Atomic Force Microscopy

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Outline

- Introduction
  - Bulk vs surface
  - Scanning probe techniques
- Atomic Force Microscopy
  - Fundamentals
    - Piezoelectric scanners, cantilevers
  - Imaging modes
    - Contact, intermittent contact, non contact
  - Force spectroscopy
- AFM in combination with other imaging modes
  - Tip enhanced Raman spectroscopy (TERS)

Bulk vs surface of materials

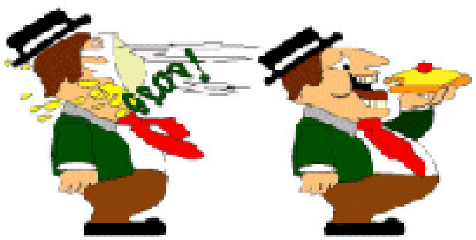
•**<u>Bulk</u>** chemical composition of total sample volume

–Morphology, which designates the space distribution of the solid (particle size, surface area, pore size distribution)

•**<u>Surface</u>** chemical composition which may or may not be different from that of the bulk

•Physico-chemical properties of surface (zeta potential, hydrophobicity) control interfacial phenomena such as adsorption, adhesion, flocculation

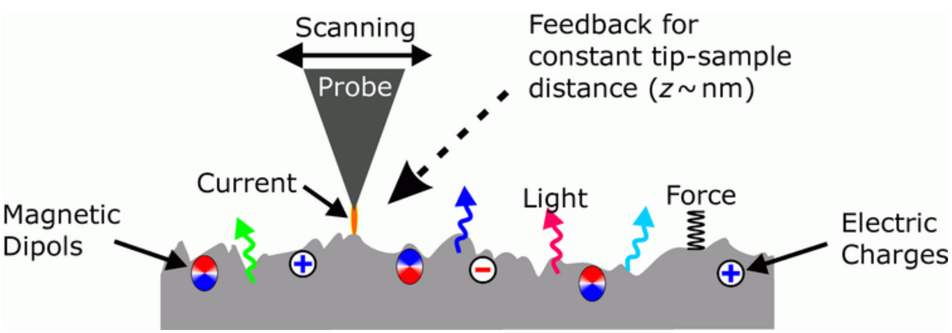
Adsorption versus Absorption

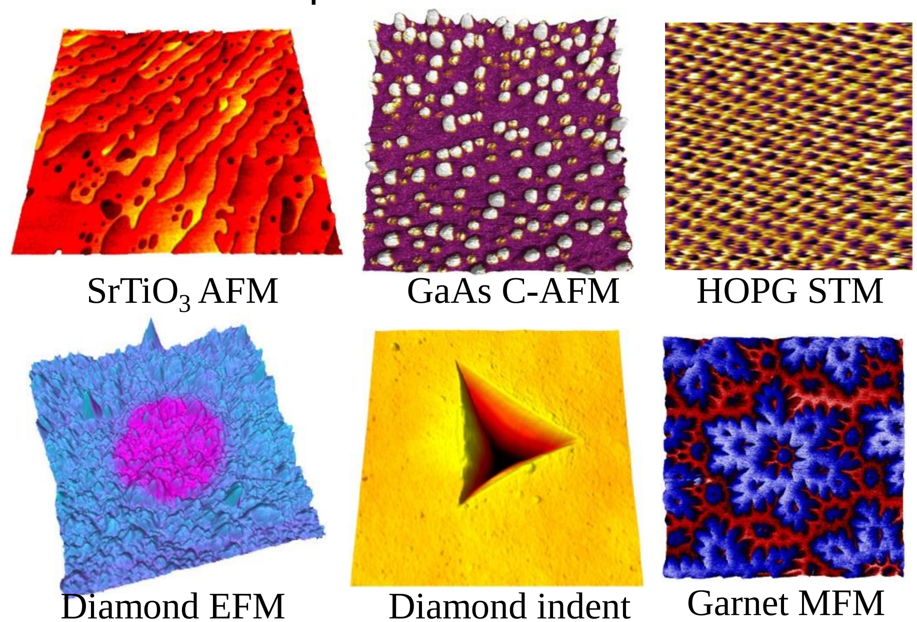


Majority of (bio)material interactions are interface (surface) based!

Scanning probe - terminology

- They all are <u>Scanning Probe</u> techniques:
  - AFM, C-AFM, STM, KPFM, MFM, EFM…
  - AFM developed to work with non-conductive materials
  - Utilize a probe tip to interact with the sample surface to probe certain response (force, potential, magnetic field, electric field etc)
  - No diffraction limit; z-axis sensitive; imaging in liquid; probing physical sample properties (adhesion, hardness, elasticity etc)
  - AFM can be operated in UHV, ambient conditions or liquids



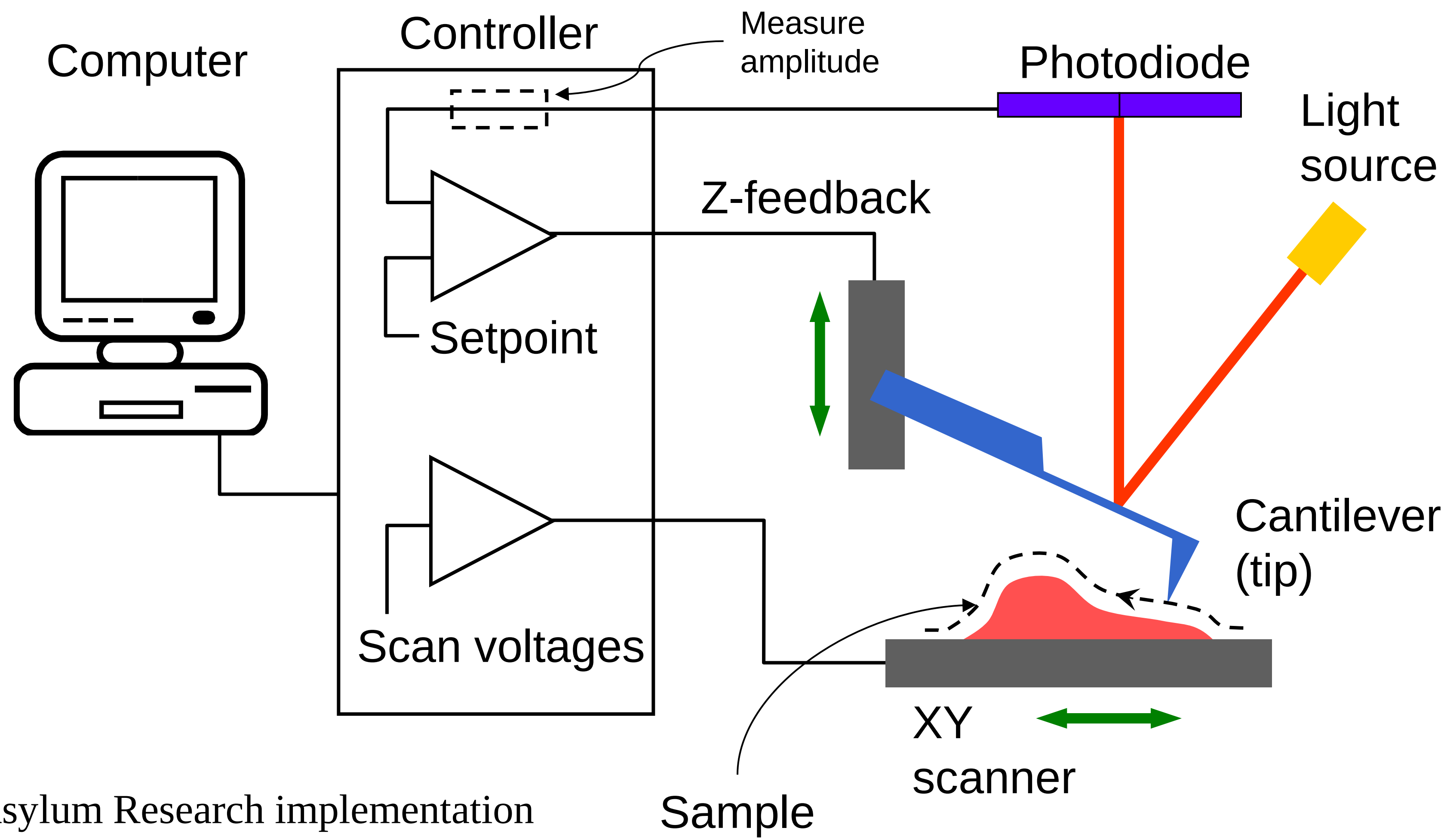


$SrTiO_3$ AFM | GaAs C-AFM | HOPG STM

Diamond EFM | Diamond indent | Garnet MFM

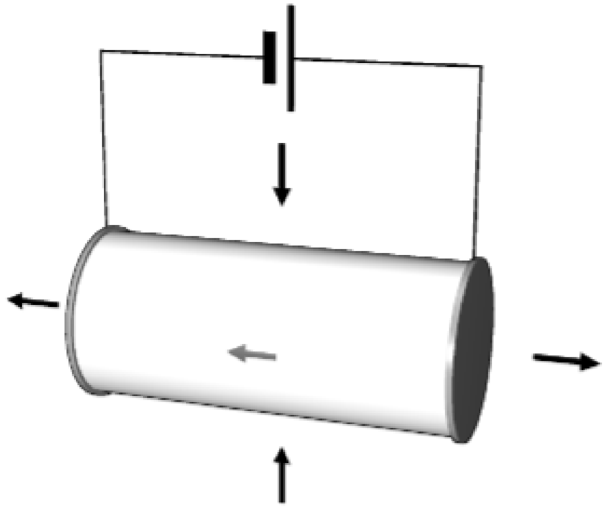
https://www.asylumresearch.com/Gallery/Materials/Materials.shtml

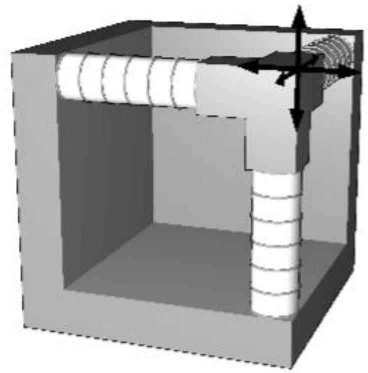
AFM working principle



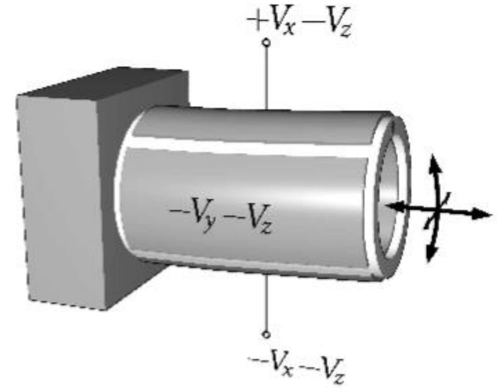
- Asylum Research implementation
- Sharp tip used to scan the sample
- Quantifiable x,y and z-axis information

Piezoelectric scanners

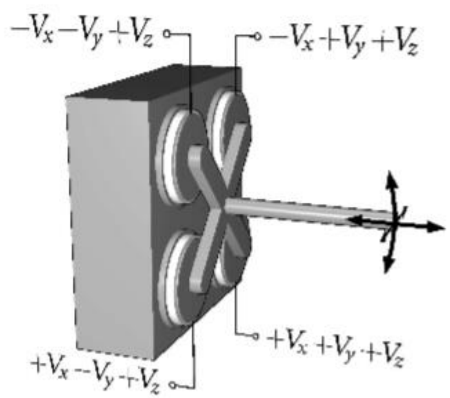




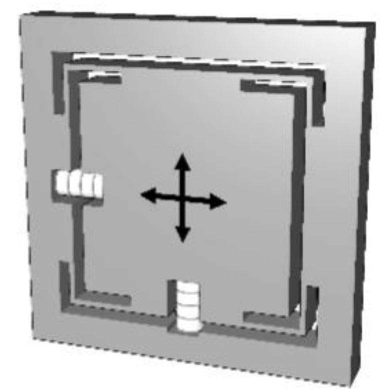
(a) Tripod



(b) Single hollow tube



(c) Lever



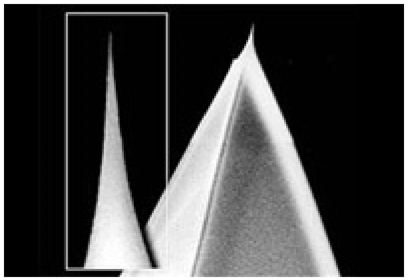
(d) Two-dimensional flexure stage

- External electric field parallel to its average polarization will cause a rod of ferroelectric material to expand or contract
- ~0.262 nm/V → 380 V to elongate 1 cm bar by 1 μm
- Nonlinearity, hysteresis and creep
- Closed-loop scanners to eliminate these problems

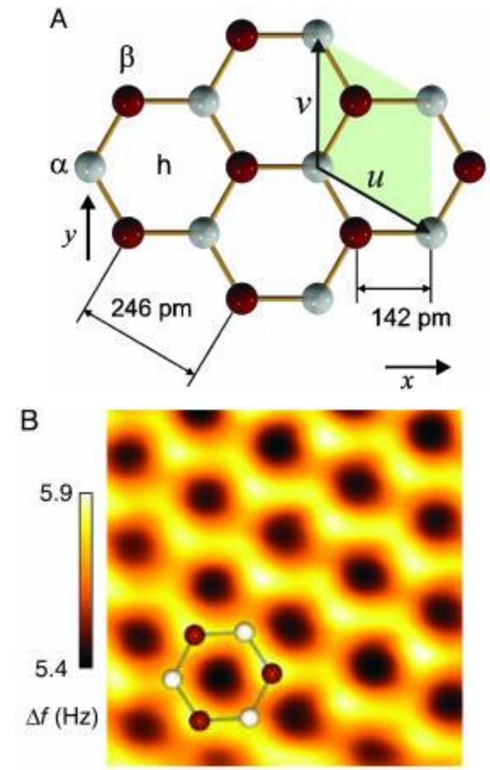
AFM resolution

- Lateral resolution of an AFM images depends on (a) step size and (b) minimum radius of the tip

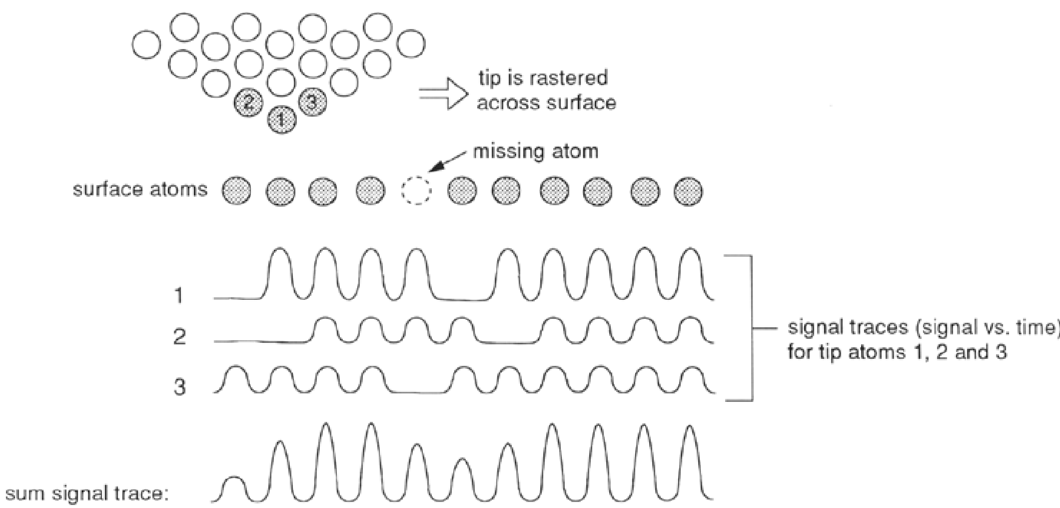
- Tip radius of 3 nm



- Image taken at 512x512 points
  - 1x1 μm image has a resolution of 2 nm (1μm/512)

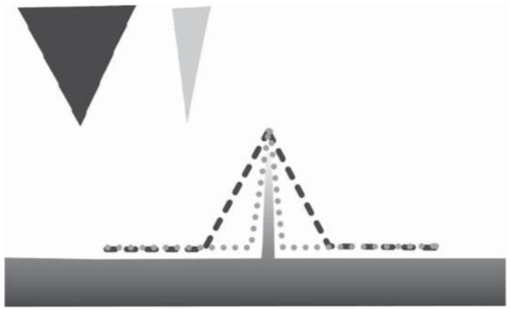


AFM is not a true atomic resolution technique!

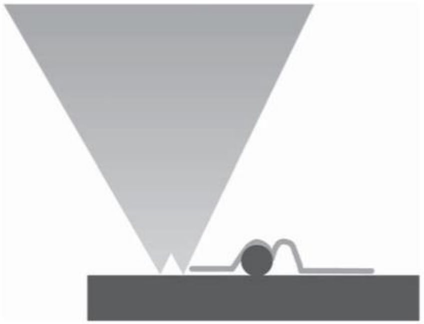


Hembacher *et al*., PNAS, 2003

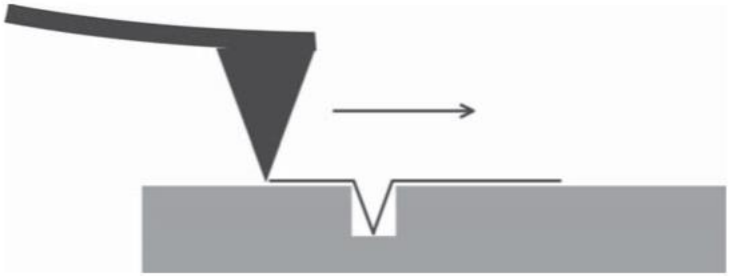
AFM image will depend on the tip



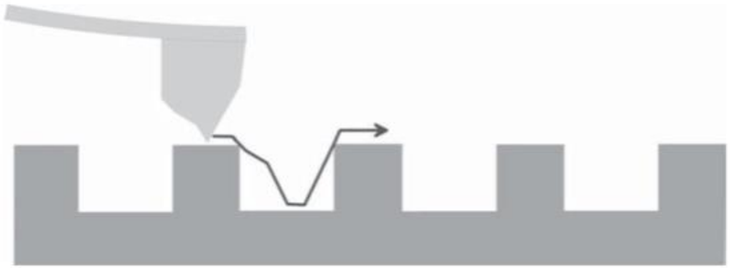
Dull or sharp probe will affect the image of the protruding featutre



Double tip will cause double imaging

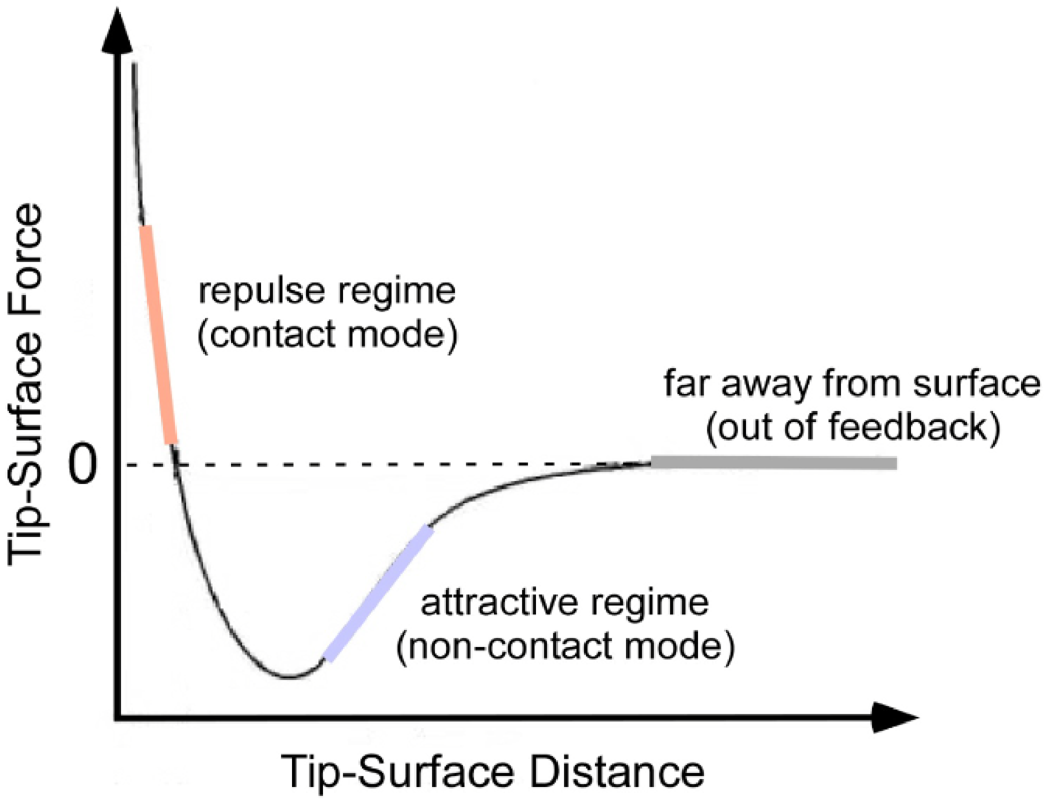


Tip width will limit the hole size



Damaged tip creates regularly irregular pattern

Interactions between the tip and the sample



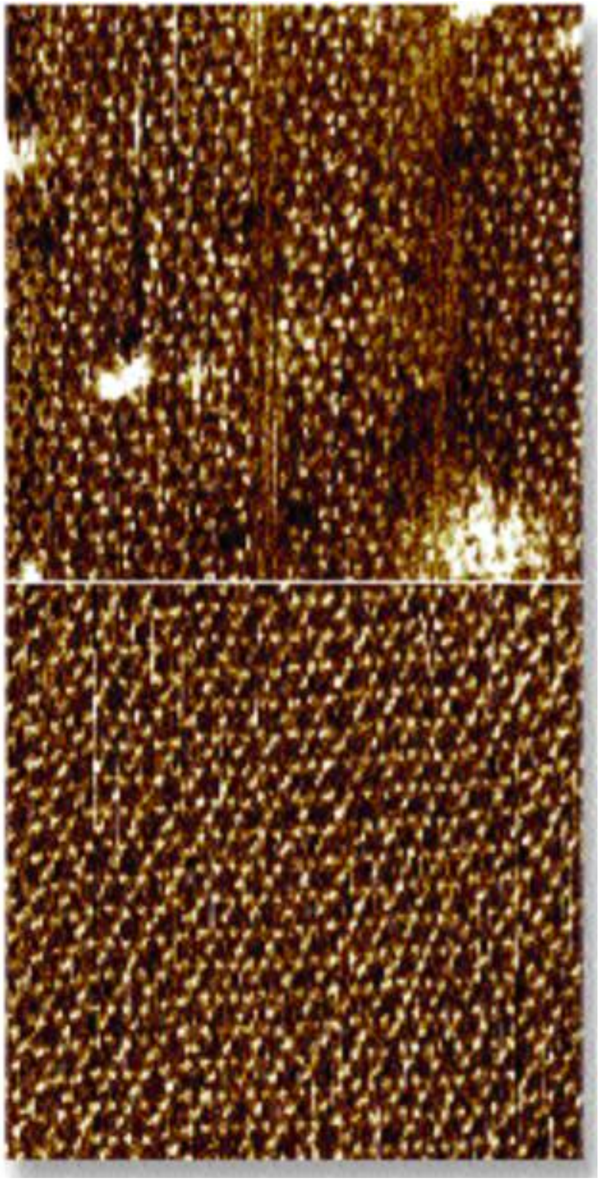
Repulsion:

At very small tip-sample distances (a few angstroms) a very strong repulsive force appears between the tip and sample atoms. Its origin is the so-called exchange interactions due to the overlap of the electronic orbitals at atomic distances. When this repulsive force is predominant, the tip and sample are considered to be in "contact".

Attraction (Van der Waals):

A polarization interaction between atoms: An instantaneous polarization of an atom induces a polarization in nearby atoms – and therefore an attractive interaction: "non contact".

Contact mode imaging

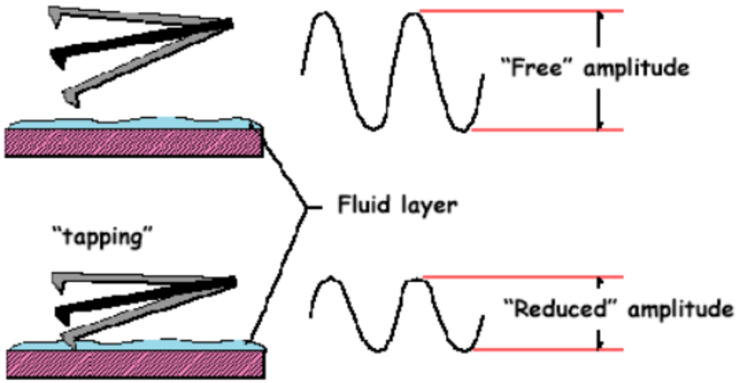


- Comparison of contact mode (top) and TappingMode (bottom) images of Bacteriorhosdopsin in liquid (buffer) (100nm scan size)
- Sample damage seen in contact mode

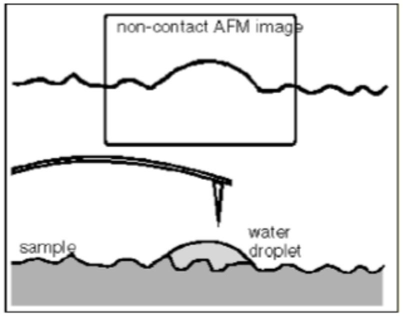
C.B. Prater, P. G. Maivald, K.J. Kjoller and M.G. Heaton, Veeco publications

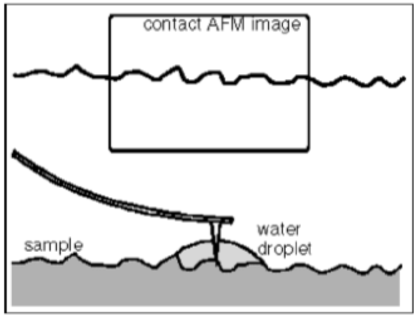
Tapping mode (non contact)

- Constant osccilation amplitude via feedback with the controller
- 50-80% of free amplitude
- High resolution – minimum sample damage
- The most used non-contact mode



Non-Contact vs. Contact Through Water



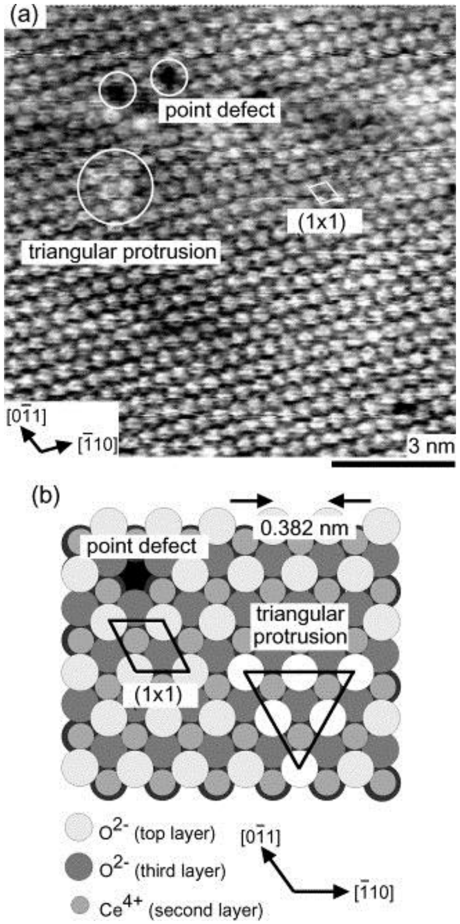


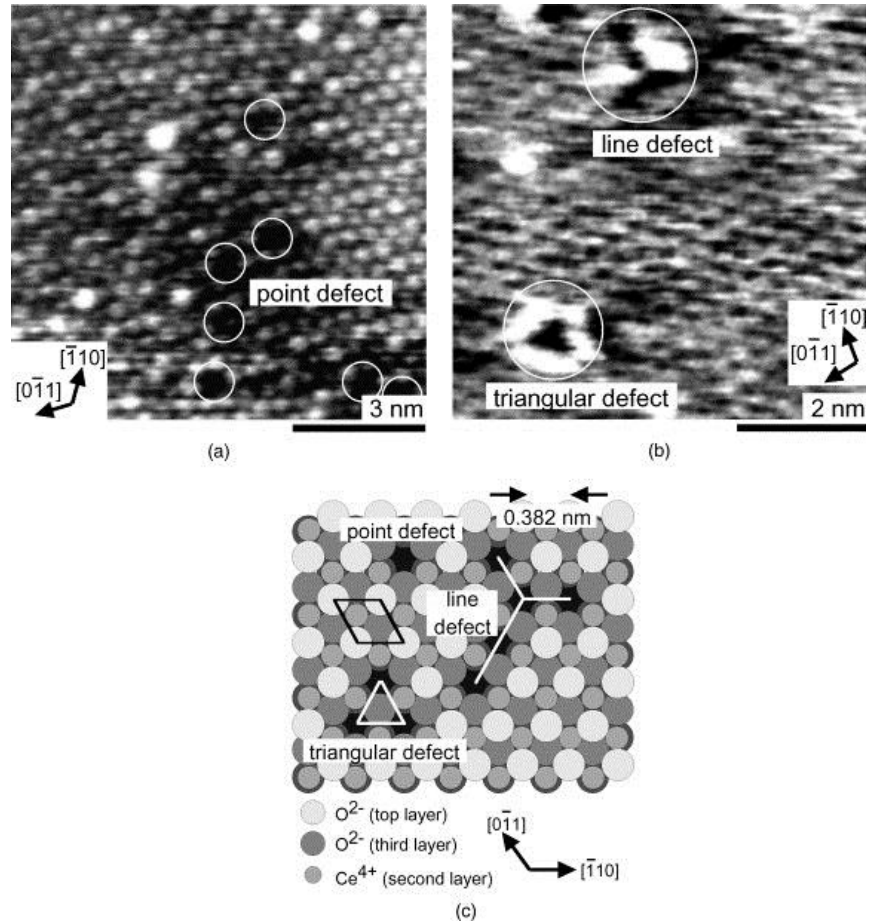
- Imaging mode often determines the results!
- Imaging in air a problem due to the adhesive forces

Non-Contact **Contact**

Stoichiometric vs reduced CeO_2 (111)

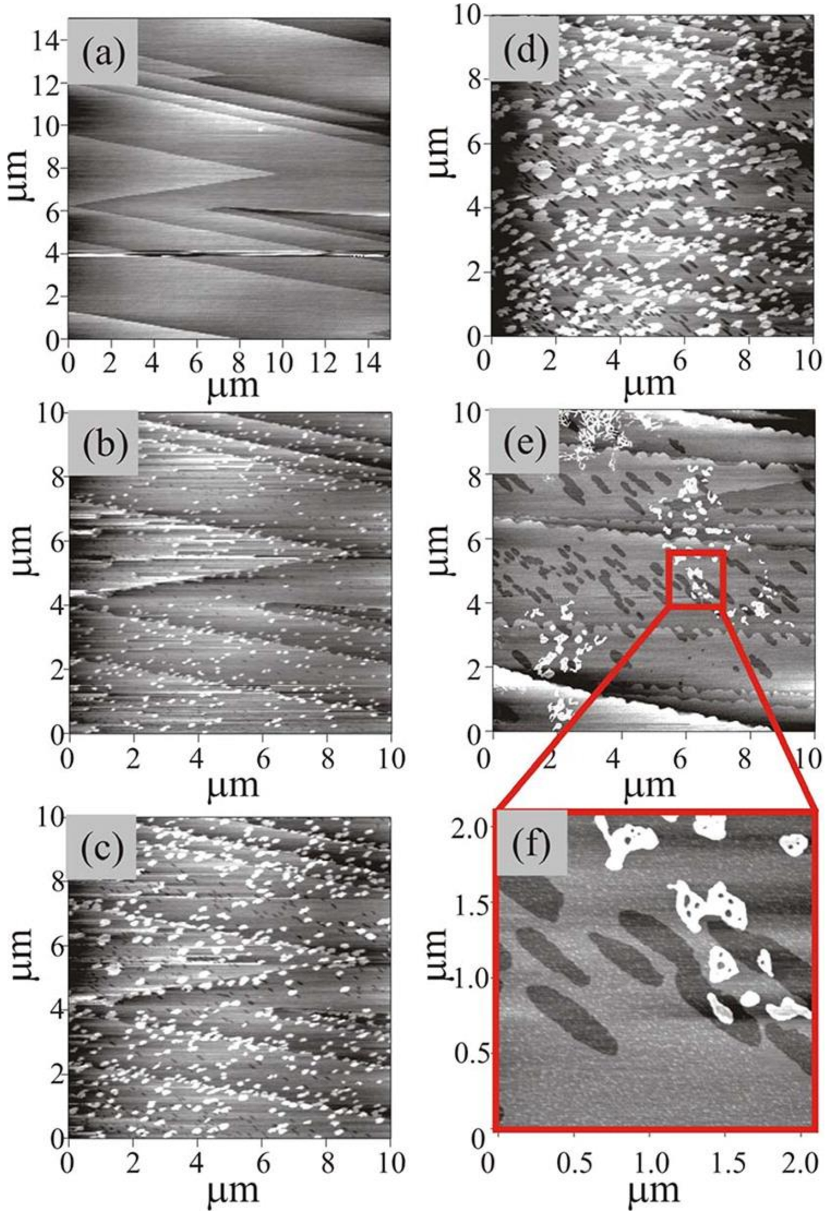
- Non contact mode of point defects in CeO_2 (111)

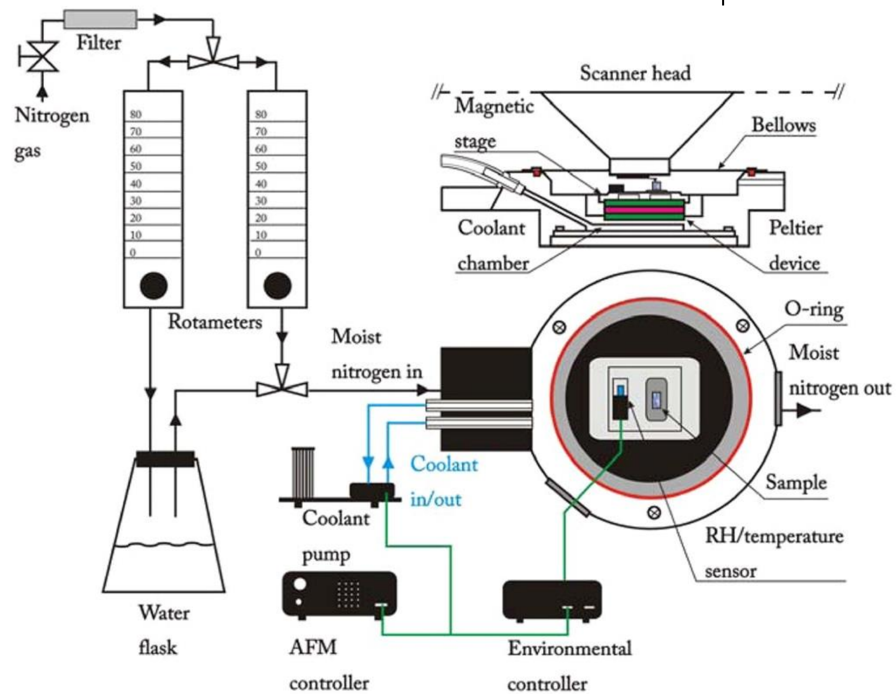




Fukui *et al.*, Applied Surface Science, 2002

Surface properties adsorbed thin films



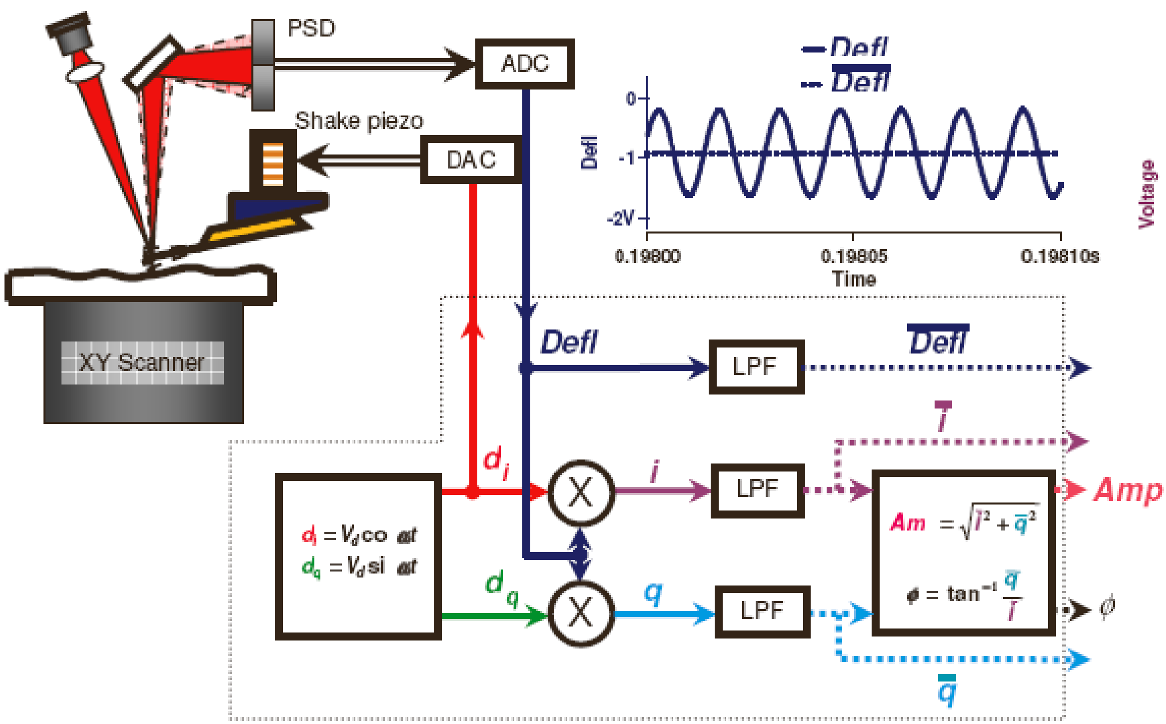


- Cleaved $CaCO_3$ crystal
- Controlled RH and temperature
- Time resolved evolution of topographical properties
- Limited compositional data – force measurements and complementary XPS

Baltrusaitis *et al*., J. Phys. Chem. A, 2012

Phase and amplitude in AFM: beyond topography

- Complementary information about sample properties using amplitude and phase
- Amplitude – lag in the piezo response: can optimize either topo or amplitude but not both simultaneously
- Phase – lag due to the varying sample properties – energy dissipation measure



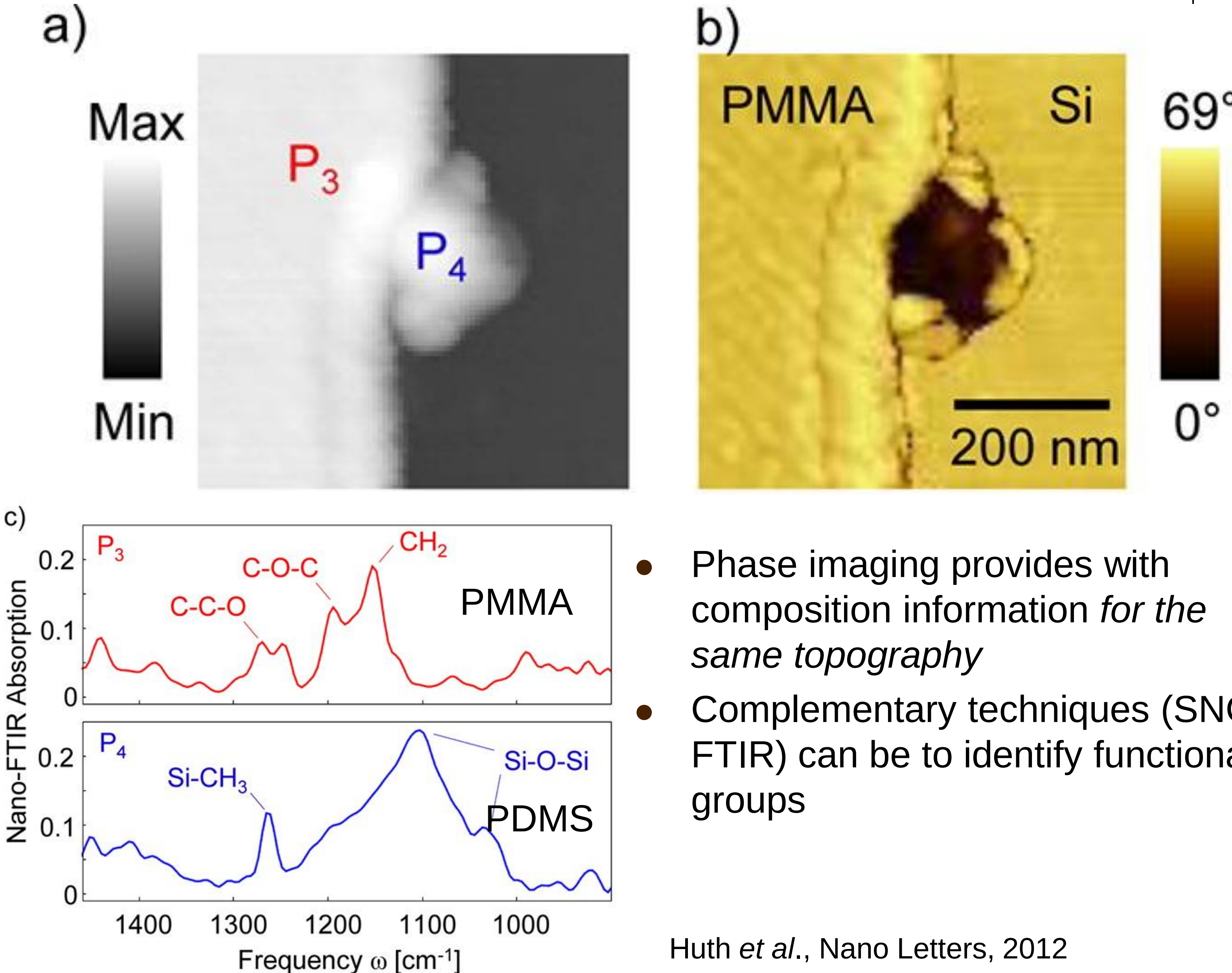
$$\bar{q} = -\frac{1}{2} V_{resp} V_d \sin\varphi \,.$$

$$\bar{i} = \frac{1}{2} V_{resp} V_d \cos\varphi \,.$$

$$A = \sqrt{\bar{i}^2 + \bar{q}^2}$$

$$\varphi = \tan^{-1} \frac{\bar{q}}{\bar{i}}$$

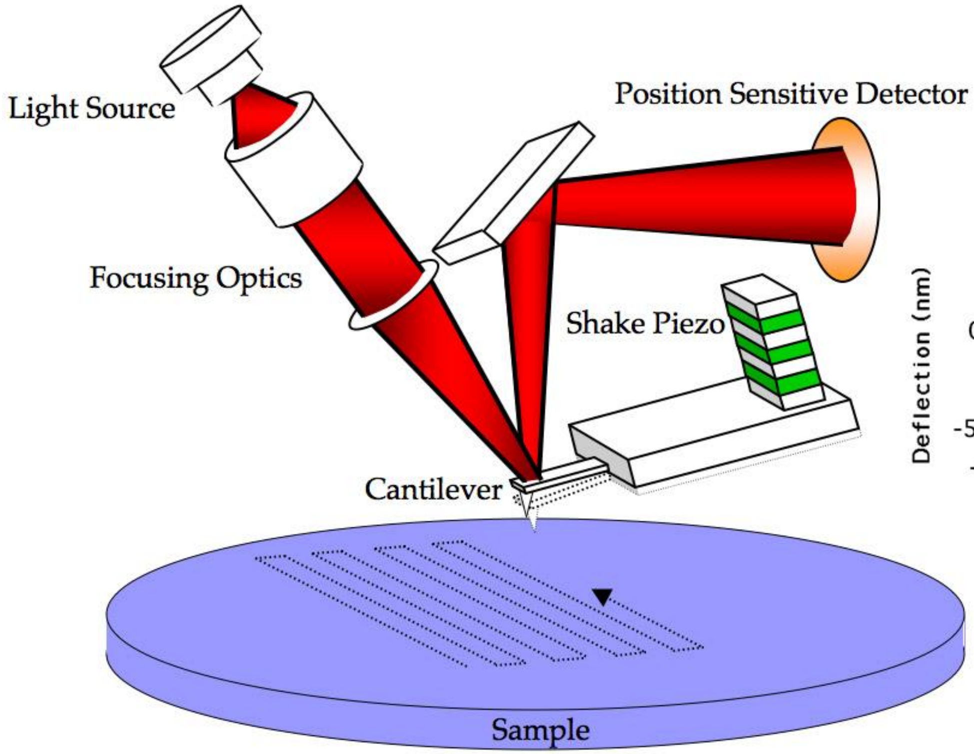
AFM phase imaging to test structural inhomogeneity in polymers

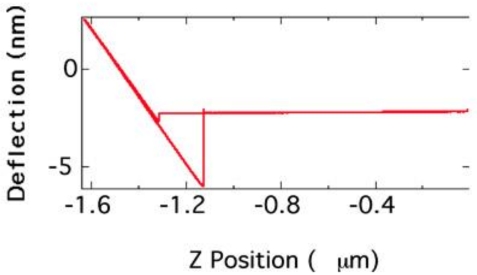


- Phase imaging provides with composition information *for the same topography*
- Complementary techniques (SNOM FTIR) can be to identify functional groups

Huth *et al*., Nano Letters, 2012

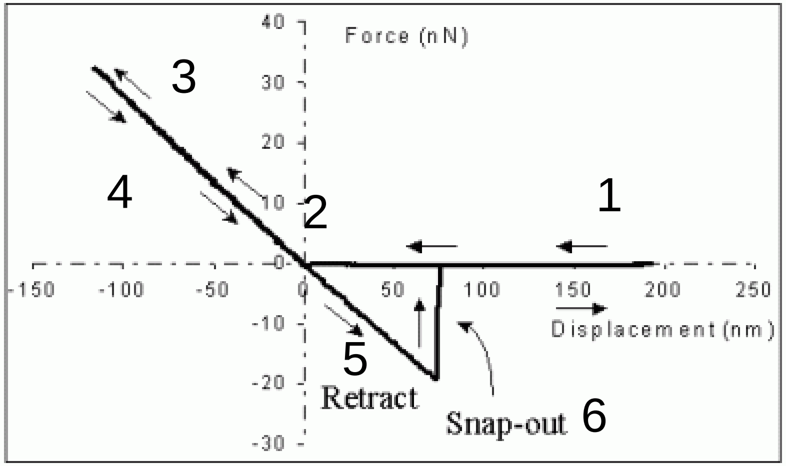
Force Measurements with AFM





- Applications:
    - Adhesion, receptor-ligand binding
    - Hardness and Young’s modulus

Typical force curves

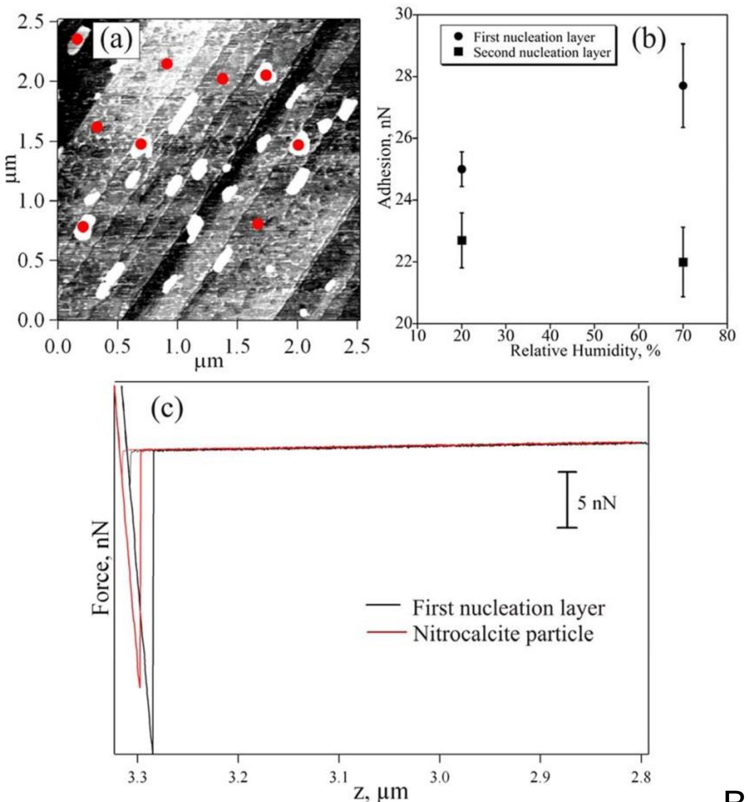


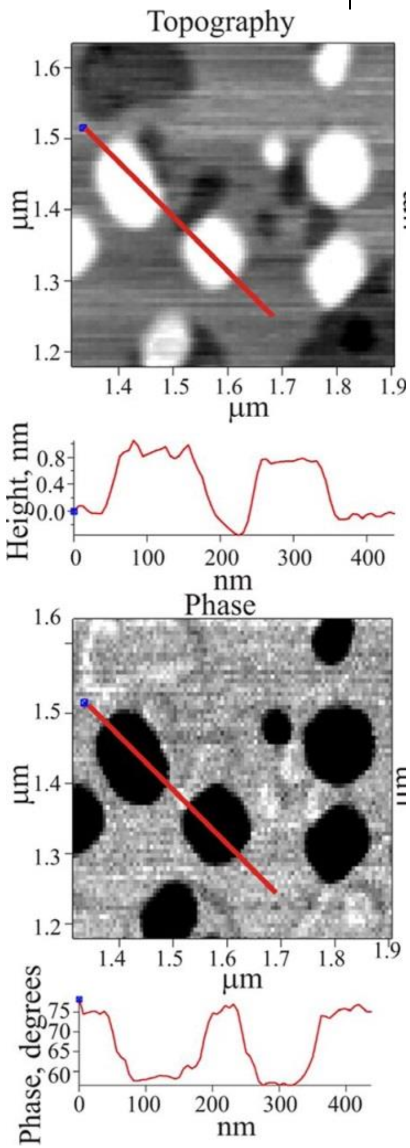
Typical events:

1. approaching sample in air
2. snap in (any attractive interactions)
3. pressing onto the sample (indentation)
4. pressing away from the sample (indentation)
5. adhesion
6. snap out

Force spectroscopy for surface adhesion

- $CaCO_3$(10-14) cleaved and reacted with NO_2
- Layer stratification with distinct crystallites forming
- Phase topography shows higher energy dissipation on new crystallites (nitrocalcite via XPS)
- Force spectroscopy confirms preferential hydration of calcite but not nitrocalcite

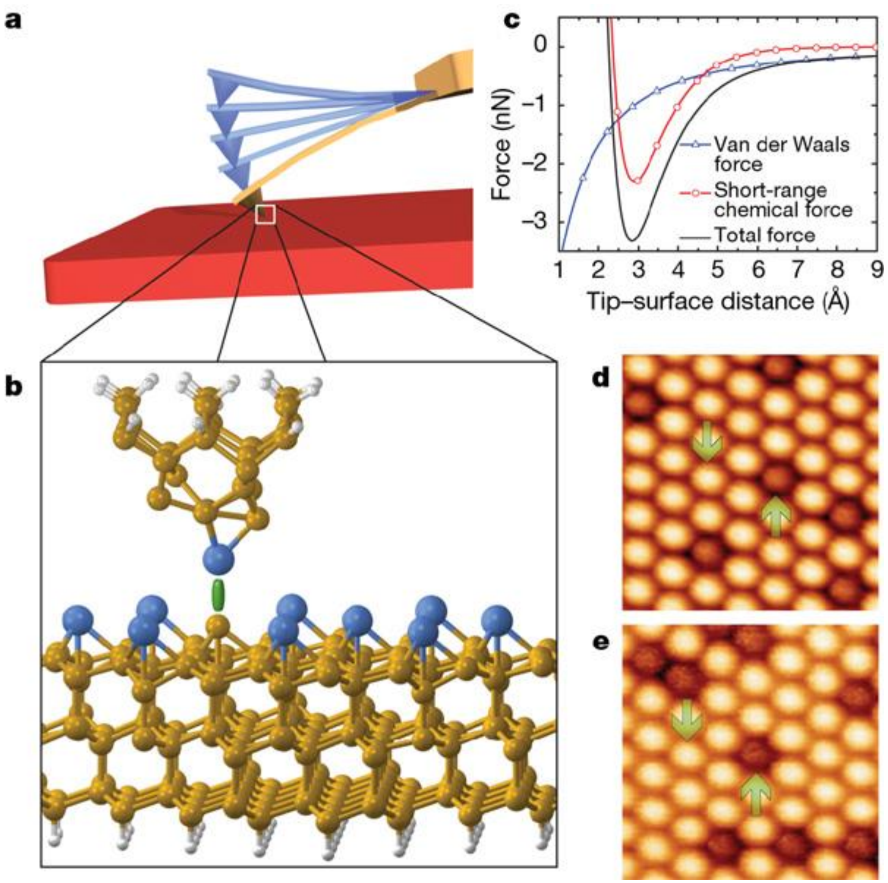


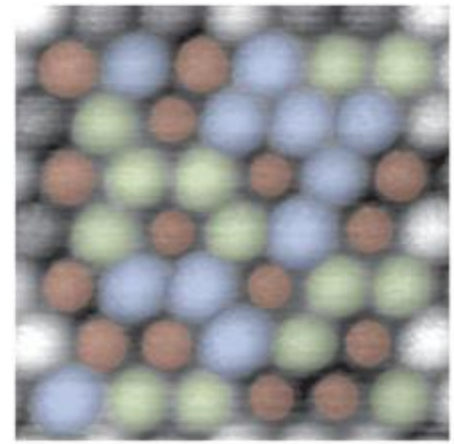


Baltrusaitis *et al*., J. Phys. Chem. A, 2012

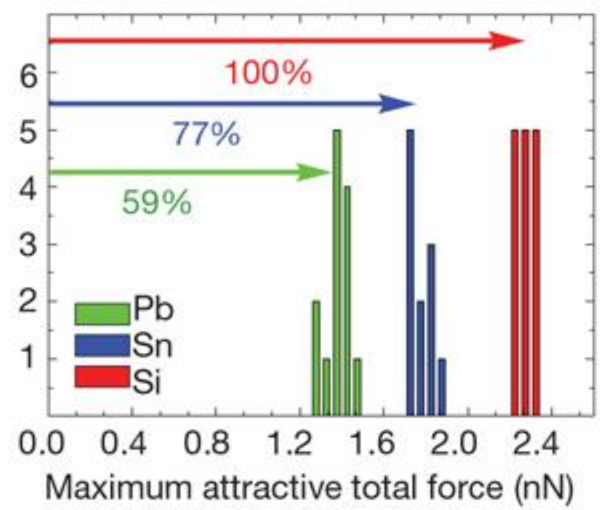
Identification of individual surface atoms using AFM

- Modifying the tip with binding specific moiety
- Rastering or performing force spectroscopy



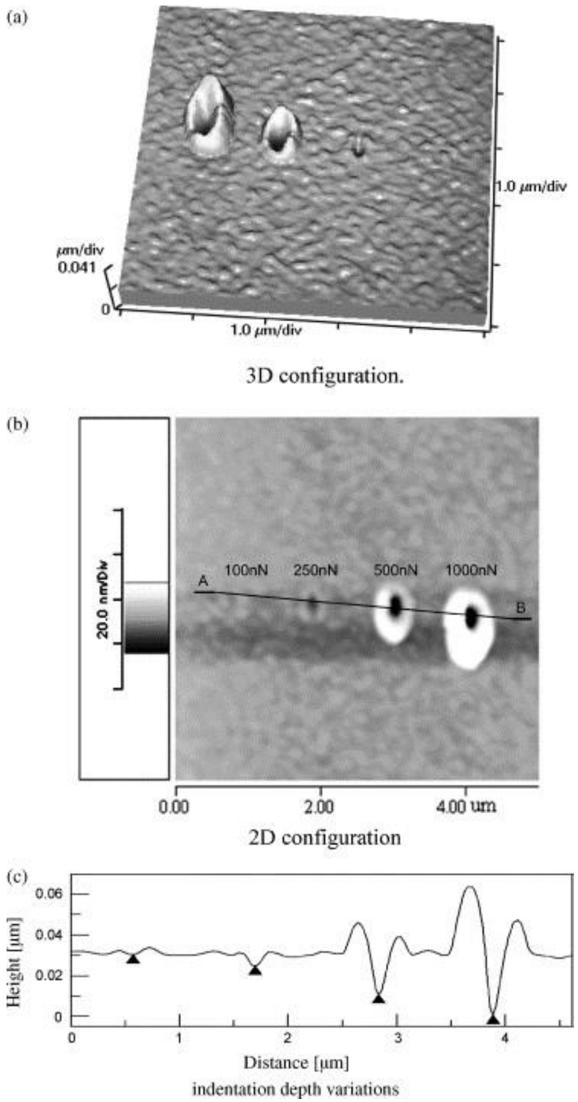


4.3 x 4.3 nm scan



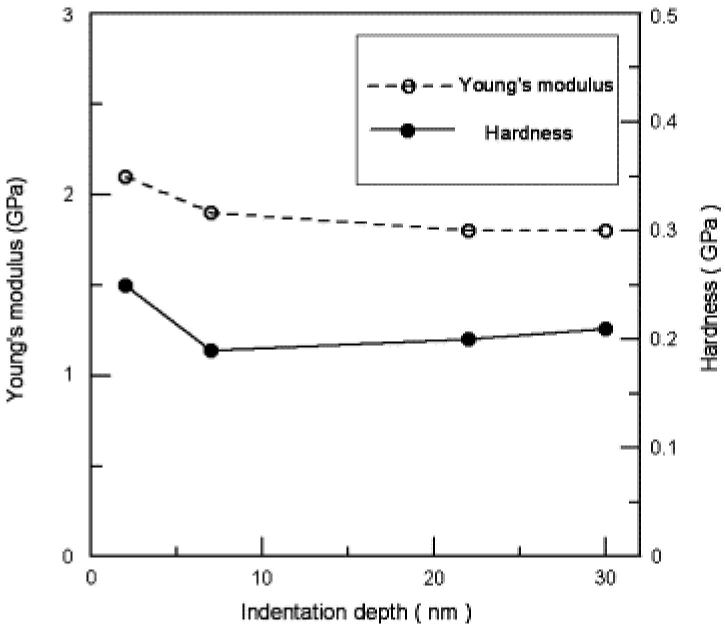
Sugimoto, Nature, 2007, 446, 64

Hardness and Young's modulus: nanoindentation



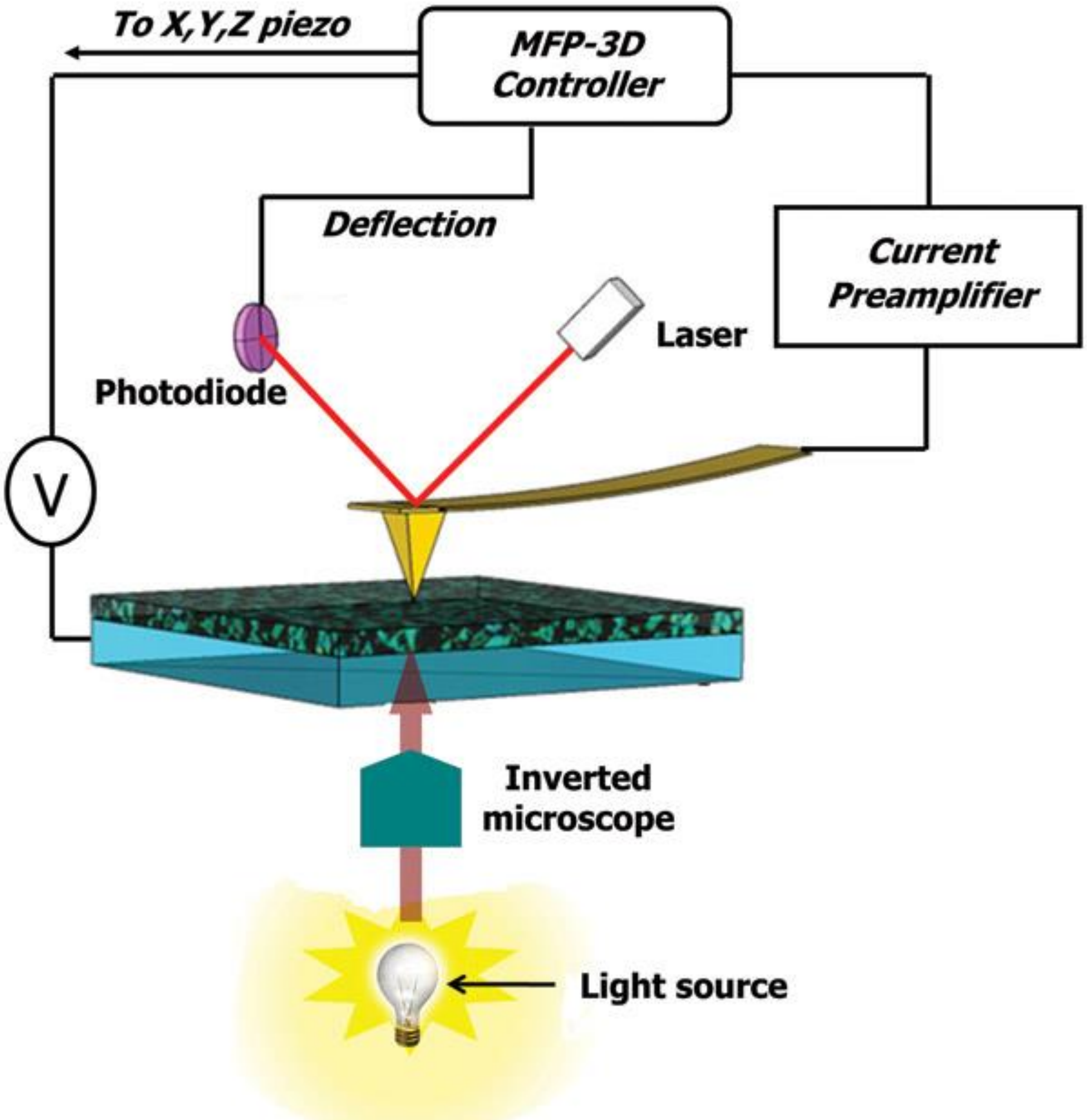
Hardness, H $$H = \frac{P_{max}}{A}$$

Young's modulus, E $$E_j = (1 - \upsilon_j^2)\left[\frac{1}{E^*} - \frac{1 - \upsilon_i^2}{E_i}\right]^{-1}$$



Fang *et al*., Microelectronics Journal, 2005

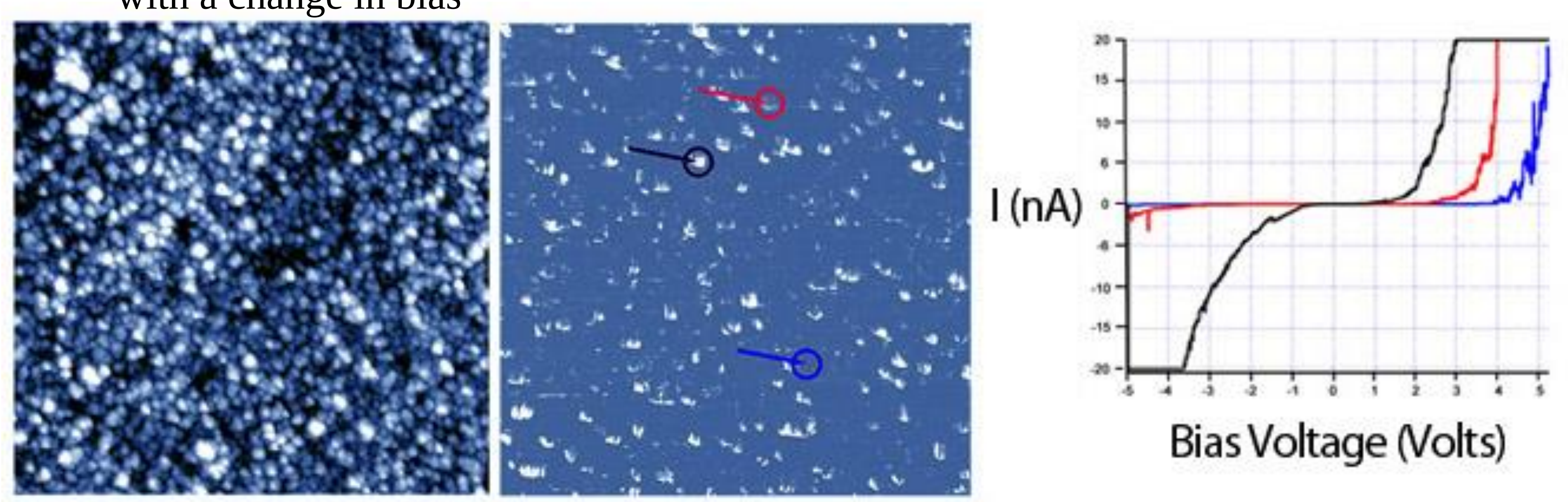
Conductive Measurements with AFM



- contact mode, using a conductive AFM probe such as gold or platinum-coated silicon tip
- Bias applied and current is measured
- Light source on an inverted microscope for photocurrent experiments

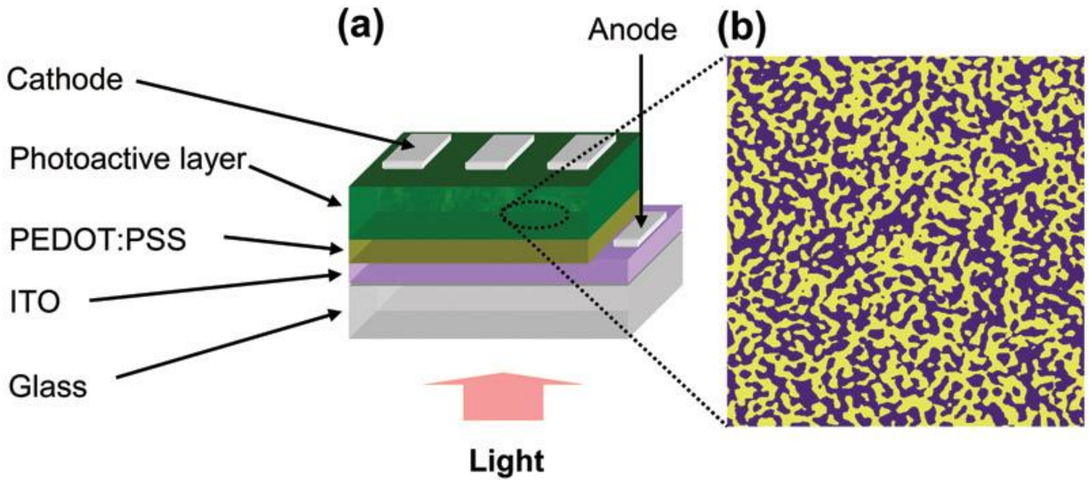
Conductive Probe Microscopy: metal oxides

- Bias is applied to the sample and changes in sample conductivity are measured using the conductive tip
- I-V curves can be taken to measure the current at the specific point on the samples with a change in bias

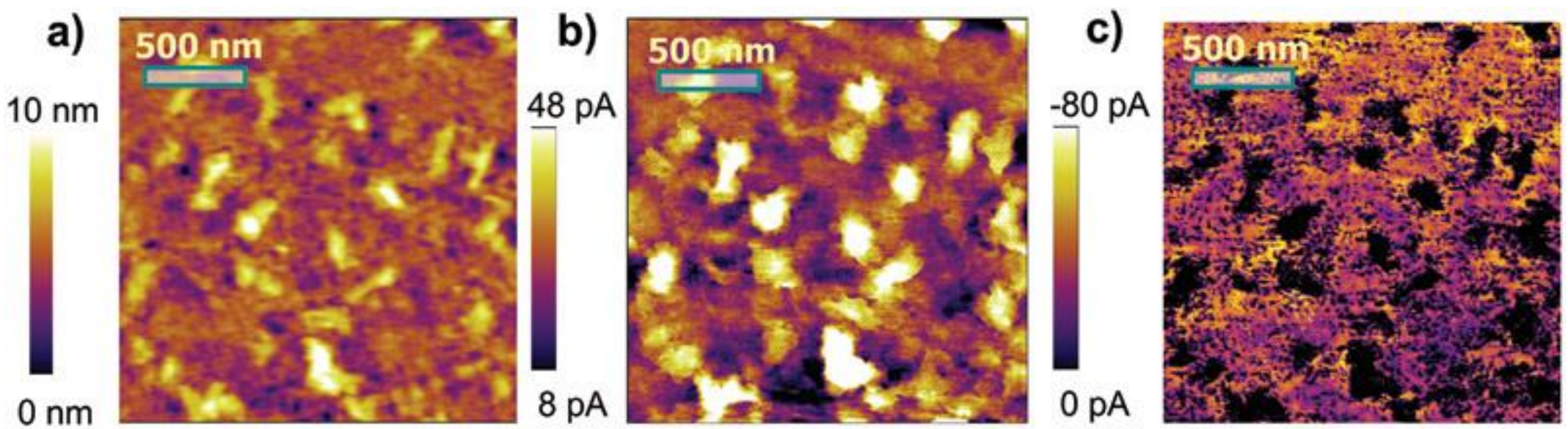


- Topography (left) and current (right) images of a Europium-doped ZnO sample with pinholes at a bias of 1.5 volts. I-V curves were taken at three locations on the image (Jason Li, Asylum Research)

Conductive Probe Microscopy: solar cells



- Typical solar cell with AFM topography images
- A nanoscale phase separation of donor and acceptor materials in the active layer is needed to achieve efficient exciton dissociation and charge transport



Images of topography (a), current collected at +1V (b) and current collected at –1V (c) of 30:70 DPPBFu:$PC_{71}BM$ films

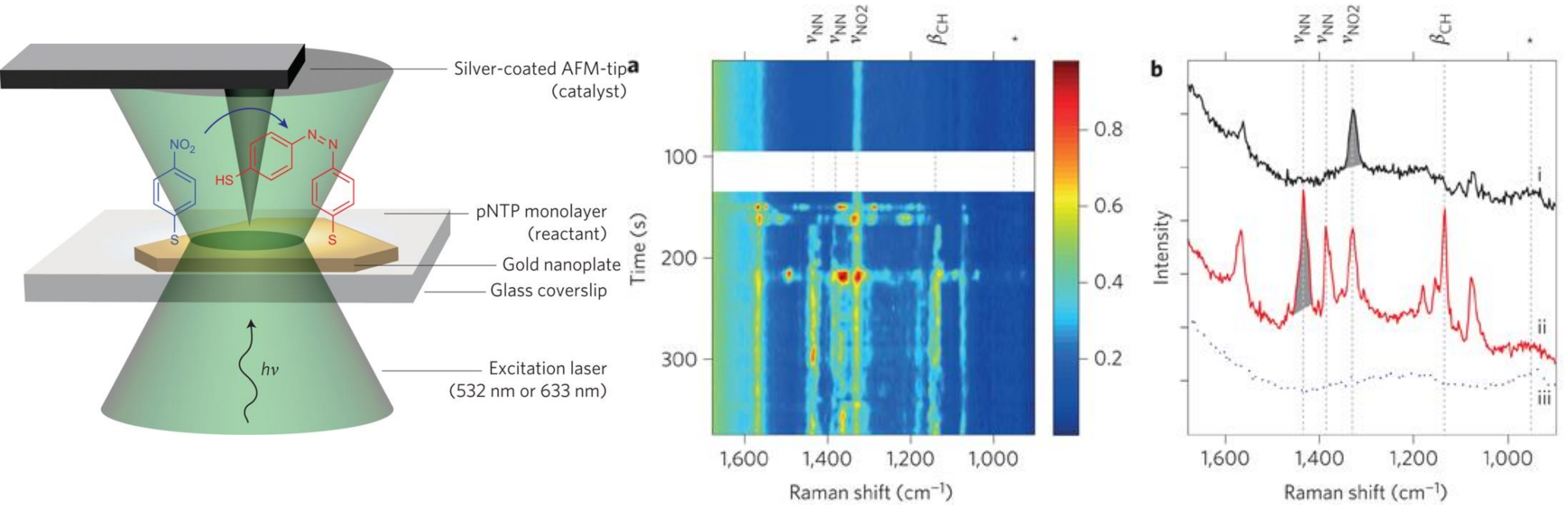
Atomic force microscopy: need for spectral capabilities

- AFM provides for indirect compositional information of the sample surface
  - Phase imaging, EFM, KPFM, force microscopy
  - No chemical specificity
  - Very good spatial resolution (routinely to <10 nm)

- Conventional spectroscopies are spatially limited to the light diffraction limit
  - FTIR (~2 μm)
  - Raman (360 nm for 532 nm laser)

- Can the resolving spatial power of AFM be combined with the chemical specificity of FTIR or Raman?

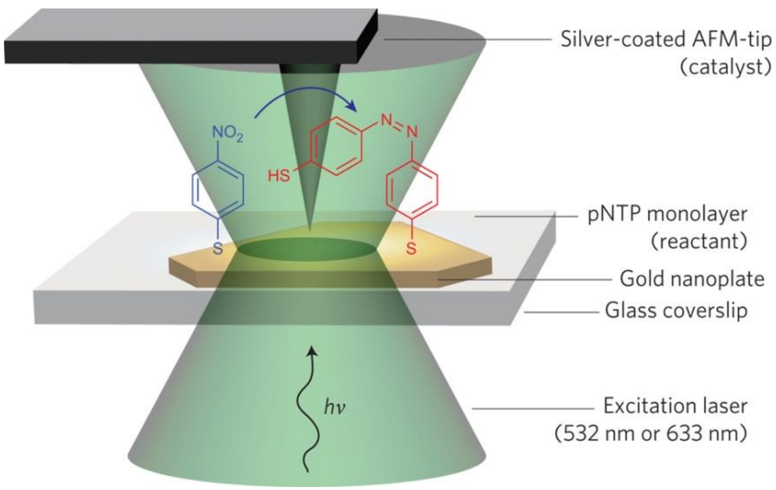
TERS for spatially and temporally dependent measurements



- Tip enhanced measurement
- 532 nm laser to induce reactions, 633 nm to probe changes
- <10 nm observation area
- p-nitrothiophenol (1335 cm^{-1}) to p,p′-dimercaptoazobisbenzene (1440 cm^{-1}) evolution
- Fluctuations due to the monolayer perturbation

Nature Nanotechnology, 2012, 7, 583

TERS for spatially and temporally dependent measurements



- Pros
  - Spatially resolved to a nanoscale region
  - Direct spectroscopical data
  - Atomic scale active sites in heterogeneous catalysis
- Cons
  - SERS active metal needs to be used (Au, Ag)
  - Integration time limits temporal resolution to 1 to 10 s
  - Solution phase experiments difficult due to the reactant/product molecules being in proximity of the near surface region
  - Laser modifies the reactive moiety

Nature Nanotechnology, 2012, 7, 583

Conclusions and acknowledgments

- Conclusions
  - Scanning probe techniques are used for spatially resolved surface information
  - Can provide z-axis imaging information with the resolution to a single molecule (atom)
  - AFM can be performed under various environmental conditions
  - Advancements in instrumentation (SNOM, TERS) allow for spatially and temporally resolved chemical information to be obtained

- Acknowledgments
  - Symposium organizers
  - Lehigh *in operando* group and Prof. Wachs

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