Atomic Force Microscopy

CHEM-E4205 Crystallography Basics and Structural Characterization

Matilda Antila, Joakim Kattelus

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Aalto University
School of Chemical
Engineering

Atomic Force Microscopy

1. History
2. Principles and equipment
3. Type of information gained
4. Research examples
5. Pros and Cons

History

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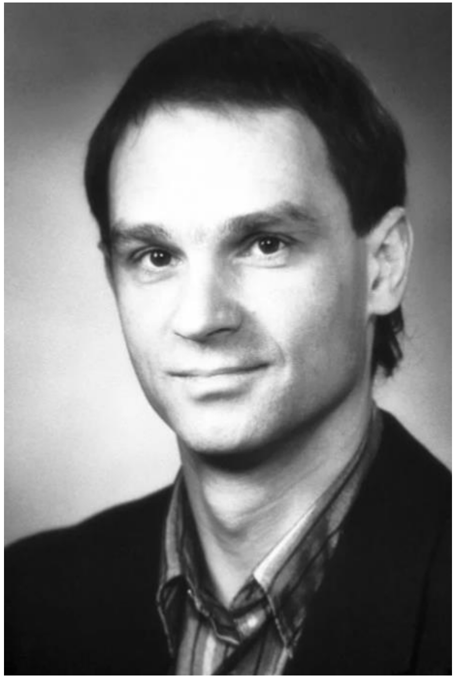
Atomic force microscopy – Historical perspective

Scanning Tunneling Microscope (STM)

- **In 1981**
- **IBM research - Zurich**
- **Gerd Binnig and Heinrich Röhrer**
- Nobel Prize in Physics in 1986

Atomic Force Microscope (AFM)

- **In 1986 by Binnig**
- **Commercially available in 1989**



Giessibl, Franz J. "Advances in atomic force microscopy." *Reviews of modern physics* 75.3 (2003): 949, https://link.aps.org/doi/10.1103/RevModPhys.75.949
Gerd Binnig – Facts, the Nobel prize, https://www.nobelprize.org/prizes/physics/1986/binnig/facts/, [Accessed 27.4.2023]

Scanning tunneling microscope (STM)

- **A voltage is applied to the sample, under high vacuum**
- **A tunneling tip (conducting wire) is brought close to surface**
- **Once the tip is close to the surface, quantum tunnelling allows an electrical current to “jump” the gap**
- **The current as a function of the z coordinates of the tip is used to generate an image of the sample surface**

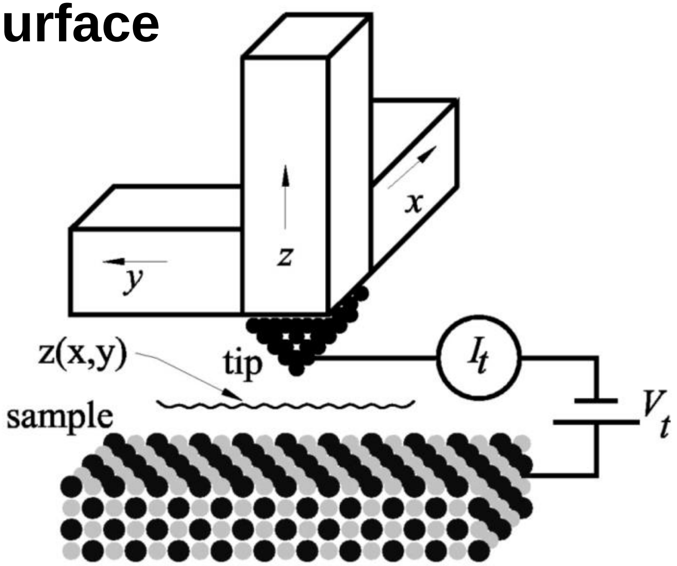
1 Å^{-1} for metals

$$I(z) = I_0 e^{(-2\kappa z)}$$

1 Å increase in z -> order of magnitude decrease in I

↓

Atomic scale resolution

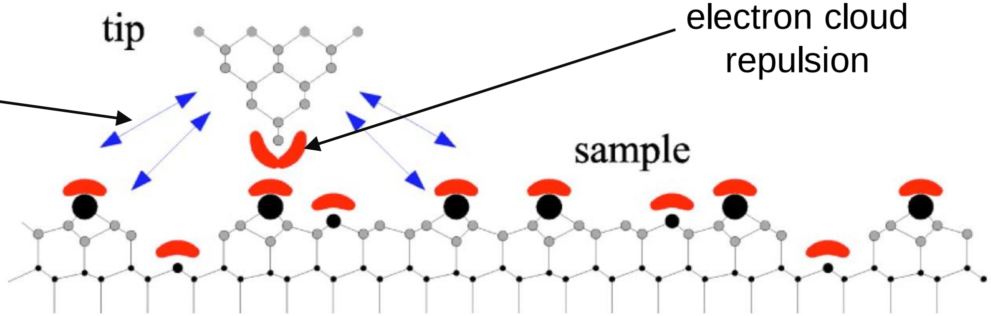


Giessibl, Franz J. "Advances in atomic force microscopy." *Reviews of modern physics* 75.3 (2003): 949, https://link.aps.org/doi/10.1103/RevModPhys.75.949

Principles and Equipment

Atomic Force Microscope – principles

- STM allows for atomic resolution imaging, but only for conducting samples at ultrahigh vacuum
- Atomic force microscopy (AFM) was developed to solve this problem
- AFM instrumentation is similar to STM, but the conducting tip is replaced by a force sensor
- The force in the z-direction is used as the signal used to create a three dimensional image



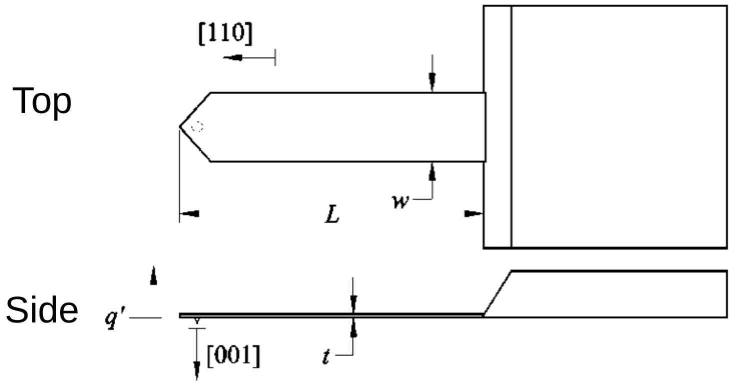
Long-range attractive dispersion forces

Short range electron cloud repulsion

Giessibl, Franz J. "Advances in atomic force microscopy." *Reviews of modern physics* 75.3 (2003): 949, https://link.aps.org/doi/10.1103/RevModPhys.75.949

The force sensor

- A cantilever geometry is commonly used for the force sensor
- Historically: gold foil, aluminium foil, tungsten wires
- Current: micromachined silicon cantilever with integrated tip
- The cantilever acts as a spring, deflection is thus: $d = F/k$
- Cantilever tip movement is commonly measured by measuring the deflection of a reflected light beam



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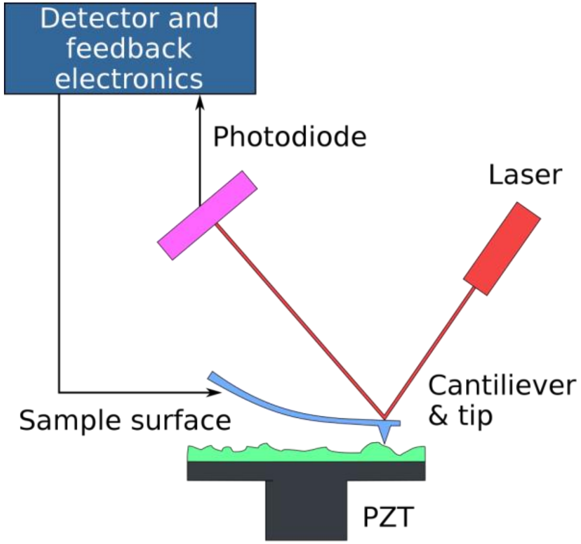
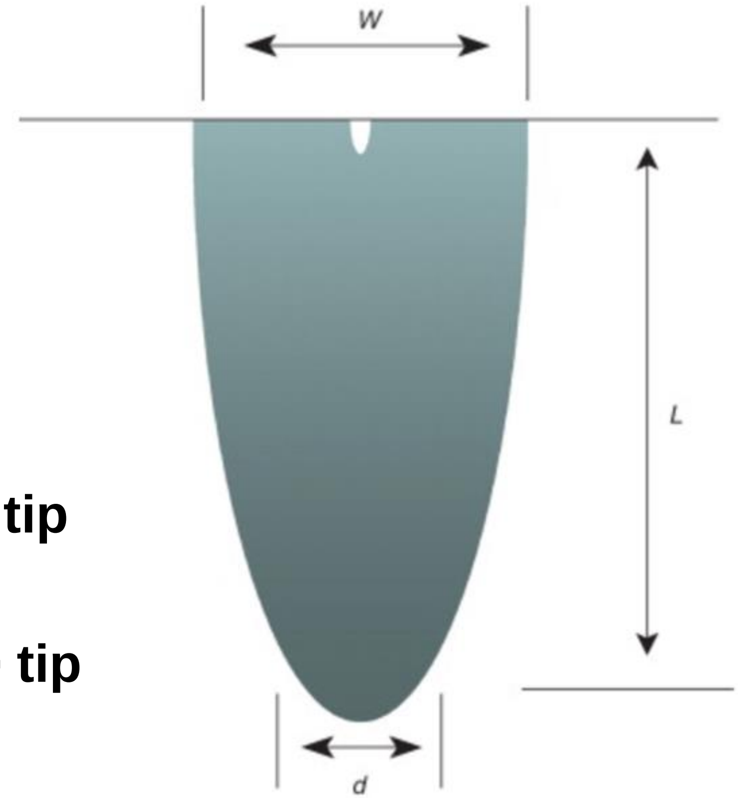


Image source: Wikipedia, created by OverlordQ, public domain.

The tip

- **Ideally, only front atom on tip interacts strongly with sample**
- **Around 10-20 nm in diameter**
- **Aspect ratio = L/W**
  - Small aspect ratio
    -> smeared out slopes
- **Load of the tip**
- **Height measurements insensitive to the tip geometry**
- **Too much interaction with the surface -> tip abrasion & sample damage**



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Suprakas Sinha Ray,4 - Techniques for characterizing the structure and properties of polymer nanocomposites, In Woodhead Publishing Series in Composites Science and Engineering, Environmentally Friendly Polymer Nanocomposites, Woodhead Publishing, 2013, P. 74-88. https://doi.org/10.1533/9780857097828.1.74.

Modes of operation

Static mode

- **Cantilever touches sample, bends, constant force**
- **Short range repulsive interactions**
- **Cantilever spring must bend easily to not damage sample -> low *k***
- **Advantages:**
    - Directly gives sample surface topography z(x, y)
- **Challenges:**
    - Thermal expansion
    - Long-range attraction forces

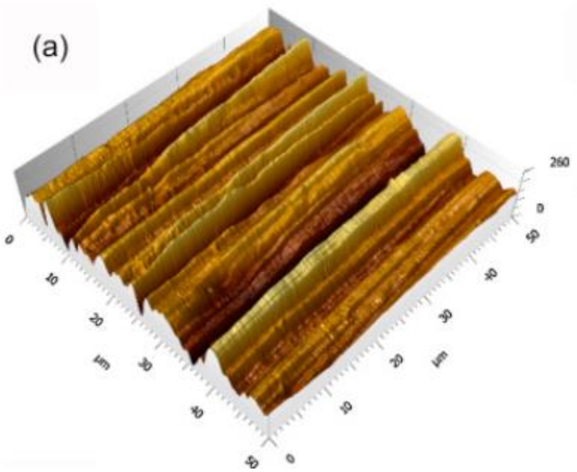
Dynamic mode

- **Cantilever is vibrated, further away from sample**
- **Medium range attractive interactions**
- **Advantages:**
    - Less damage to sample surface
    - Long-range attraction forces can be removed by changing amplitude
- **Challenges:**
    - More complex method and instrumentation
    - Often requires long measurement times

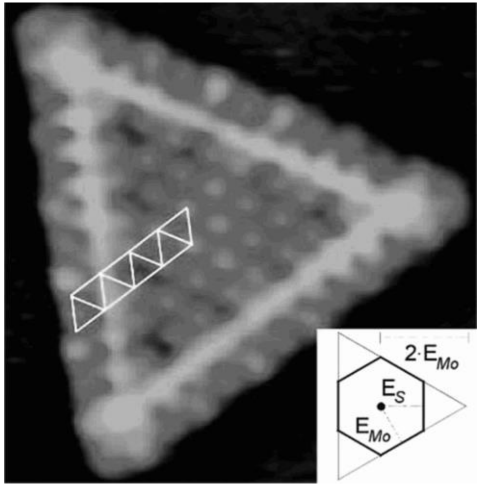
Giessibl, Franz J. "Advances in atomic force microscopy." *Reviews of modern physics* 75.3 (2003): 949, https://link.aps.org/doi/10.1103/RevModPhys.75.949

Type of information gained

Topography



https://www.sciencedirect.com/science/article/pii/S0169433216001185#bib0230



https://www.tandfonline.com/doi/full/10.1080/01614940500439776

- **The main objective**
- **Surface map**
  - Lateral = x & y
  - Height = z
- **Resolution higher than with optical microscope**
  - Vertical resolution less than 0.1 nm
  - Lateral resolutions around 1-5 nm
- **Atomic scale resolution challenging, but achievable. Allows for “seeing” individual atoms, determining crystallite size, defects etc.**

Giessibl, Franz J. "Advances in atomic force microscopy." *Reviews of modern physics* 75.3 (2003): 949, https://link.aps.org/doi/10.1103/RevModPhys.75.949

Marinella Farré, Damià Barceló, Chapter 1 - Introduction to the Analysis and Risk of Nanomaterials in Environmental and Food Samples, Comprehensive Analytical Chemistry, Elsevier, Volume 59, 2012, P. 1-32, https://doi.org/10.1016/B978-0-444-56328-6.00001-3.

Surface roughness

- **3D needed**
  - SEM doesn't give this!

Aritmethical mean

$$\mathrm{Sa} = \frac{1}{n}\sum_{i=1}^{n}|y_i|$$

Root mean square

$$\mathrm{Sq} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}y_i^2}$$

Skewness of the sample

- **Asymmetry of the surface topography**

$$\mathrm{Ssk} = \frac{1}{nRq^3}\sum_{i=1}^{n}y_i^3$$

Kurtosis

- **"Tailedness" of distribution**

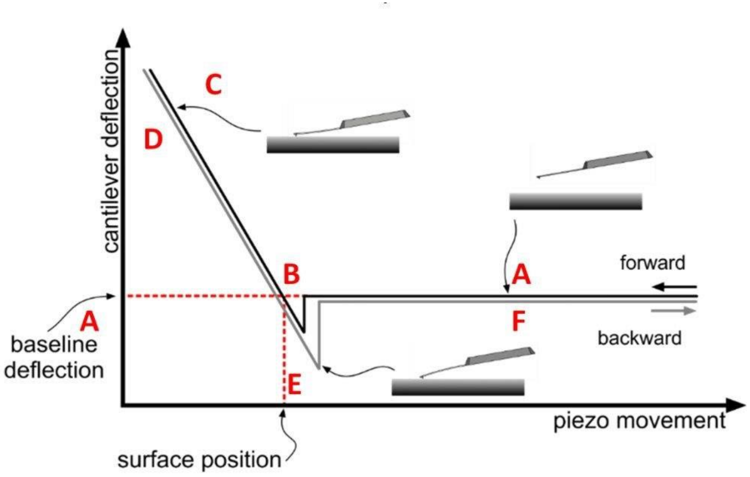
$$\mathrm{Sku} = \frac{1}{nRq^4}\sum_{i=1}^{n}y_i^4$$

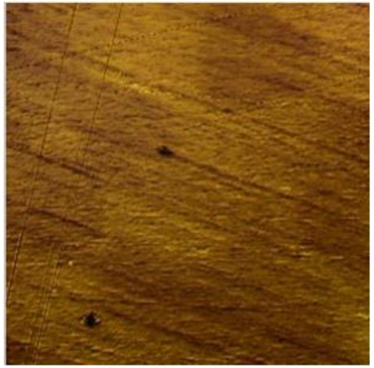
y = height, i = pixel

Topography and surface roughness measurements, Nanosurface, https://www.nanosurf.com/en/support/afm-modes-overview/topography-and-surface-roughness-measurements, [Accessed: 27.4.2023]

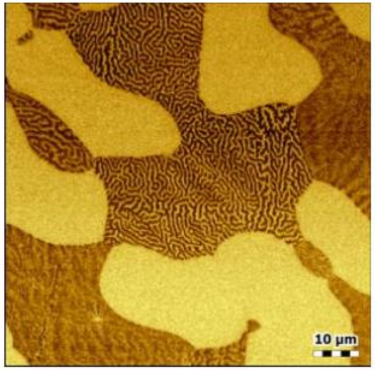
Additional information

- **Force Spectroscopy**: **Mechanical properties**
- **Magnetic Force Spectroscopy (MFM)**: **Magnetic properties**
- **AFM-IR**: **Chemical properties**





Topography of a polished stainless steel sample. Scan size: 80 µm. Height range: 50 nm.



Magnetic force microscopy (MFM) of the same 80 µm × 80 µm area. Phase range: 10°.

Force Spectroscopy, Nanosurf, https://www.nanosurf.com/en/support/afm-modes-overview/force-spectroscopy. [Accessed 27.4.2023]

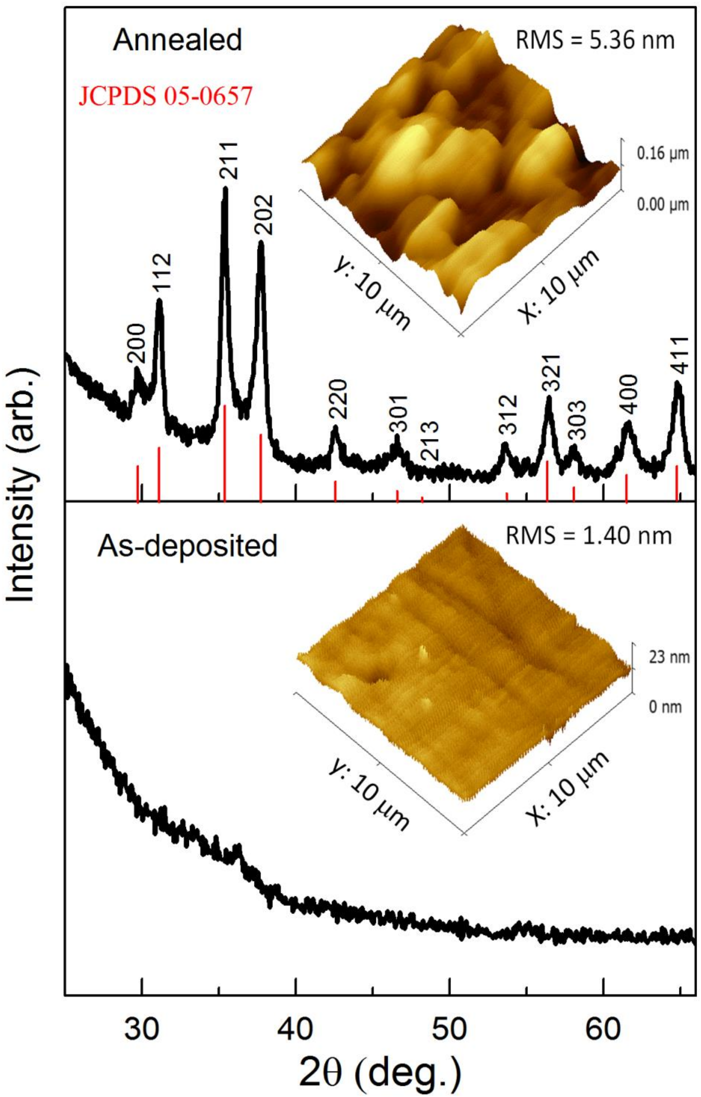
Magnetic Force Microscopy, Nanosurf, https://www.nanosurf.com/en/support/afm-modes-overview/magnetic-force-microscopy-mfm [Accessed 27.4.2023]

Research examples

Example 1

- **AFM was used to compare 3D surface topography for fresh and annealed ALD thin films**
- **With AFM, it could be shown that the roughness of the film increased during annealing**
- **RMS roughness 1.40 nm -> 5.36 nm**

T. S. Tripathi, C. S. Yadav, M. Karppinen; Transparent ferrimagnetic semiconducting $CuCr_2O_4$ thin films by atomic layer deposition. *APL Mater* 1 April 2016; 4 (4): 046106. https://doi.org/10.1063/1.4946884



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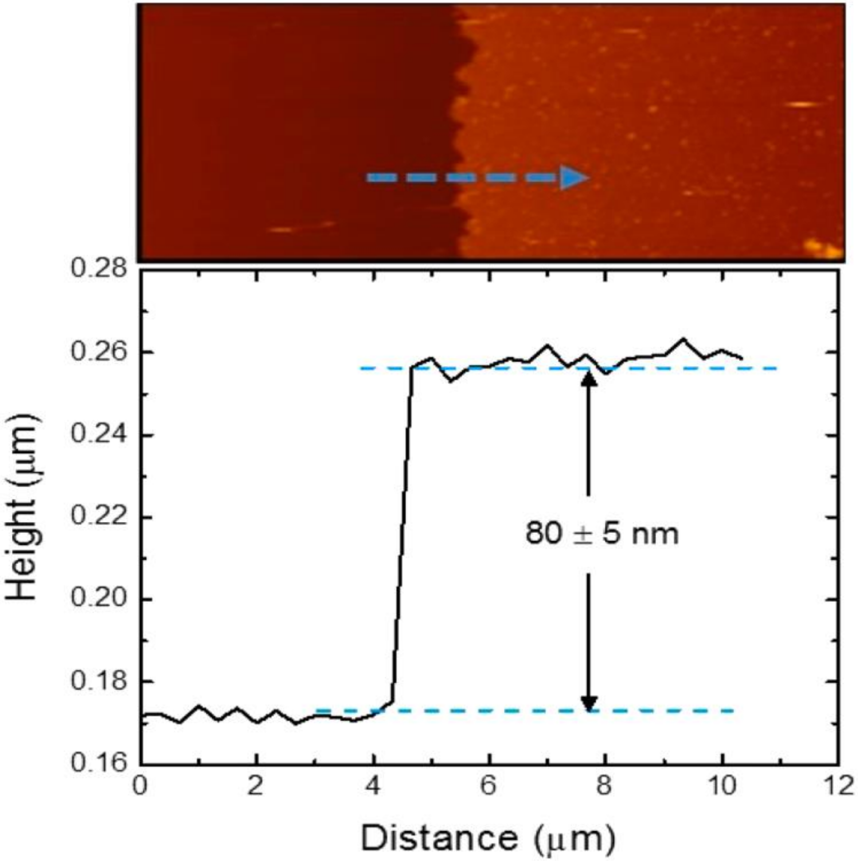
Example 2

- **AFM was used to determine the thickness and roughness of deposited copper thin films**
- **No fringes seen in XRR, thus AFM was used instead**
- **A scratch was made through the film, and AFM was used across the scratch to determine the thickness**



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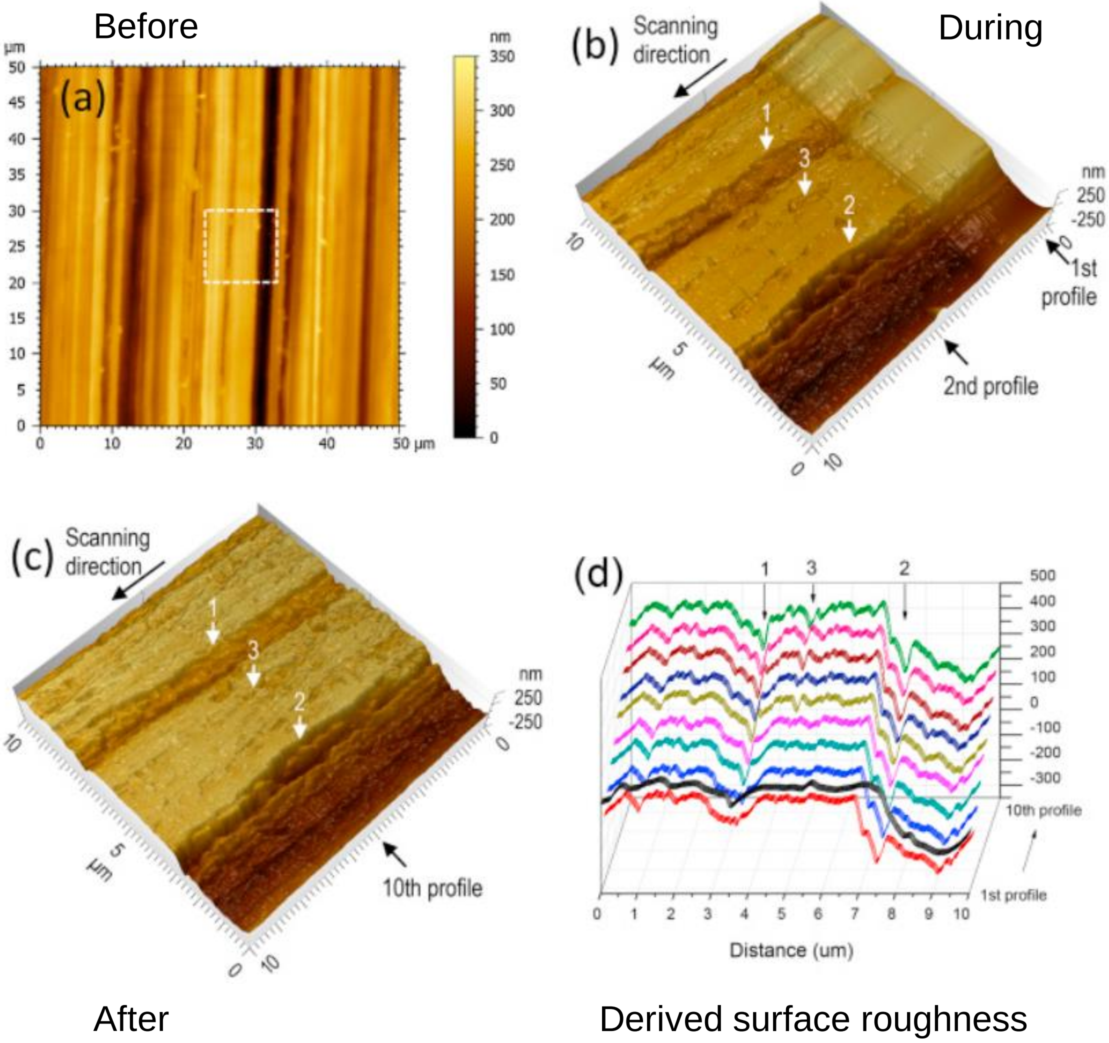
Tripurari S. Tripathi and Maarit Karppinen, Efficient Process for Direct Atomic Layer Deposition of Metallic Cu Thin Films Based on an Organic Reductant, *Chemistry of Materials* 2017 *29* (3), 1230-1235, https://doi.org/10.1021/acs.chemmater.6b04597

Example 3

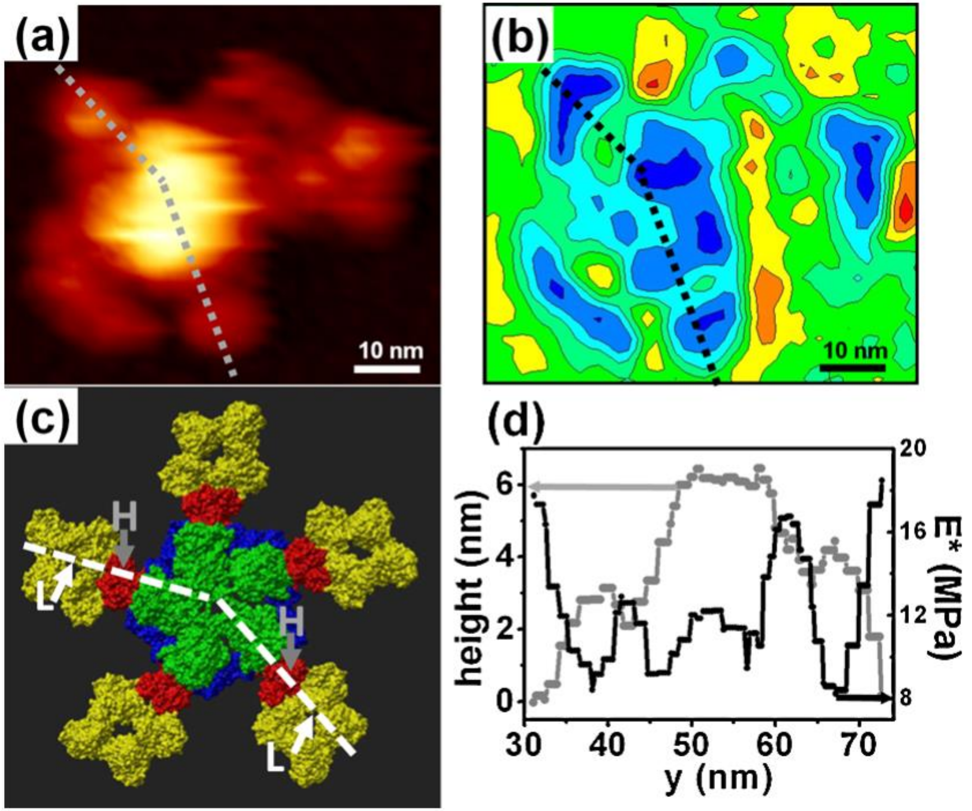
- AMF used to characterize surface roughness of a carbon steel with early-stage corrosion
- Roughness in nm scale
- Increase in corrosion activity with increasing surface roughness



2. Li, Y. Y., Frank Cheng, F., Effect of surface finishing on early-stage corrosion of a carbon steel studied by electrochemical and atomic force microscope characterizations, Applied Surface Science, Vol. 366, 2016, P. 95-103.

Example 4

- Bimodal AFM (an advanced type of dynamic AFM) was used to map protein structures in water
- High resolution of <2 nm achieved
- Low forces allowed non-destructive imaging of sensitive biomolecules
- Elastic modulus at different sections of the protein could also be measured



Martínez-Martín, David, et al. "Noninvasive protein structural flexibility mapping by bimodal dynamic force microscopy." *Physical review letters* 106.19 (2011): 198101.

Pros and cons

AFM – Pros and cons

Pros

- Allows high resolution imaging of (almost) any material (1 Å – 5 nm)
- Can be used at ambient conditions and in liquids
- Samples do not require special treatment
- Can be used to study biological macromolecules

Cons

- Achieving atomic scale resolution is difficult
- Relatively complex and expensive instruments required
- Generally, quite slow measurements

Sources

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11. 2. Li, Y. Y., Frank Cheng, F., Effect of surface finishing on early-stage corrosion of a carbon steel studied by electrochemical and atomic force microscope characterizations, Applied Surface Science, Vol. 366, 2016, P. 95-103.

12. Martínez-Martín, David, et al. "Noninvasive protein structural flexibility mapping by bimodal dynamic force microscopy." *Physical review letters* 106.19 (2011): 198101.

Questions?