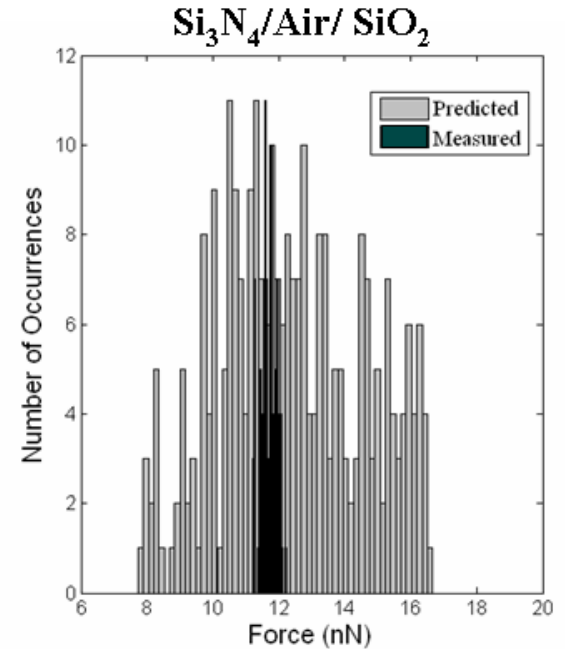
Adhesion in Nano-Scale Body-Substrate System

- Silicon nitride AFM probe on silicon dioxide surface in air and DI water
 - Tip ROC $\sim 50\text{nm}$



$F_{,av\text{-Measured}}$: 2.32 nN

$F_{,av\text{-Predicted}}$: 2.75 nN



$F_{,av\text{-Measured}}$: 11.67 nN

$F_{,av\text{-Predicted}}$: 12.47 nN

- ✓ 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**



Acknowledgement

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