**WHAT IS AFM-BASED NANOSCRAFFING**

- **AFM-based nanoscratch**, also known as scratch nanolithography, is using a functionalized cantilevered-tip for directly removing nanoscale amount of materials from target surfaces with sub-nanoscale precision under control manner.

- Nanoscratching aims at building nanoscale structures (0.1 – 100 nm), which can act as components, devices, or systems with desired properties and performance characteristics, in large quantities at low cost.
  - **Methodology or Processing Technology**
  - **Toolbox** (Equipment: hardware, software, system)
  - **Physical Product** (Components, device, system,...)

---

**AFM Nanofabrication & Mechanical Scratching**

- AFM-based nanofabrication is using an AFM-tip for performing nanofabrication of nanostructures (0.1 – 100 nm), which can act as components, devices, or systems with desired properties and performance characteristics, in large quantities at low cost.

  - **Nano-Manipulation**: Atoms, molecules, nanoparticles, nanoclusters...
  - **Material Removal**: Mechanical scratch, etching...
  - **Material Modification**: Resist exposure, local anodic oxidation.
  - **Material Deposition and Growth**: Electrical field-induced mass-transfer, electrochemical deposition.

---

**AFM: Mechanical Scratching**

- **Automation of AFM Nanofabrication**
  - Predictive model
  - CNC control with sub-nanometer precision
  - Multiple tips

---

**Typical Nanoscratch Apparatus**

- **AFM Nanoscratch**
  - **Operation in Contact mode**
  - **Triangular pyramid tip**
  - **Diamond coated**

---

**AFM Scratching of Silicon**

- **Triangular pyramid tip**
  - **Diamond coated**

- **Effect of tip normal force on scratched depth and width**

  - **Scratch depth**, \( d(F_n) = \alpha_1 \ln(F_n/F_{t1}) \)
  - \( F_n \) is the normal tip-sample force
  - \( \alpha_1 \) is scratch penetration depth
  - \( F_{t1} \) is threshold forces based on depth data
AFM Scratching of Silicon

AFM Scratching of Au-Pd Film

A Chinese poem (20 characters) of Tang Dynasty was scratched on gold-palladium film (with r.m.s. of 0.2 nm), which was deposited on cleaved mica by ion sputtering. The scratch was performed by a Si AFM tip with a force constant of 35 N/m at a normal force of 20 μN. Scratched depth is about 2 nm.


Effect of tip normal force on scratched depth and width

AFM Scratching of Ni$_{80}$Fe$_{20}$ (in backward direction)

Effect of multiple scratch on scratched depth and width

Multiple Scratching of Ni$_{80}$Fe$_{20}$ in Upward direction

AFM Scratchability of Si and Ni$_{80}$Fe$_{20}$

Archard's wear equation

Where $V$ is the volume loss caused by wear, $k$ is wear coefficient, $L$ is sliding distance, $F_n$ is applied normal force, and $H$ is hardness of material to be tested. Scratch coefficient, $k_s$

$k_s = kH = V/F_nL = dw/L$

where $L$ becomes the scratch distance. Since the cross-section of the scratched groove is in a "V" shape, its cross-section area can be approximated by $d \times w_f$ and $V = dw_fL$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Single crystal silicon</th>
<th>Ni$<em>{80}$Fe$</em>{20}$ thin film</th>
<th>Scratchability rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scratch penetration depth, $d$ (nm)</td>
<td>2.58 (nm)</td>
<td>4.46 (nm)</td>
<td>65%</td>
</tr>
<tr>
<td>Mean scratch coefficient, $k$ (nm/N)</td>
<td>2.43 (nm/N)</td>
<td>38.41 (nm/N)</td>
<td>1,072%</td>
</tr>
<tr>
<td>Scratch penetration area, $p$ (nm$^2$)</td>
<td>1.418 (nm$^2$)</td>
<td>15.079 (nm$^2$)</td>
<td>1,072%</td>
</tr>
<tr>
<td>Hardness, $H$ (GPa)</td>
<td>10.4 (GPa)</td>
<td>8.0 (GPa)</td>
<td>75%</td>
</tr>
</tbody>
</table>
Mechanical Scratching and Etching by AFM

AFM images of V-shaped grooves on mica substrate scratched by Si tip at contact mode: a) 2-nm deep and 60-nm wide grooves with one scratch at normal force of 500 nN, b) 20-30 nm groove by five repeated scratches with a normal force of 5 nN (Tseng et al., 2007).

AFM SCRATCHING OF Ni

Hertz contact theory: the contact area: \( A_c = \pi/d (R/d)^{1.5} \)

The maximum contact stress: \( \sigma_m = 3F_c/2R \sqrt{d/d} \)

where the subscripts n and c denote the property related to diamond and nickel. \( E_n = 143 \text{ GPa} \) and \( E_c = 130 \text{ GPa} \), \( \nu_n = 0.07 \) and \( \nu_c = 0.24 \), \( E_n = 171 \text{ GPa} \).

At \( F_n = 1 \mu \text{N} \) with \( R = 120 \text{ nm} \), \( \sigma_m = 7.33 \text{ GPa} \). The permanent indentation is achieved only if the indentation pressure or contact stress is exceeding a certain limit. Very often, its hardness is considered as the limit. The hardness of Ni thin films can be found from 7.0 to 7.7 GPa. The contact stress, \( \sigma_m \), is consistent with the experimental hardness.

Pauli Repulsion Between Atoms or Molecules

The repulsive forces between an AFM tip and a sample can be obtained by finding the corresponding pairwise potentials first. The potential of the interaction (V) between neutral atoms or molecules can normally be approximated as

\[ V(r) = A_0 \ln \left( \frac{r}{a} \right) \]

where \( A_0 \) is a proportionality constant and the exponent is higher than 10 for most of materials (Wagner, 2006). Note that the main repulsion between atoms is not due to electrostatic repulsion between the nuclei, but due to the Pauli exclusion principle for their electrons. If \( r < 12 \), the above potential can incorporate with the potential of the vdW interaction to form the well-known Lennard-Jones potential, which is common to almost all empirical potentials and shown below:

\[ V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

where \( \epsilon \) is the Lennard-Jones potential including both the repulsive and the attractive terms, \( \sigma \) is the depth of the potential well, \( \sigma \) is the distance at which the inter-particle potential is zero, and \( r \) is the distance between the centers of the paired particles. The basic shape of Lennard-Jones potential curve is common to almost all empirical potentials and shown below:

As shown, at short range (small \( r \)) the potential energy is very large and positive, revealing that this is a very unfavorable arrangement of the atoms, which indicates that the two atoms are strongly overlapping.

Lennard-Jones Potential and Forces

Although the attractive vdW potential is derived from dispersion interactions, the exponent 12 in describing the Pauli repulsion has no theoretical justification and was chosen because of its simplicity and good agreement with experimental data for most gases. The \( n \)-th term describes Pauli repulsion between paired electrons. The typical values of \( \sigma \) and \( \epsilon \) for O interaction are 1.07 Å and 0.355 eV and for R = 200 Å the potential is 8.136 eV and \( \epsilon = 0.163 \text{ eV} \) for N.C. By integration, the interaction force between a sphere and a plane using the Lennard-Jones potential can be found as

\[ F_I = \frac{d\Phi}{dn} = \frac{d\Phi}{dn} \]

where \( \Phi \) is the total interaction to form the well-known Lennard-Jones potential constant equal to \( 22 \epsilon \).

If the tip can be approximated by a circular cone, Du and Li (2007) found that the combined repulsive and attractive interaction force can be expressed as

\[ F_I = \frac{d\Phi}{dn} \]

where \( \Phi \) is the total interaction to form the well-known Lennard-Jones potential constant equal to \( 22 \epsilon \).
Scratch coefficient, $k_s = \frac{V}{L F_n} = \frac{d_w f}{F_n}$

Assume the cross-section of scratched groove is in a “V” shape, $V = d_w f L$

$A_t = d_w f$

The cross-section of the tip end segment, $A_t$

$A_t = R^2 (\theta - \sin \theta)$

where $\theta = 2 \cos^{-1} (1 - d_i / R)$.

$d_i =$ the impressed depth of the semispherical tip into the sample, and $d_i = d$.

$R = 120 \text{ nm}$

A.A. Tseng et al., JVSB (2010)

AFM Scratchability of Si and Ni

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Si</th>
<th>Ni</th>
<th>Si thin film</th>
<th>Ni thin film</th>
<th>Si/Al</th>
<th>Al/As2S3</th>
<th>PGMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring constant $[\text{N/m}]$</td>
<td>42.0</td>
<td>239</td>
<td>42.0</td>
<td>42.0</td>
<td>165</td>
<td>239</td>
<td>0.68</td>
</tr>
<tr>
<td>Scratch speed $[\text{mm/s}]$</td>
<td>0.10</td>
<td>30</td>
<td>0.10</td>
<td>0.10</td>
<td>9.0</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>Scratch coeff. $\alpha_1 [\text{nm}]$</td>
<td>0.765</td>
<td>38.65</td>
<td>4.96</td>
<td>3.94</td>
<td>80.51</td>
<td>18.09</td>
<td>4.538</td>
</tr>
<tr>
<td>Threshold force $F_{t_1} [\mu\text{N}]$</td>
<td>1.01</td>
<td>52.09</td>
<td>1.01</td>
<td>1.20</td>
<td>11.17</td>
<td>48.55</td>
<td>0.017</td>
</tr>
<tr>
<td>Coefficient $R^2$</td>
<td>0.96</td>
<td>0.97</td>
<td>0.98</td>
<td>0.92</td>
<td>0.97</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>Scratch ratio, $\alpha_1 / F_{t_1} [\text{nm/\mu N}]$</td>
<td>0.756</td>
<td>0.034</td>
<td>4.555</td>
<td>3.272</td>
<td>6.962</td>
<td>0.399</td>
<td>123.44</td>
</tr>
<tr>
<td>Scratch ratio rating [%]</td>
<td>100</td>
<td>97</td>
<td>603</td>
<td>433</td>
<td>921</td>
<td>53</td>
<td>16,328</td>
</tr>
<tr>
<td>Hardness $H [\text{GPa}]$</td>
<td>10.35</td>
<td>7.35</td>
<td>2</td>
<td>141</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rating based on hardness [%]</td>
<td>100%</td>
<td>100%</td>
<td>125%</td>
<td>136%</td>
<td>1000%</td>
<td>204%</td>
<td>—</td>
</tr>
<tr>
<td>Scratch ratio rating/Hardness rating</td>
<td>1.01</td>
<td>0.97</td>
<td>4.82</td>
<td>3.18</td>
<td>0.93</td>
<td>0.26</td>
<td>—</td>
</tr>
</tbody>
</table>

* With respect to Si properties

** Scratch ratio rating/Hardness rating

Comparison of Scratch Properties

A.A. Tseng, Surface Science (2010)

SCRATCH DIRECTION OR TIP SHAPE

a) Upward b) Forward c) Downward d) Backward

Tip Normal Force = 9μN

AFM Scratch Coefficient and Volume??

Scratch coefficient, $k_s = \frac{V}{L F_n} = \frac{d_w f}{F_n}$

Assume the cross-section of the scratched groove is in a “V” shape, $V = d_w f L$

$A_t = d_w f$

The cross-section of the tip end segment, $A_t$

$A_t = R^2 (\theta - \sin \theta)$

where $\theta = 2 \cos^{-1} (1 - d_i / R)$.

$d_i =$ the impressed depth of the semispherical tip into the sample, and $d_i = d$.

$R = 120 \text{ nm}$

A.A. Tseng et al., JVSB (2010)

AFM Scratching can be a promising technique for creating or repairing Ni-based masks, stamps and molds

AFM Scratching can be used to scratch electroplated Ni structures that can act as major components and devices in different MEMS/NEMS and masks for NGL

AFM Scratchability of Si and Ni

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Si (100)</th>
<th>Si (100)</th>
<th>Si/Al/As2S3</th>
<th>Si/Al</th>
<th>Al/As2S3</th>
<th>Polymeric photoresist</th>
<th>Zr55Cu30Al10Ni5</th>
<th>PGMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring constant $[\text{N/m}]$</td>
<td>42.0</td>
<td>239</td>
<td>42.0</td>
<td>165</td>
<td>239</td>
<td>0.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scratch speed $[\text{mm/s}]$</td>
<td>0.10</td>
<td>30</td>
<td>0.10</td>
<td>9.0</td>
<td>30</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scratch coeff. $\alpha_1 [\text{nm}]$</td>
<td>0.765</td>
<td>38.65</td>
<td>4.96</td>
<td>80.51</td>
<td>18.09</td>
<td>4.538</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Threshold force $F_{t_1} [\mu\text{N}]$</td>
<td>1.01</td>
<td>52.09</td>
<td>1.20</td>
<td>48.55</td>
<td>0.017</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coefficient $R^2$</td>
<td>0.96</td>
<td>0.97</td>
<td>0.97</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scratch ratio, $\alpha_1 / F_{t_1} [\text{nm/\mu N}]$</td>
<td>0.756</td>
<td>0.34</td>
<td>4.555</td>
<td>6.962</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scratch ratio rating [%]</td>
<td>100</td>
<td>97</td>
<td>603</td>
<td>921</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness $H [\text{GPa}]$</td>
<td>10.35</td>
<td>7.35</td>
<td>2</td>
<td>48.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Scratch ratio rating/Hardness rating

A.A. Tseng, Surface Science (2010)
**AFM Scratching Versus Oblique Cutting**

- **SEM image of 6 scratched grooves with chips using $F_n = 1, 2, 3, 5, 7,$ and 9 µN.**
- **SEM image of 5 machined grooves with chips using $F_n = 9$ µN with number of scan (No) equal to 1, 3, 5, 7, and 9.**

**Finite Element Modeling of AFM Scratching**

- **Static Model for normal AFM tip (negative rake angle).**
- **Dynamic model For better tip design (positive rake angle).**

**Mechanical Scratching and Etching by AFM**

- **AFM images of V-shaped grooves on mica substrate scratched by Si tip at contact mode: a) 2-nm deep and 60-nm wide grooves with one scratch at normal force of 50 nN, b) 20-30 nm groove by five repeated scratches with a normal force of 5 µN (Tseng et al., 2007).**

**Polymeric Materials by AFM Scratch**

- **Scratched resist thin film can be used as masked for subsequent etching or deposition processes.**
- **Material removal rate can be increased by aiding chemical with chemical etching.**

**Scratch of Nanochannel on Gold Films and Wires**

- **AFM images of trenches of on polymer films by Si tip at contact mode: 150-225 nm deep with one scratch on PMMA film using normal force of 17.5 µN, b) 150-nm deep with one scratch on PI film using normal force of 8.5 µN.**

**Roadmap for Tip-Based Nanofabrication**

*Developed in 2007 for Commercialization*

<table>
<thead>
<tr>
<th>Metric</th>
<th>2010</th>
<th>2012</th>
<th>2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feature Position Accuracy [nm]</td>
<td>50</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>Feature Size Variation (% of dimension)</td>
<td>10%</td>
<td>3%</td>
<td>1%</td>
</tr>
<tr>
<td>Heterogeneity in Parameters: Size, Shape, or Orientation</td>
<td>Two values of one parameter</td>
<td>Five values of two parameters</td>
<td>Continuous control over two parameters</td>
</tr>
<tr>
<td>Feature Fabrication Rate (No. of structure/min/tip with array tips)</td>
<td>1 min</td>
<td>5 min/tip</td>
<td>Five-tip array</td>
</tr>
<tr>
<td>Tip Shape Variation (% of dimension with required operations)</td>
<td>Height &lt; 10%, Radius &lt; 30%</td>
<td>Height &lt; 5%, Radius &lt; 10%</td>
<td>Height &lt; 1%, Radius &lt; 3%, 10 operations</td>
</tr>
<tr>
<td>In-situ Tip Height Sensing [nm]</td>
<td>20</td>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>

Develop closed-loop control strategy to reduce the geometric errors induced by equipment including hysteresis creep by piezo scanner, AFM tip, mechanical drift, thermal drift...
- To reduce the hysteresis creep, feedback signal uses direct-measuring, non-contact capacitive position sensors (high motion linearity, long-term stability, phase fidelity)
- To reduce mechanical drift, positioning and scanning use frictionless flexure guidance (within 0.01 nm/s)
- To reduce thermal drift, invar or low thermal expansion materials is used for the stage (within 0.01 nm/s)
- The total inaccuracy should be less than 1 nm/mm and 0.01 nm/s.

Dimension and accuracy of patterns are highly affected by operating parameters: contact mode, tip material, scanning speed, humidity, applied voltage...
- Accuracy of patterning scheme requires further refining, and better processing procedures need to be developed.
- Height and width modulation by adjusting the phase and the duration time of pulsed voltage (short pulse voltage restricting lateral diffusion while high voltage pulse producing fast growing in height).
- Develop CAD software for the design and control of SPM (including AFM, STM, SNOM) oxidation and scratching patterning.

Parallel Processing & Multi-Resolution (IBM Millipede and Special Tip Design)
Schematics of three main classes of sensory used for deflection detection in AFM
1) external sensor: sensor is not integrated in the cantilever,
2) self sensing: sensor is integrated in the cantilever,
3) Tip-surface interaction sensor: other tip-surface than force interactions are detected, e.g. thermal or electrochemical interactions (Courtesy of J. Polesel-Maris).

Factors in Nanoscratching
- Tool/Workpiece Interaction (physical, chemical, biological....)
  Relevant techniques: Science with Manufacturing
- Tool/Workpiece Manipulation (position, movement, force, ....)
  Relevant techniques: CNC, Automation
- Desired Product Requirements (properties of surface, shape, ....)
  Relevant techniques: On-line monitoring and sensing
- Productivity (reliability, system....)
  Relevant techniques: Equipment design, management

Computer Integrated Manufacturing for TBN
Desk Top Based System
For All of Us in Nano Worlds

Life Is Limited!
Learning Is Unlimited!

Thank You!!

<table>
<thead>
<tr>
<th>General Nanotechnology Related Markets</th>
</tr>
</thead>
<tbody>
<tr>
<td>US National Science Foundation has made predictions of the future of nanotechnology by 2015</td>
</tr>
<tr>
<td>• $340 billion for nanostructured materials,</td>
</tr>
<tr>
<td>• $600 billion for electronics and information-related equipment,</td>
</tr>
<tr>
<td>• $180 billion in annual sales from nanopharmaceuticals</td>
</tr>
</tbody>
</table>