



# MS31007: Materials Science

## Chapter 4-III: Defects in Solids /Characterization Techniques

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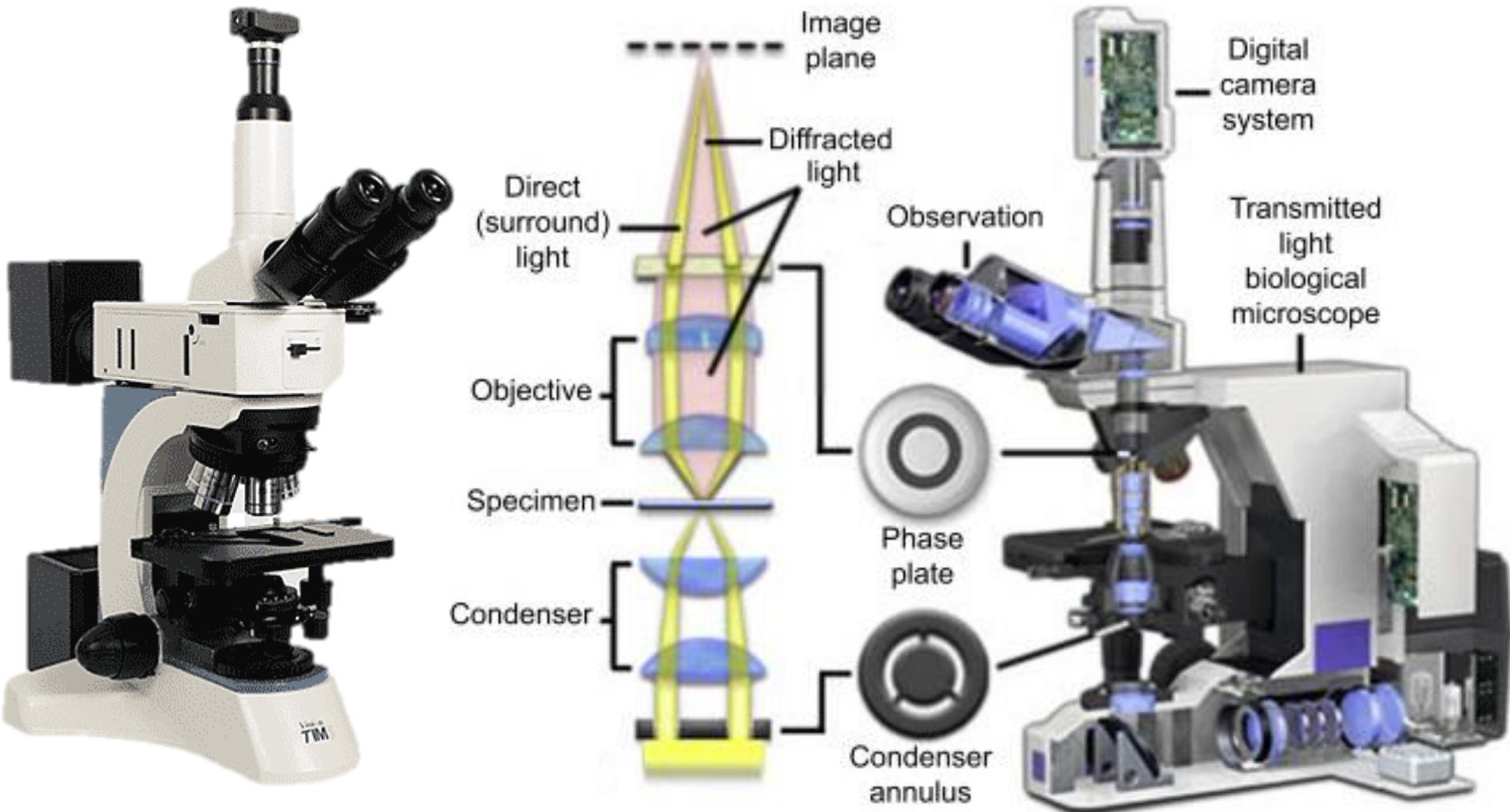
40  $\mu\text{m}$



# Objectives

- Classify various types of crystalline imperfections and explain the role of defects on the mechanical and electrical properties of crystalline materials.
- Determine the ASTM grain size number and average grain size diameter and describe the importance of grain size and grain boundary density on the behavior of crystalline materials.
- Learn how and why optical microscopy, SEM, TEM, HRTEM, AFM, and STM techniques are used to understand more about the internal and surface structures of materials at various magnifications.

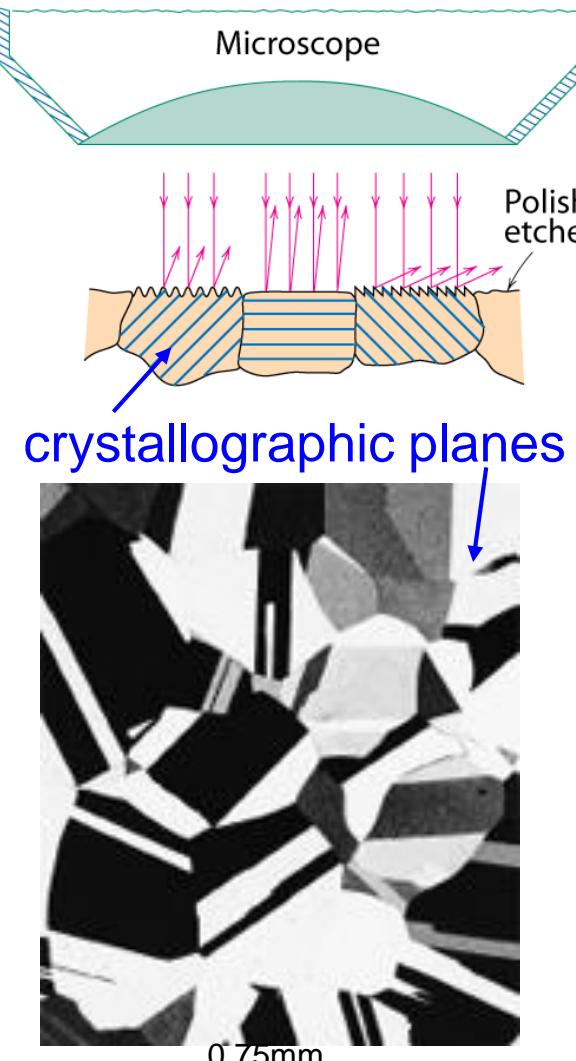
# Optical Microscope



# Grain-size Determination

## Optical Microscopy

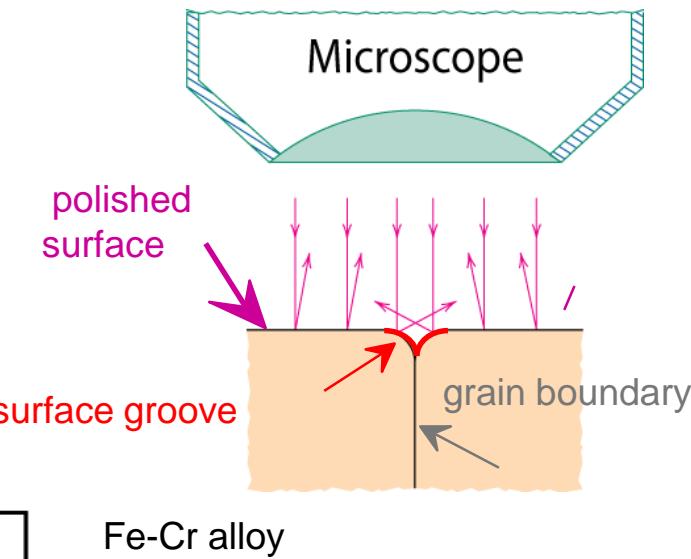
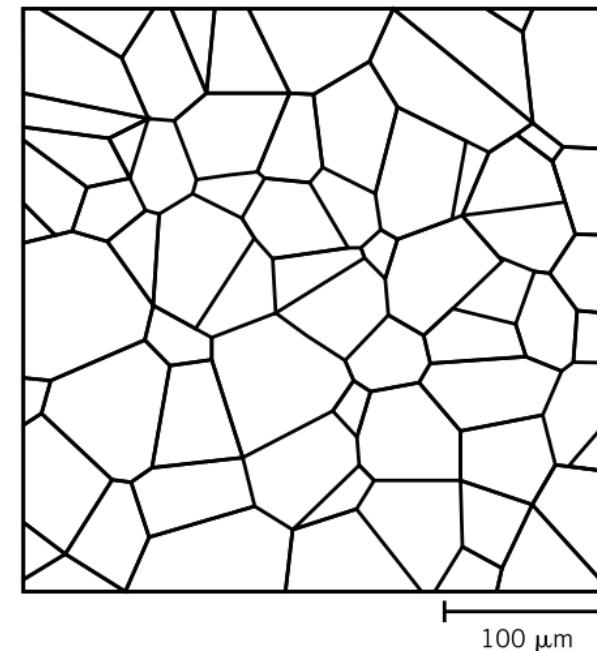
**Grain size** is often determined when the properties of polycrystalline and single phase materials are under consideration



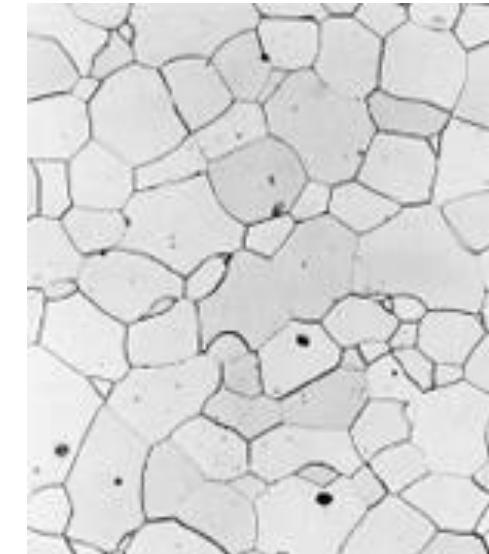
Micrograph of brass (a Cu-Zn alloy)

- Useful up to 2000X magnification.
- Polishing removes surface features (e.g., scratches)

- Etching changes reflectance, depending on crystal orientation.



Fe-Cr alloy



# Grain-size Determination

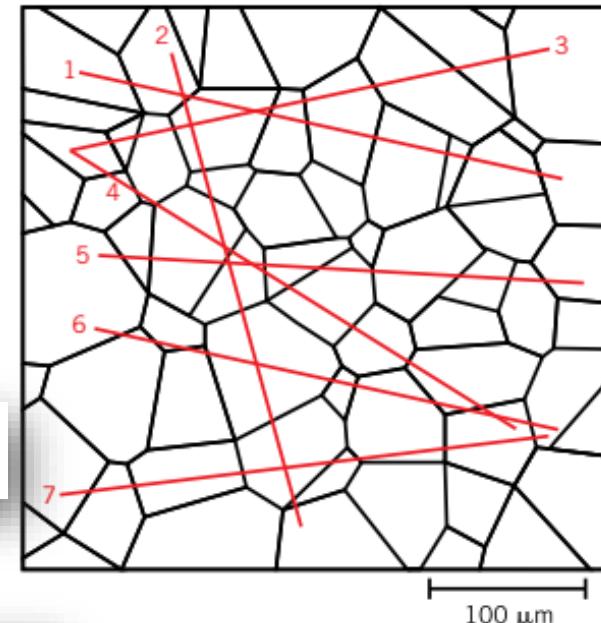
To compute magnification from a scale bar, the following procedure may be used:

1. Measure the length of the scale bar in millimeters using a ruler.
2. Convert this length into microns [i.e., multiply the value in step (1) by 1000 because there are 1000 microns in a millimeter].
3. Magnification  $M$  is equal to

$$M = \frac{\text{measured scale length (converted to microns)}}{\text{the number appearing by the scale bar (in microns)}}$$

First determine the magnification of the micrograph. The scale bar length is measured and found to be 16 mm, which is equal to 16,000  $\mu\text{m}$ ; and because the scale bar number is 100  $\mu\text{m}$ , the magnification is

$$M = \frac{16,000 \mu\text{m}}{100 \mu\text{m}} = 160\times$$



## (1) Linear intercept—counting numbers of grain boundary intersections by straight test lines;

Mean intercept length  $\bar{\ell}$ ,  $P$ : sum of the total number of intersections,  $L_T$  total length of all the lines,  $M$  is the magnification

$$\bar{\ell} = \frac{L_T}{PM}$$

Line Number	Number of Grain-Boundary Intersections
1	8
2	8
3	8
4	9
5	9
6	9
7	7
Total	58

**Example:** (7 lines)(50 mm/line) = 350 mm

The mean intercept length  $\bar{\ell}$  (in millimeters in real space)

$$= \frac{350 \text{ mm}}{(58 \text{ grain-boundary intersections})(160\times)} = 0.0377 \text{ mm}$$



## American Society for Testing and Materials (ASTM)

(2) comparison— comparing grain structures with standardized charts, which are based upon grain areas (i.e., number of grains per unit area)

$$n = 2^{G-1}$$

- $G$  represent the grain-size number,
- $n$  be the average number of grains per square inch at a magnification of 100×

The comparison method of grain-size determination was devised by the  
**American Society for Testing and Materials (ASTM)**

For other magnification ( $M$ )

$$n_M \left( \frac{M}{100} \right)^2 = 2^{G-1}$$

- $n_M$  is the number of grains per square inch at magnification  $M$ .
- the inclusion of the  $(M/100)^2$  term makes use of the fact that, whereas magnification is a length parameter, **area is expressed in terms of units of length squared**. Hence, the number of grains per unit area increases with the square of the increase in magnification.



# Resolution Limit of Microscopy

$$d = \frac{0.61 \lambda}{NA}$$

Usually a wavelength of 550 nm is assumed, which corresponds to green light. With air as the external medium, the highest practical  $NA$  is 0.95, and with oil, up to 1.5.

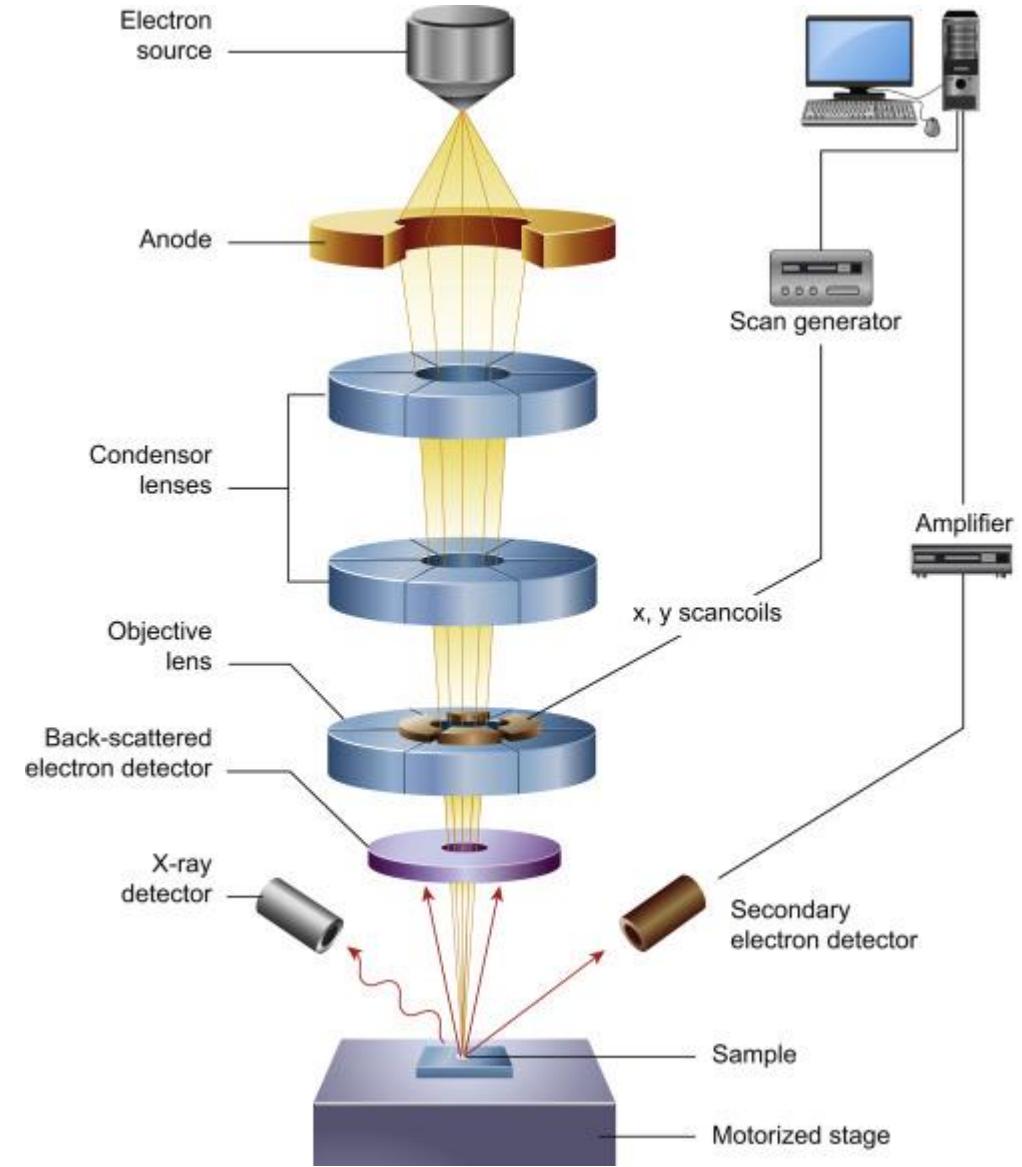
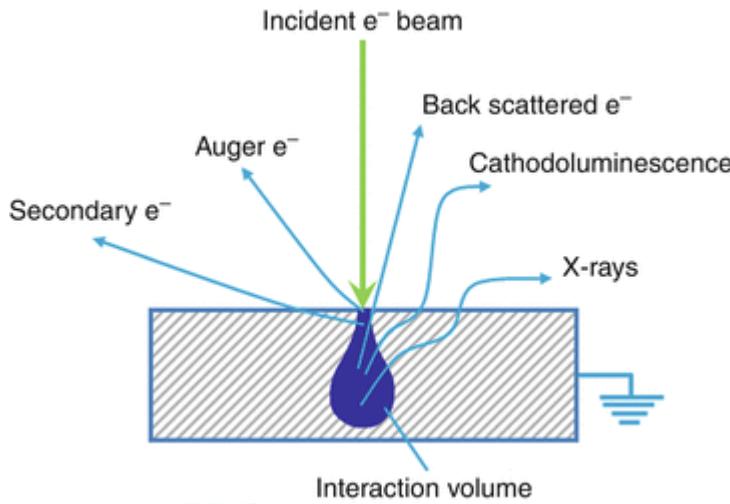
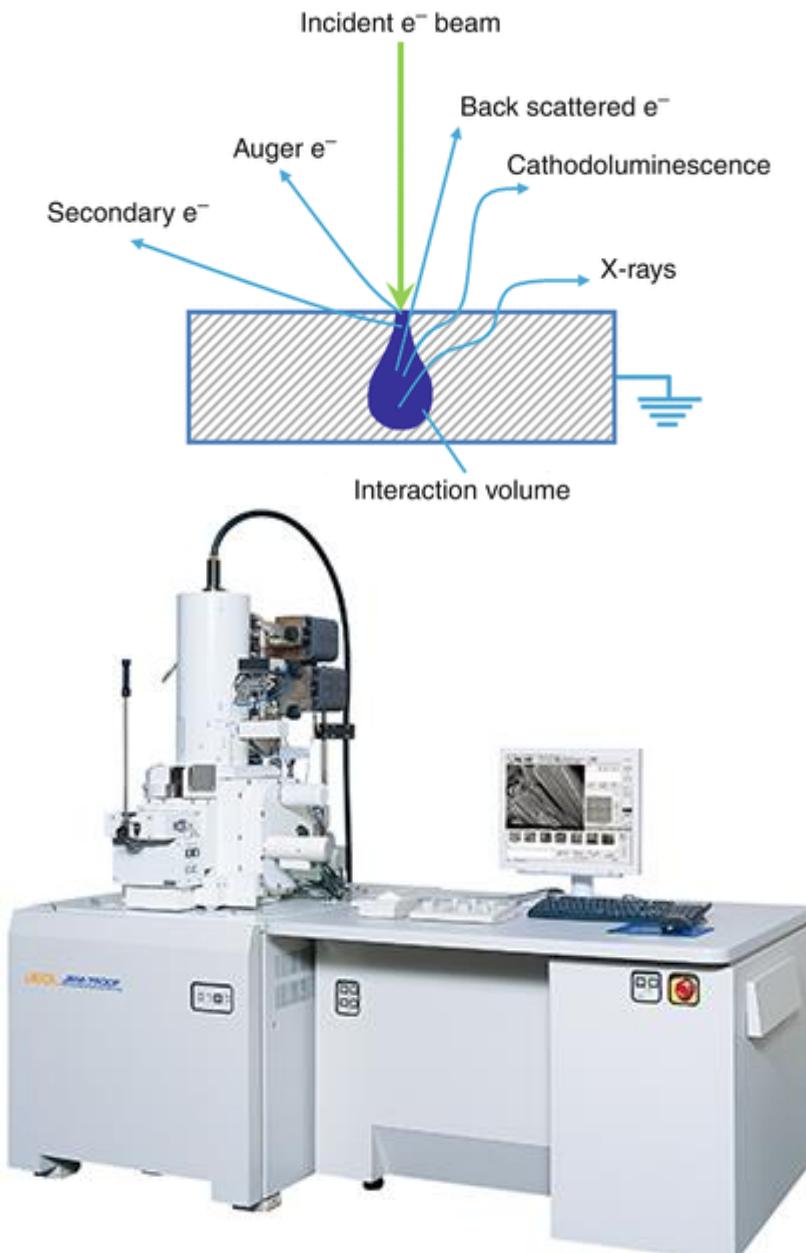
**In practice the lowest value of  $d$  obtainable with conventional lenses is about 200 nm.**

Optical resolution  $\sim 0.2 \mu\text{m} = 200 \text{ nm}$

For higher resolution need higher frequency

- X-Rays? Difficult to focus.
- Electrons
  - Wavelengths ca. 3 pm (0.003 nm)
    - (Magnification - 1,000,000X)
  - Atomic resolution possible
  - Electron beam focused by magnetic lenses.

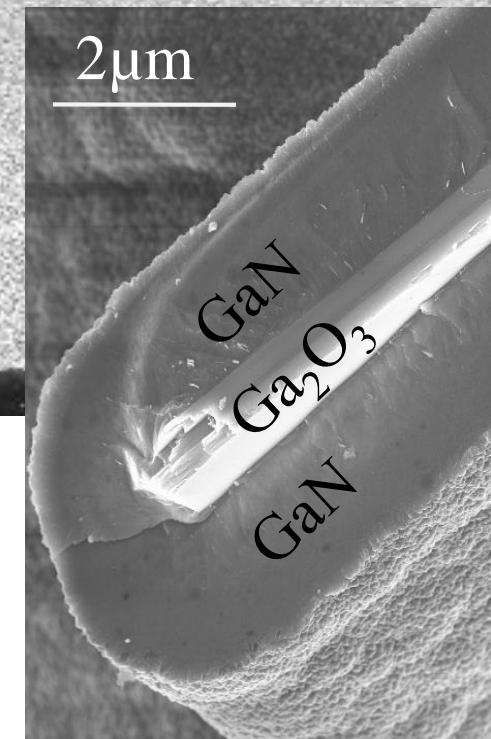
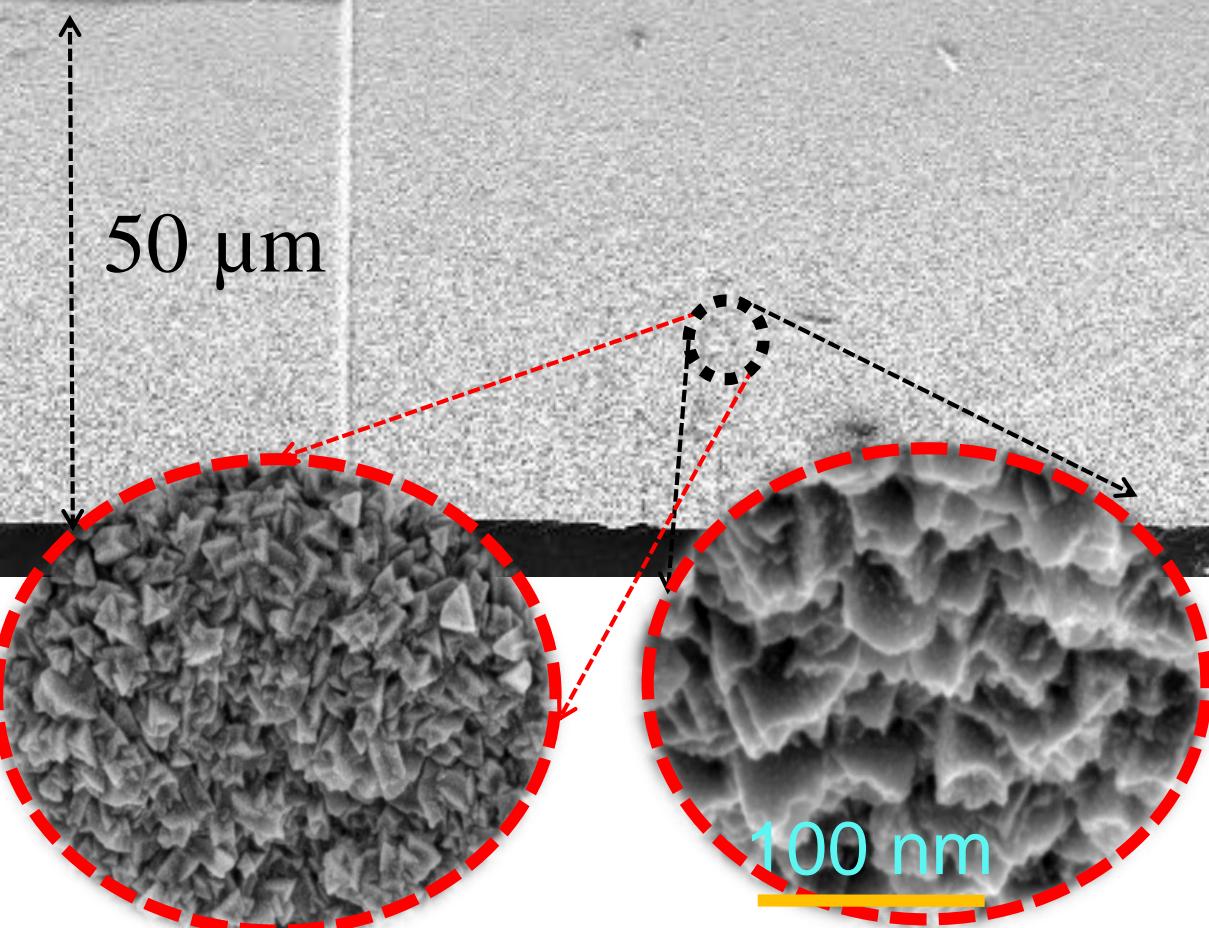
# Scanning Electron Microscope (SEM)



# FE-SEM Surface Characterization

## Surface morphology of GaN Belt

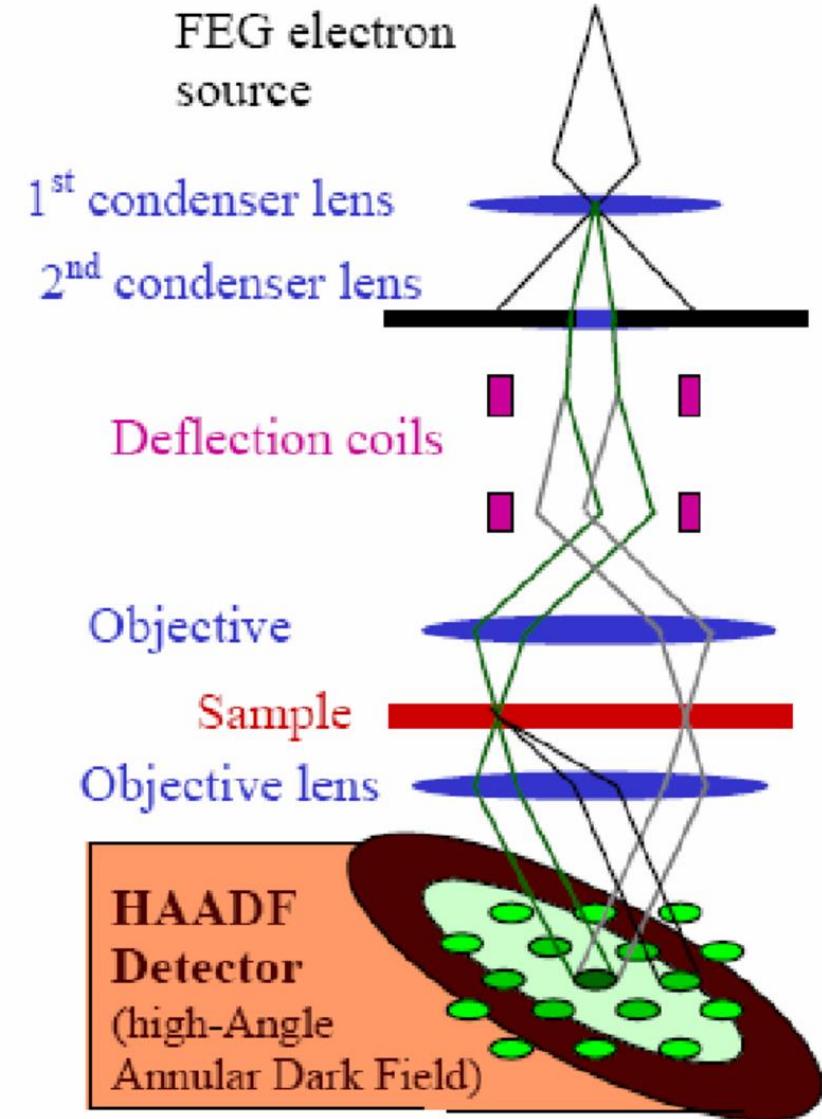
P. Sahoo et al. Applied Physics Letter 2011



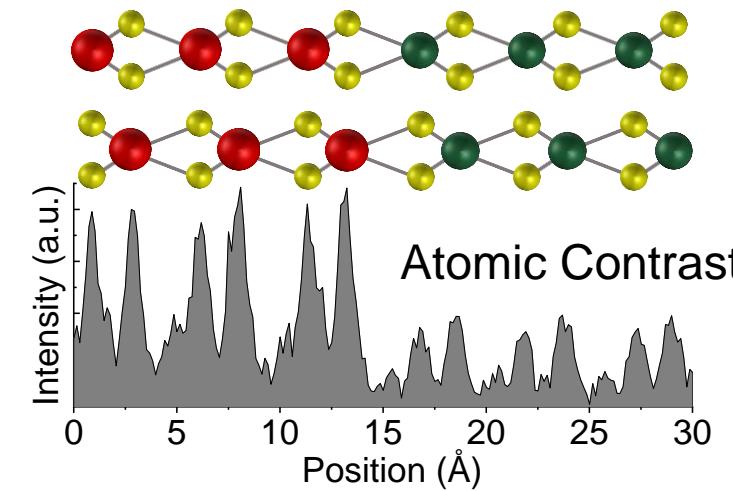
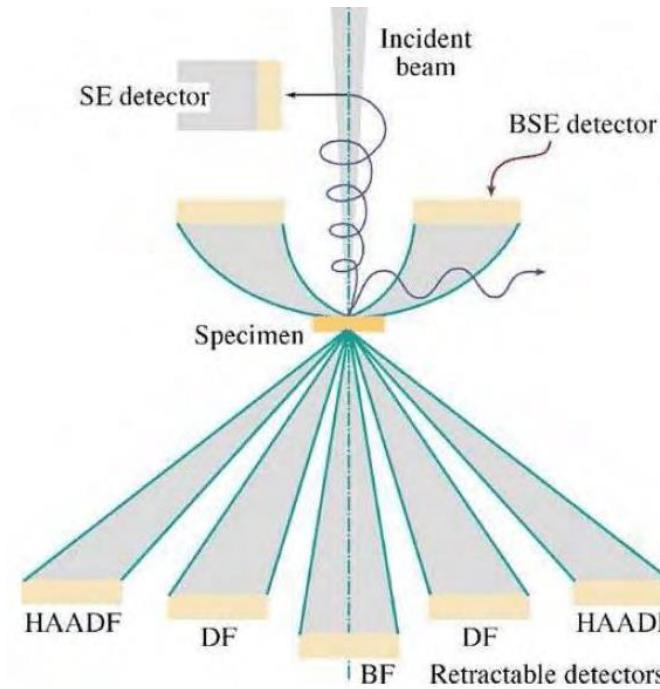
# Transmission Electron Microscopy (TEM)

Types:

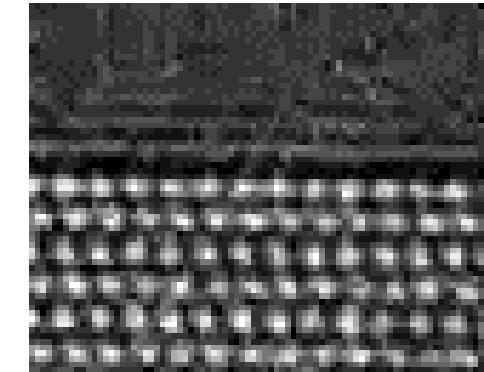
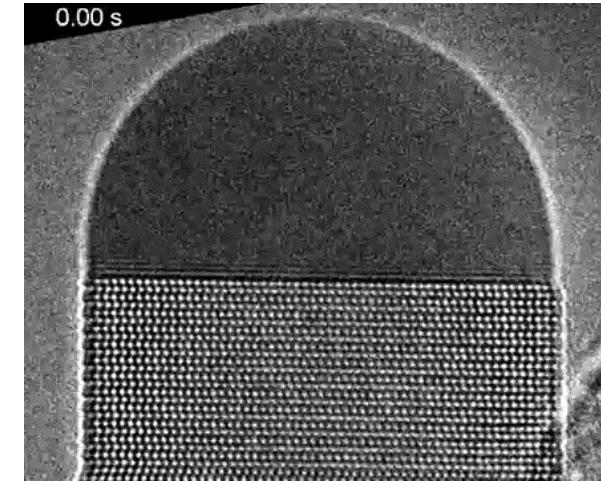
1. TEM
2. HRTEM
3. HAADF-STEM



# High Angle Annular Dark Field Scanning TEM (HAADF-STEM)

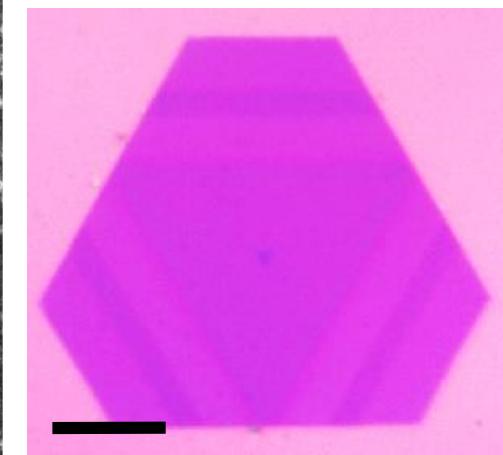
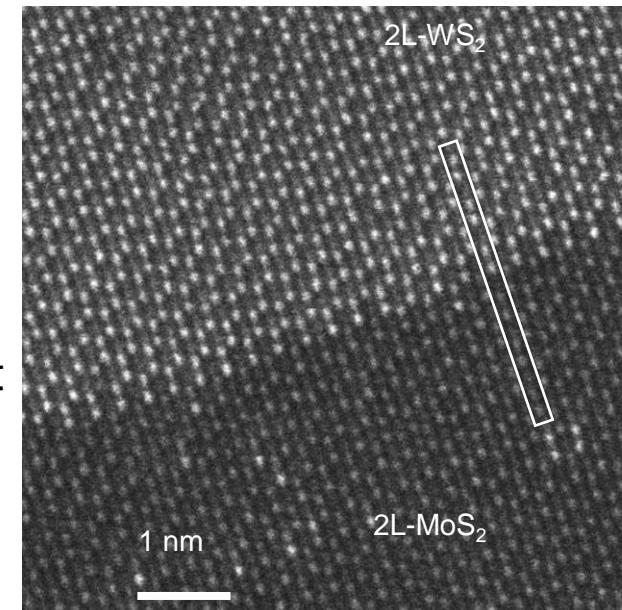


## HRTEM Image of Nanowire



## InP Nanowire

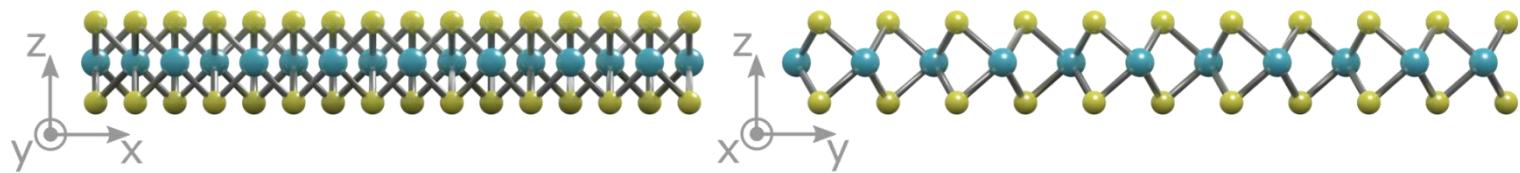
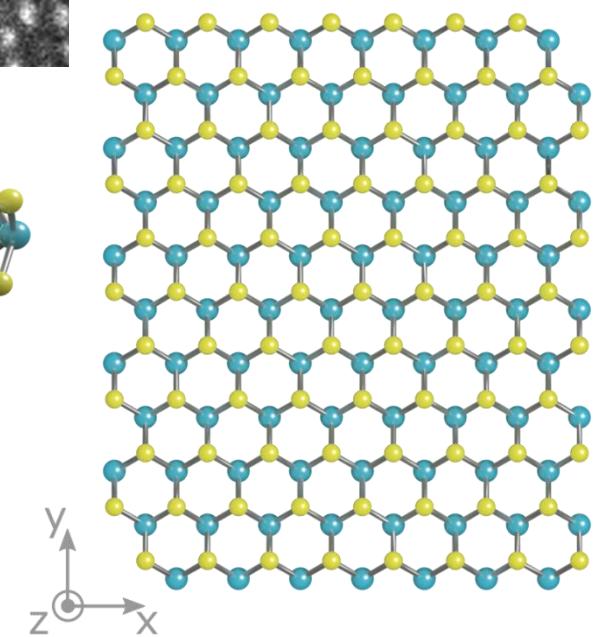
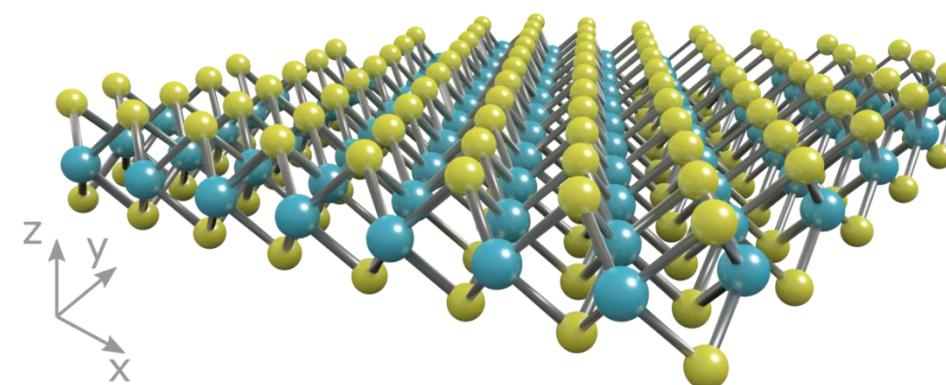
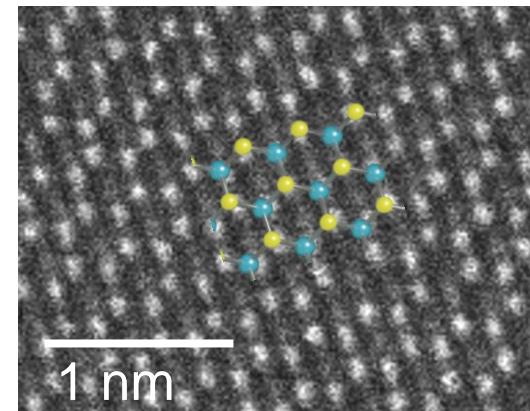
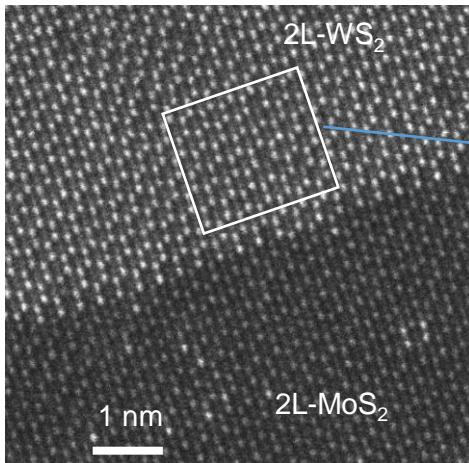
### HAADF-STEM image of ultrathin 2D materials



P. Sahoo Nature 2018

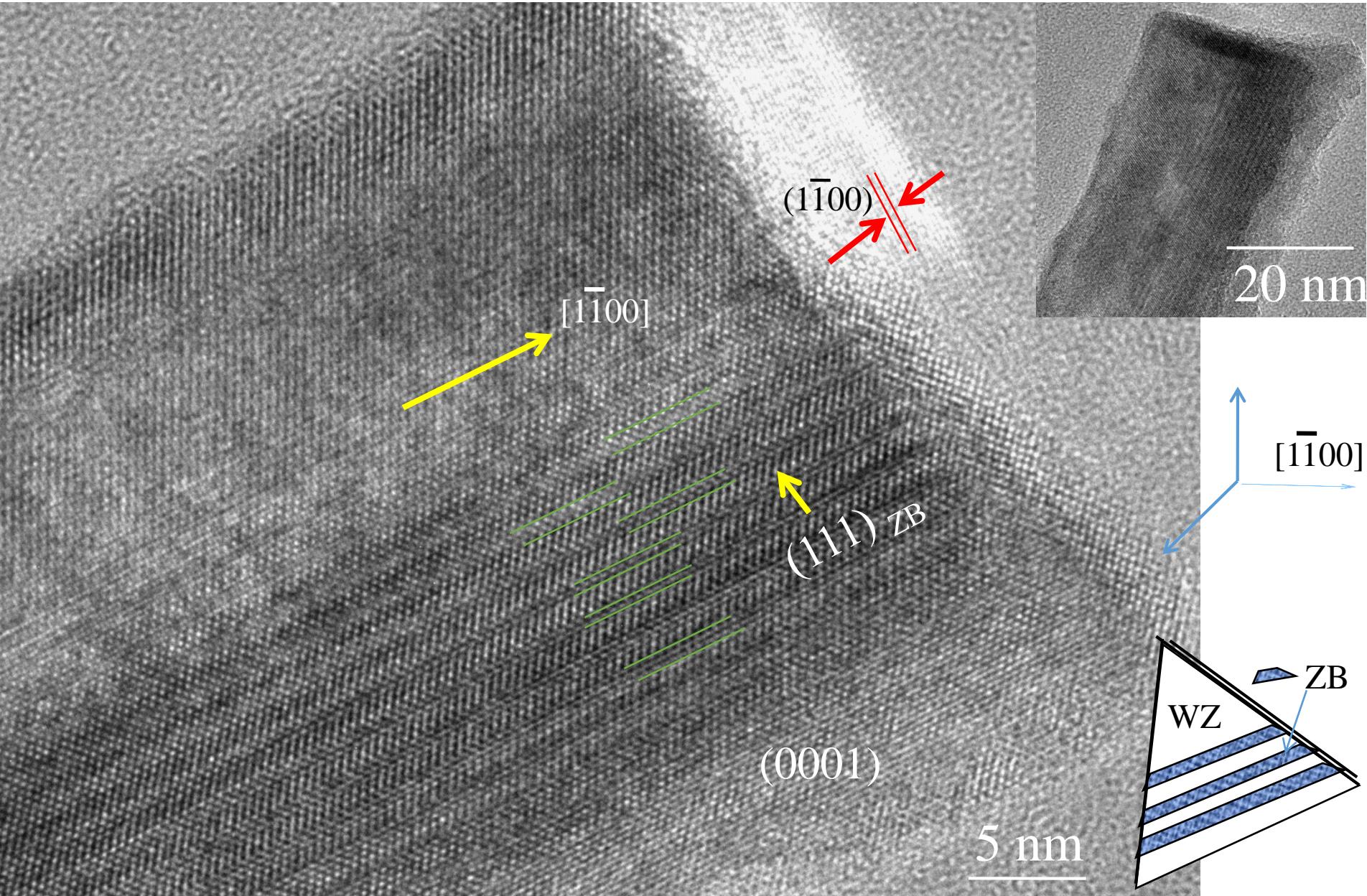
P. Sahoo ACS Nano 2018

## HAADF-STEM image of ultrathin 2D materials



# Wurtzite/Zincblende Stacking faults/Twin Boundaries in GaN Nanowires

P. Sahoo CryGrowthDesign 2012

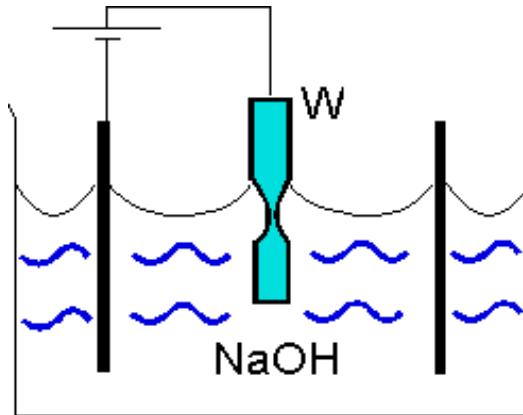


# Scanning Probe Microscopy

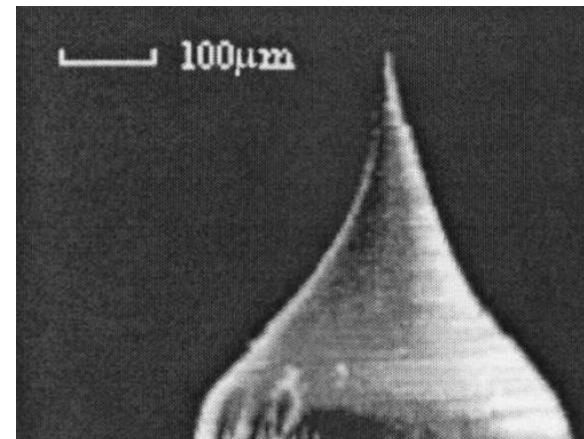
## Probes

### Scanning tunneling microscopy probes

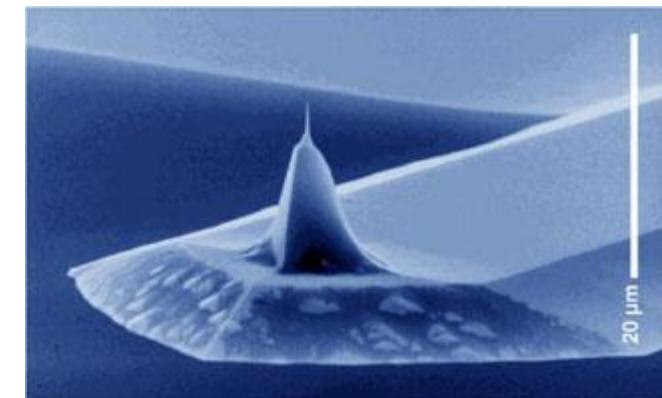
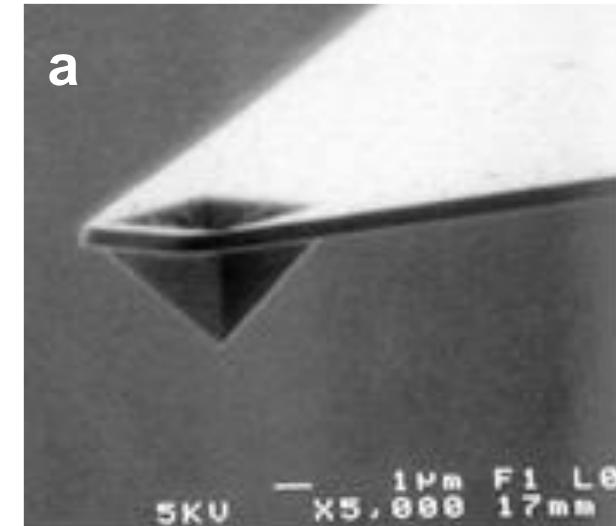
- *Cutting and grinding*
- *Electrochemical etching*



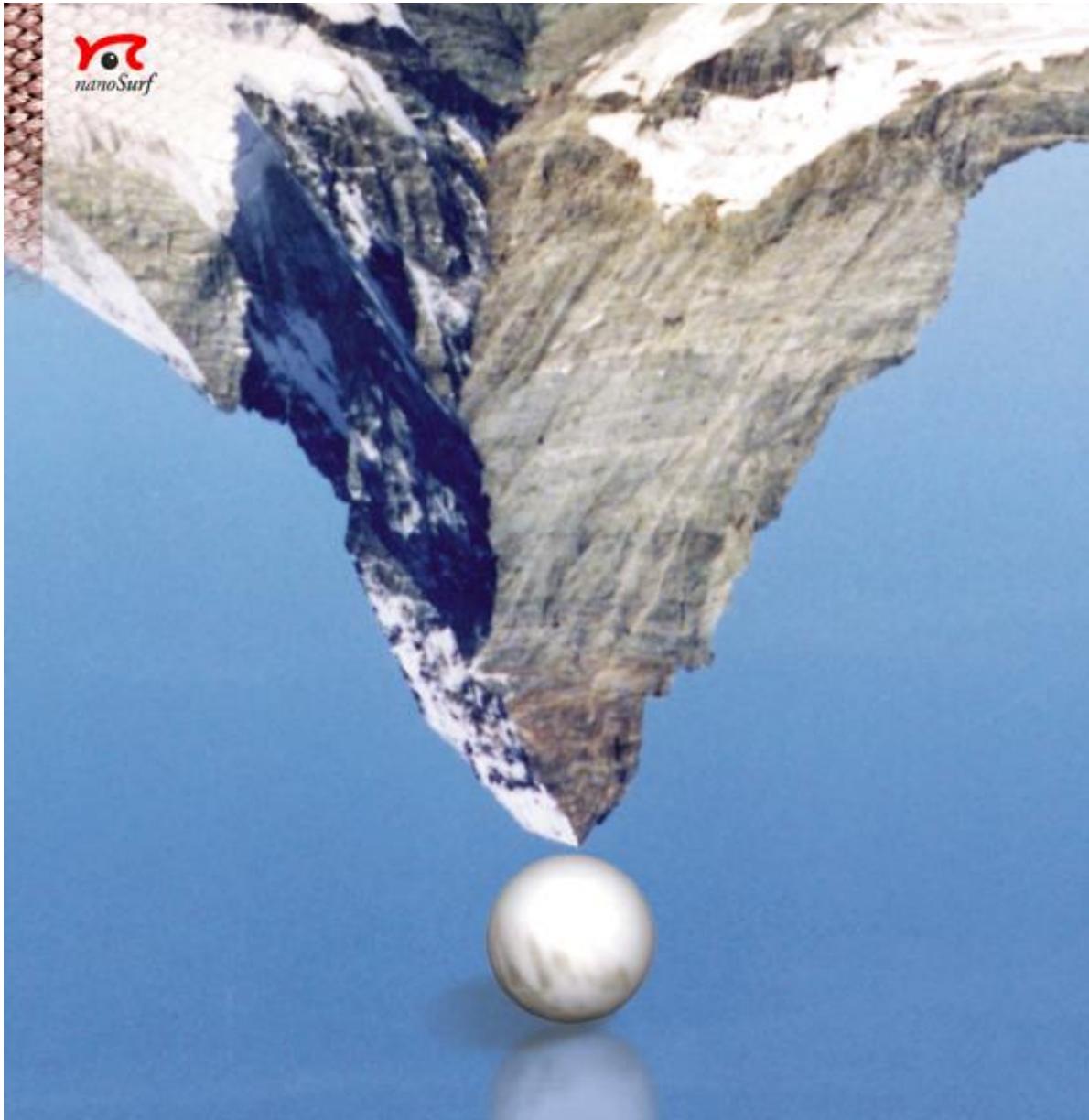
Scanning electron microscopy image of a tungsten tip



### Atomic force microscopy probes



# Scanning Probe Microscopy

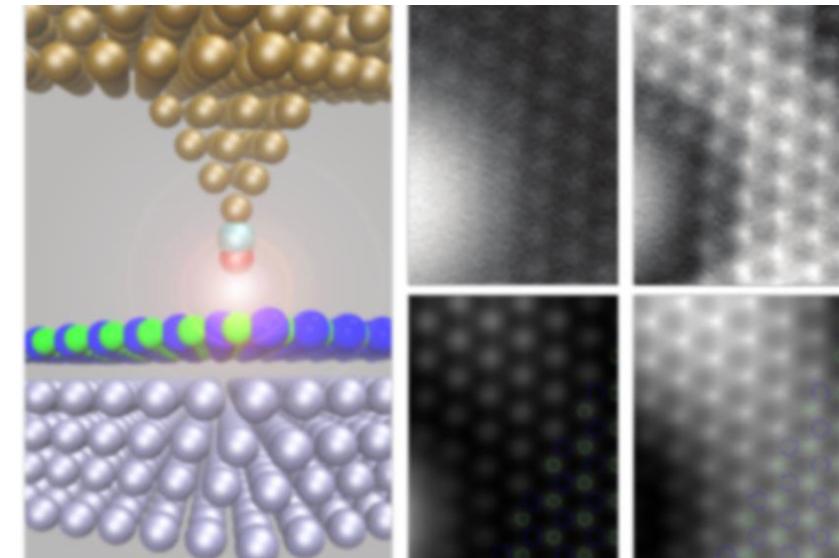
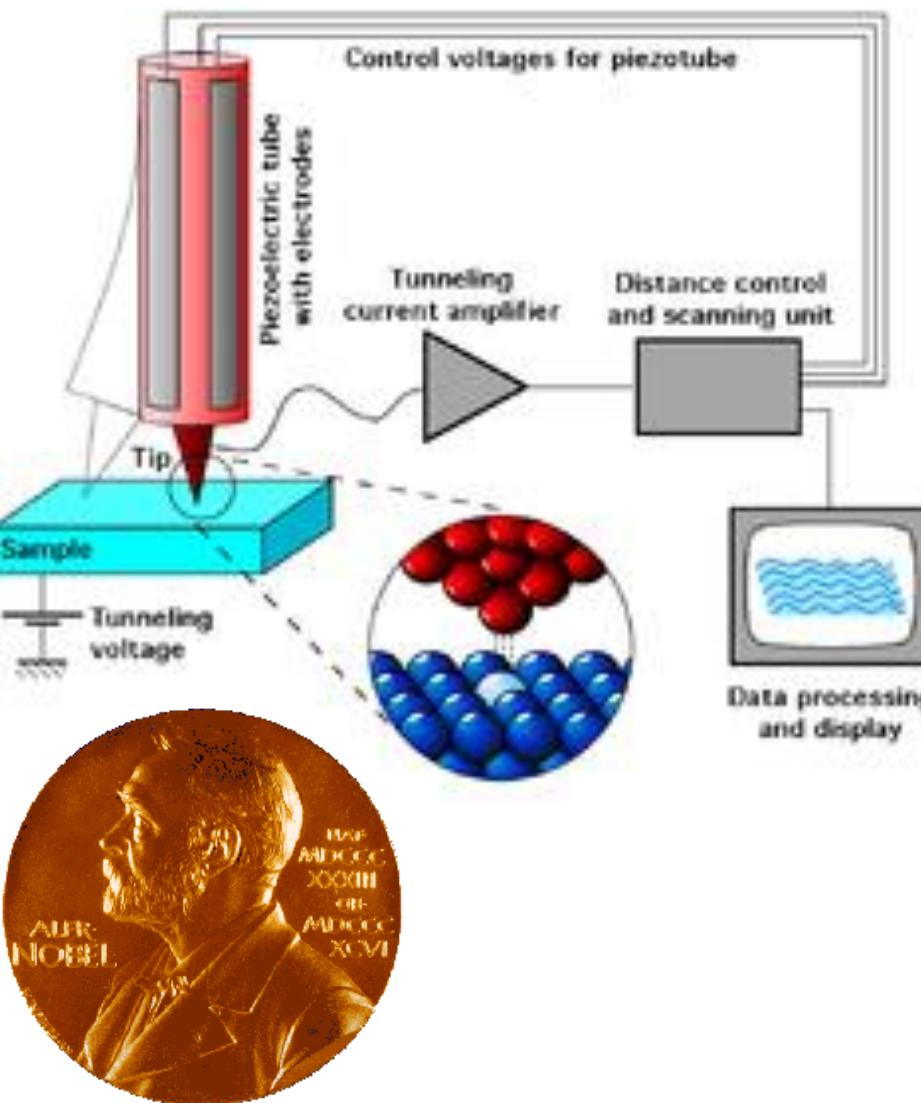


**Usually, only one atom at the end of the tip carries most of the current. This is the atom that sticks out the most.** (Remember the factor 100 decrease in the tunneling current per atom diameter.)

**The atom at the end of the tip compares to a ping-pong ball at the top of the Matterhorn.** (The STM was invented in Switzerland !)

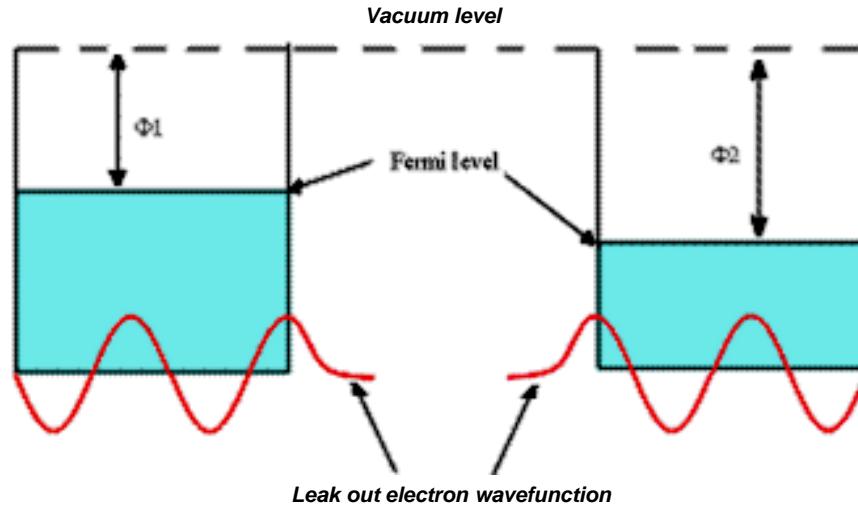


# Scanning Tunneling Microscopy- STM

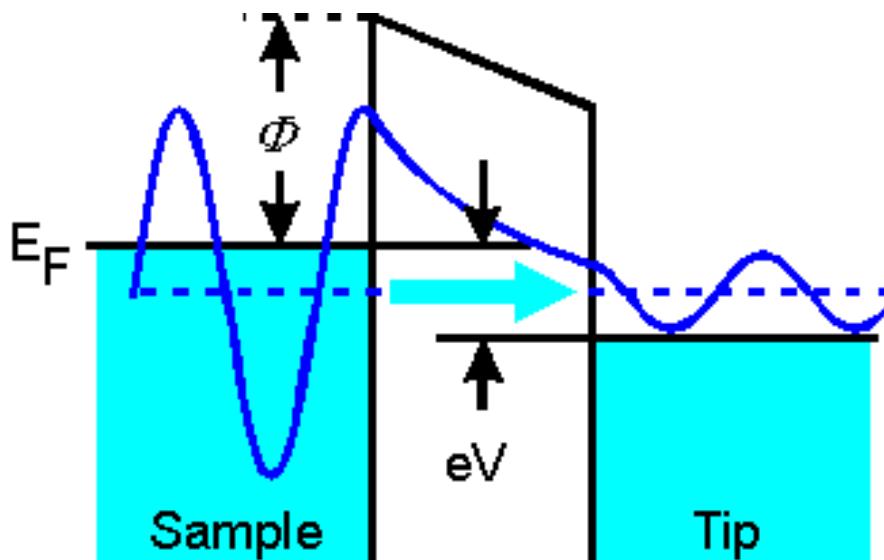


# Scanning Tunneling Microscopy

## Theory of the electron tunneling

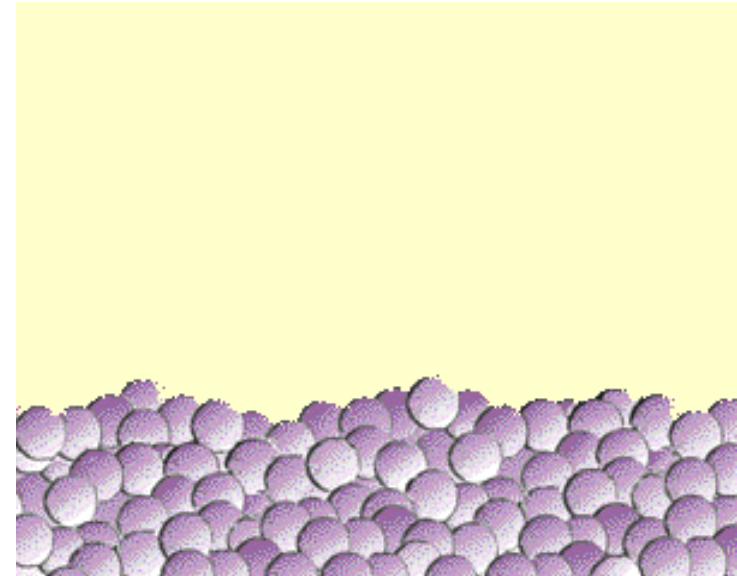
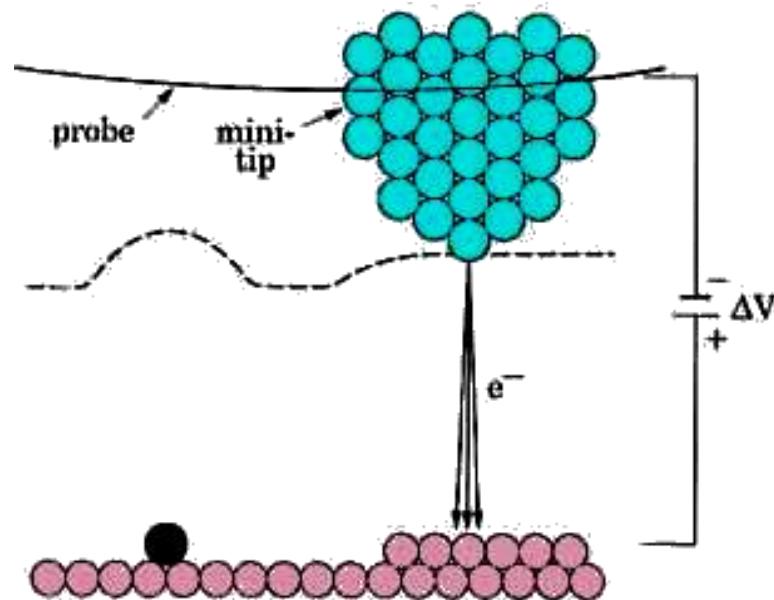


When an electron is incident upon a vacuum barrier with potential energy larger than the kinetic energy of the electron, there is still a non-zero probability that it may traverse the forbidden region and reappear on the other side of the barrier. It is shown by the leak out electron wavefunction in the picture.



In scanning tunneling microscopy a small bias voltage  $V$  is applied so that due to the electric field the tunneling of electrons results in a tunneling current  $I$ . The height of the barrier can roughly be approximated by the average workfunction of sample and tip.

# Scanning Tunneling Microscopy

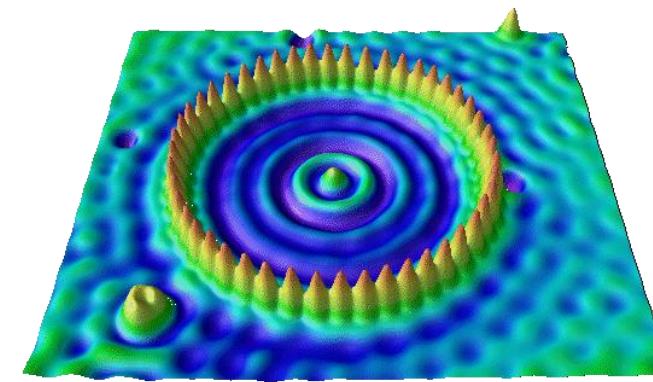
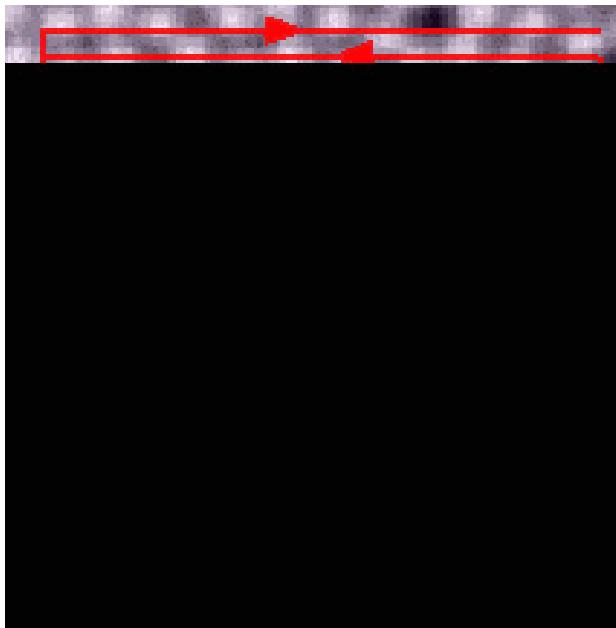


**Measurement of the tunneling current while scanning thus generates a map of the LDOS of the sample**

Scanning is a movement of the tip across the surface in X and Y directions. In order to scan, the STM must position the tip within tunneling distance at each instant. The STM measures at discrete X,Y points while scanning.. Its resolution is a function of tip radius, tunneling distance, speed, and the distance between measurements. Its vertical resolution is limited by electrical and mechanical noise and by thermal effects.

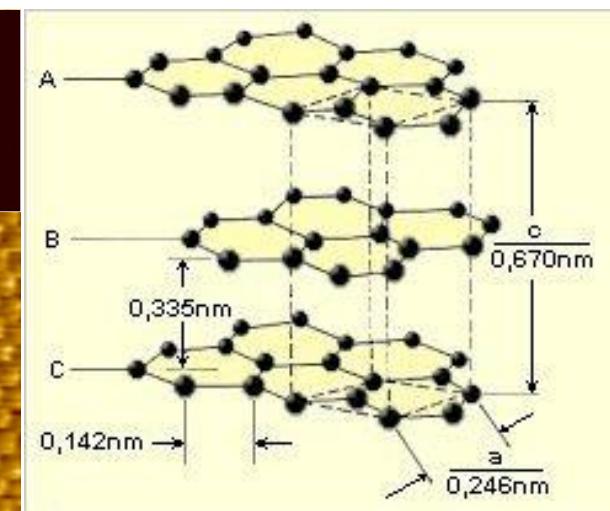
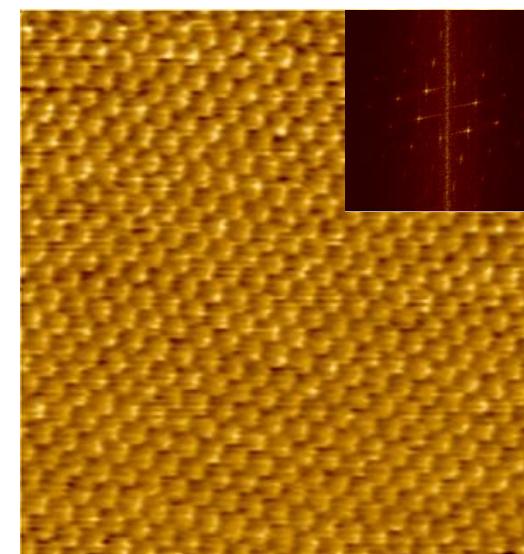
# Scanning Probe Microscopy

As the tip is rastered over the sample surface, the lateral (x, y) location and the height or property value at that position (z) is recorded. Once the z-profile for each of the raster lines are put together, an image of the surface can be constructed and visualized.



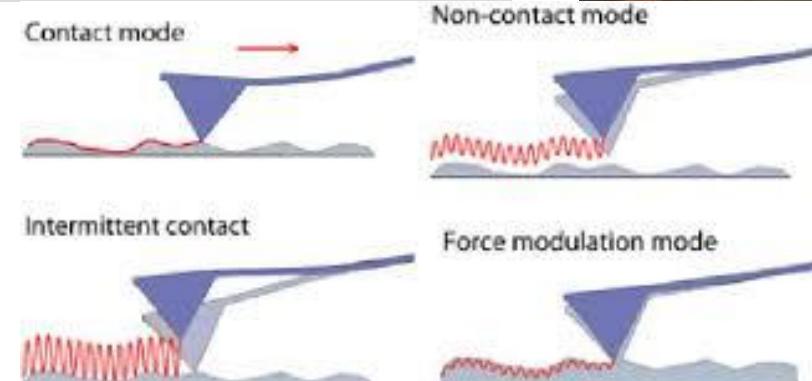
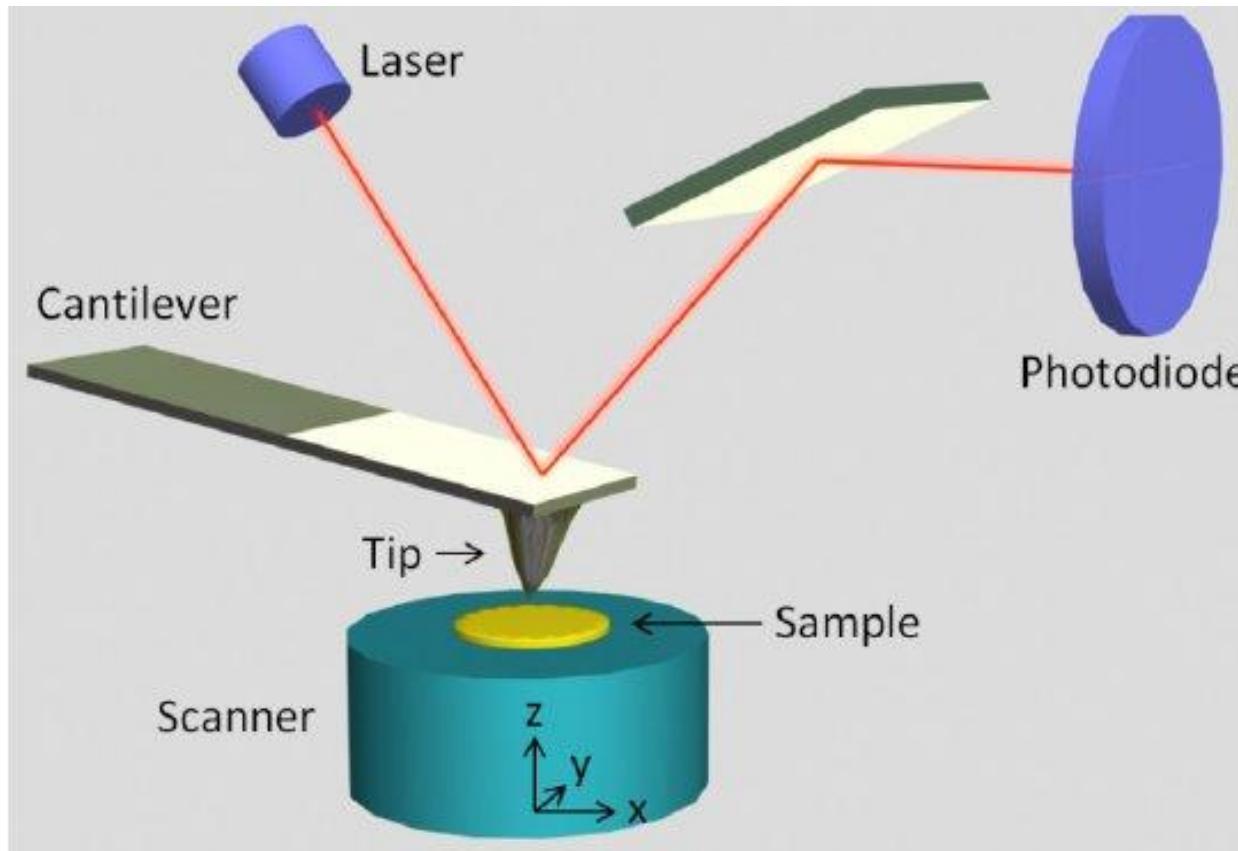
Surface state electrons on Cu(111) were confined to closed structures (corrals) defined by barriers built from Fe adatoms. The barriers were assembled by individually positioning Fe adatoms using the tip of a low temperature scanning tunneling microscope (STM). A circular corral of radius 71.3 Angstrom was constructed in this way out of 48 Fe adatoms.

***STM image of graphite***



**STM rastering to form an image of silicon atoms on a surface**

# Atomic Force Microscopy-AFM

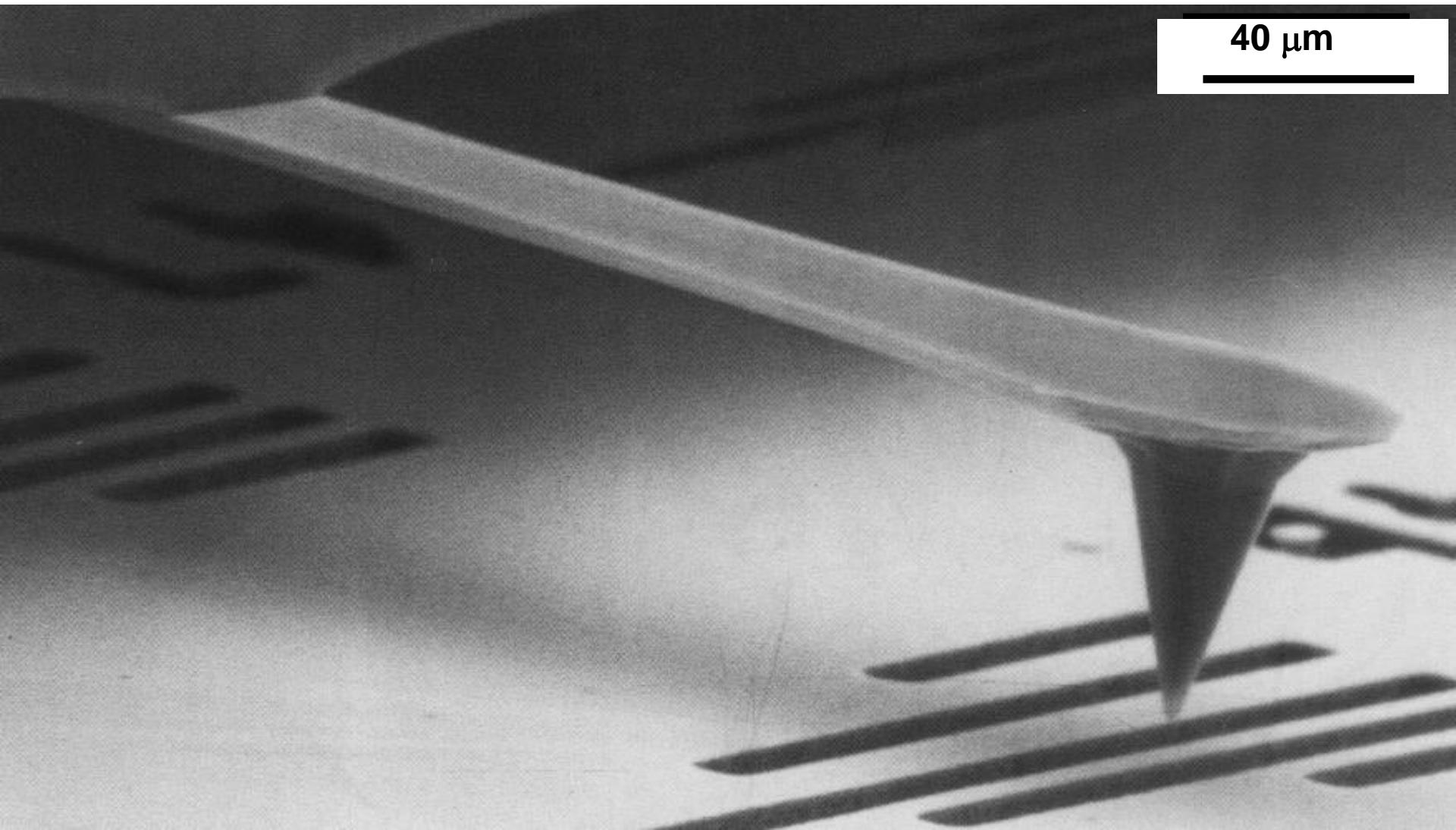




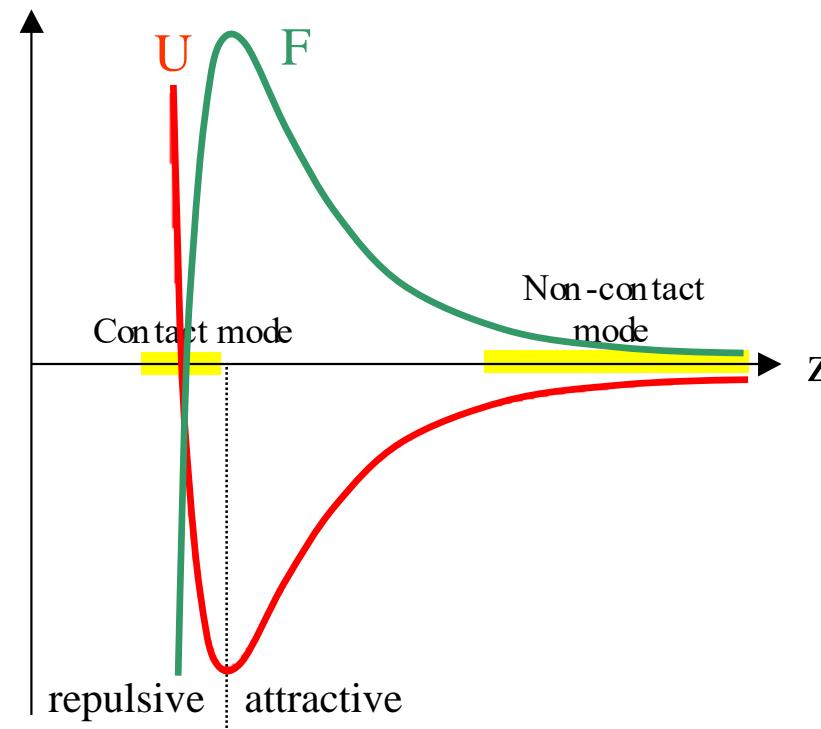
## AFM Cantilever and Tip

To obtain an extra sharp AFM tip one can attach a carbon nanotube to a regular, micromachined silicon tip.

40  $\mu\text{m}$



# Principle of AFM

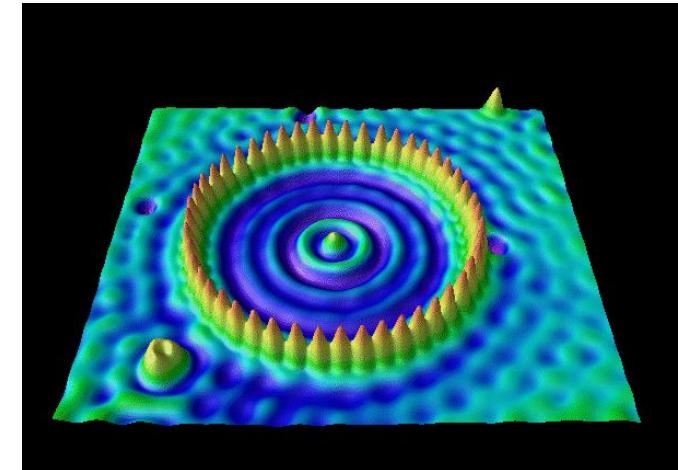


**Energy  $U$  and force  $F$  between tip and sample as a function of their distance  $z$ .**  
The force is the derivative (= slope) of the energy. It is attractive at large distances (van der Waals force, non-contact mode), but it becomes highly repulsive when the electron clouds of tip and sample overlap (Pauli repulsion, contact mode).

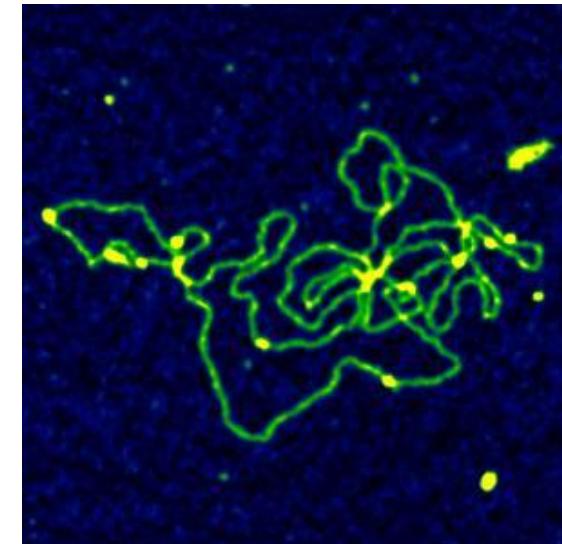
In AFM the force is kept constant, while in STM the current is kept constant.

# STM versus AFM

STM is particularly useful for probing electrons at surfaces, for example the electron waves in quantum corrals or the energy levels of the electrons in dangling bonds and surface molecules.

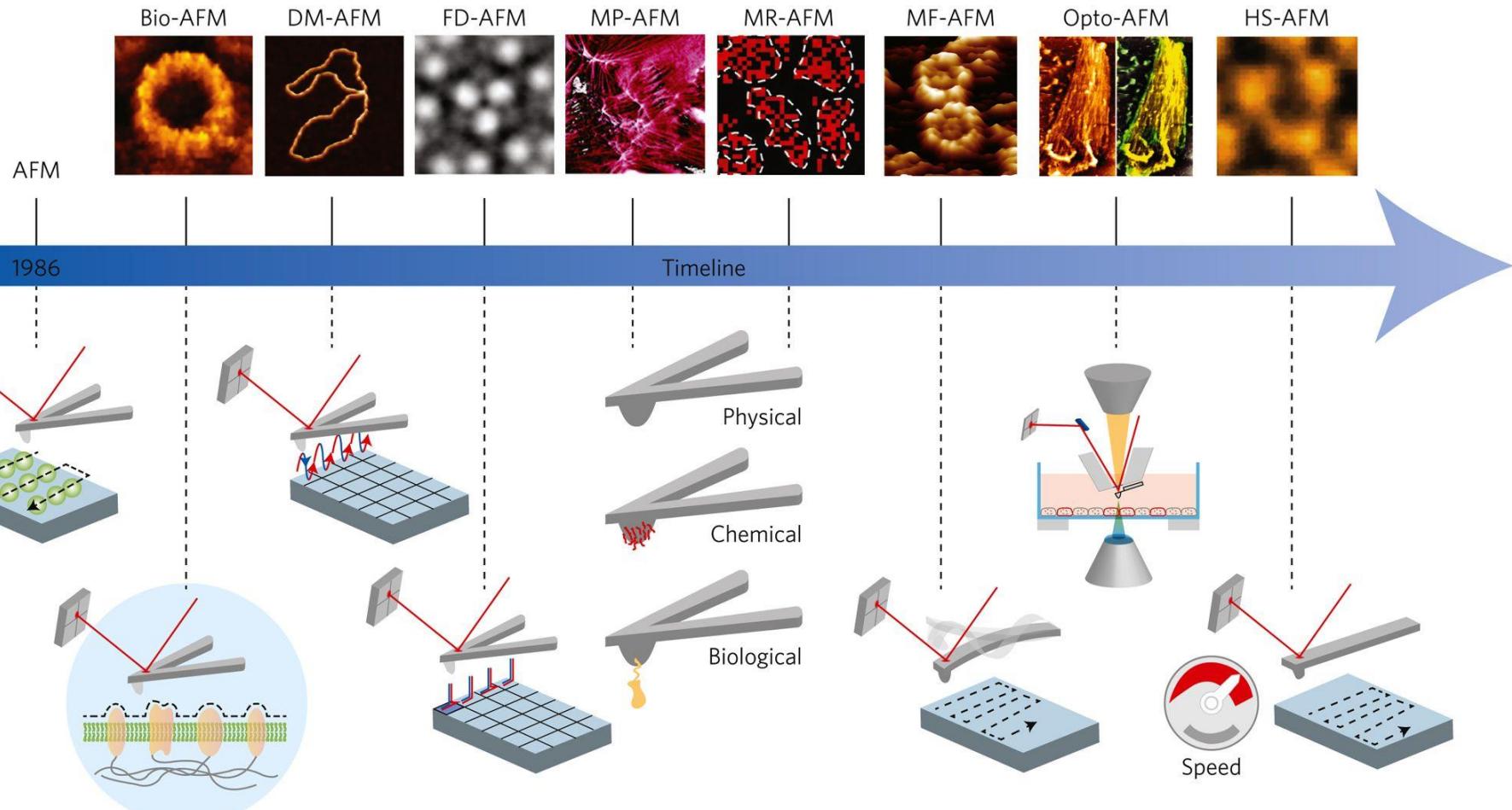


AFM is needed for insulating samples. Since most polymers and biomolecules are insulating, the probe of choice for soft matter is often AFM. This image shows DNA on mica, an insulator.



# AFM based Different modes of Operation

*Nature Nanotechnology* volume 12, pages 295–307(2017)

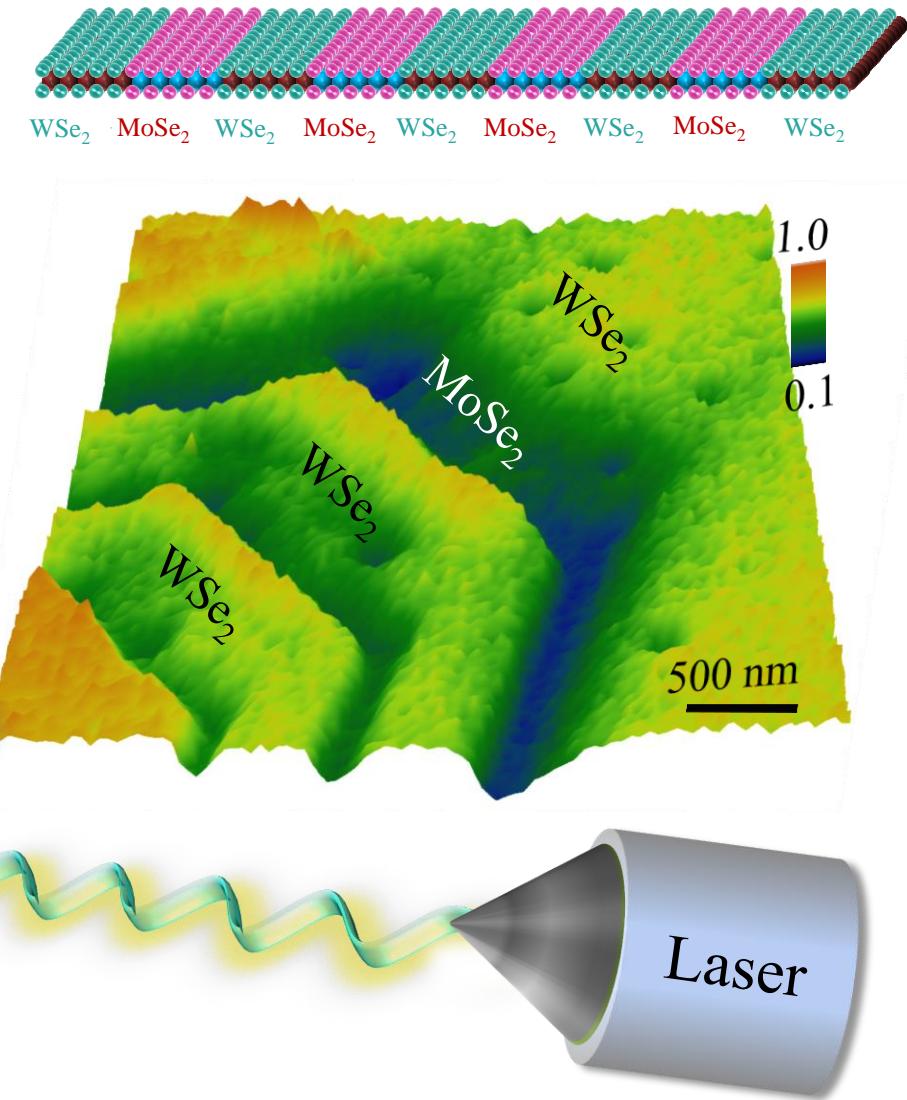
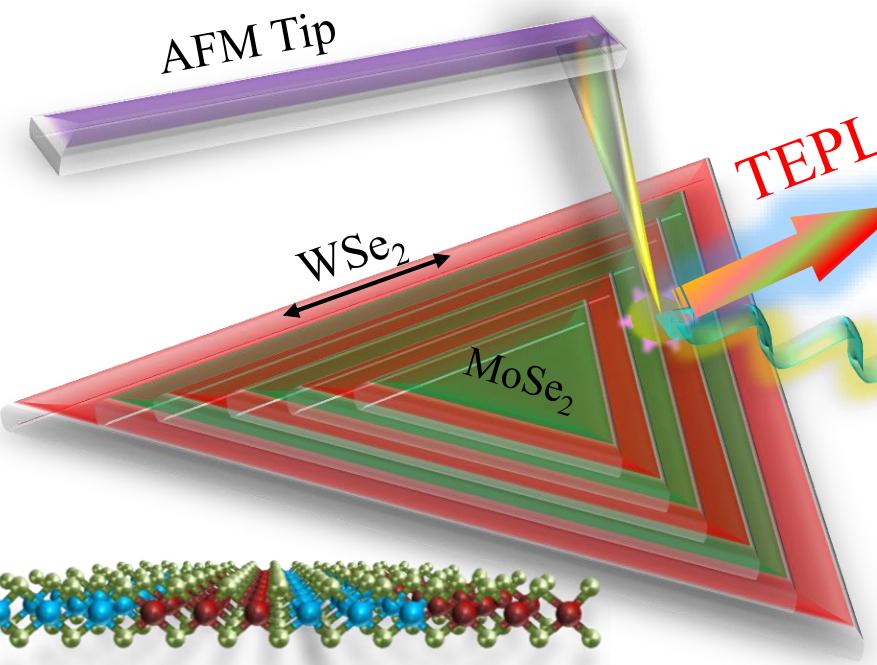
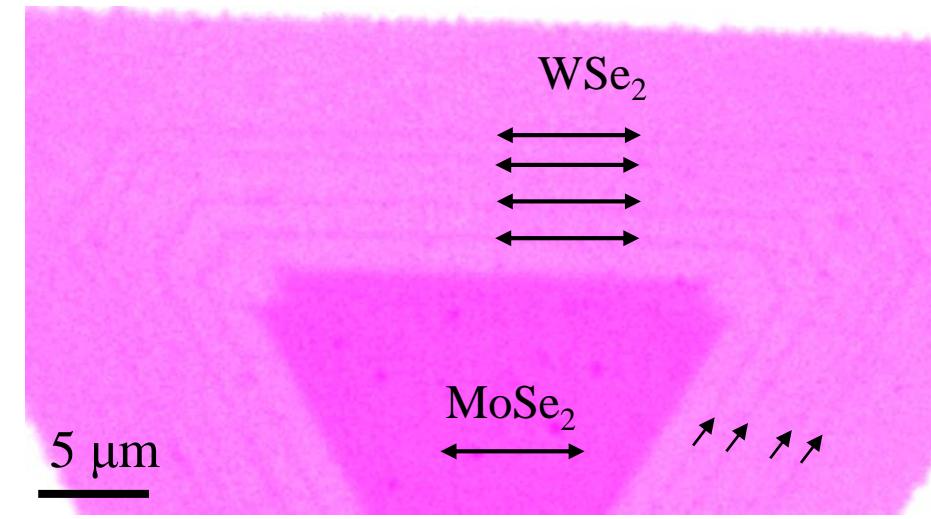


Key inventions developed over the years include: an optical detection system and fluid cell enabling contact mode AFM to operate in aqueous solution (Bio-AFM); dynamic mode AFM (DM-AFM), which oscillates the AFM tip to reduce friction while contouring the biological sample; force-distance curve-based AFM (FD-AFM), which contours the surface of a biological system while recording pixel-by-pixel a full force-distance curve; multiparametric AFM (MP-AFM), which contours the sample while mapping multiple physical or chemical properties; molecular recognition AFM (MR-AFM), which images and maps specific interactions of biological samples; multifrequency AFM (MF-AFM), which contours the sample while oscillating the cantilever tip at multiple frequencies, thus mapping various physical parameters; correlating advanced optical imaging and AFM (Opto-AFM) for the imaging of complex biological systems; high-speed AFM (HS-AFM), which speeds up the image acquisition time by a factor of ~1,000, providing access to dynamic processes in biology. Most modes cross-fertilized each other, ultimately leading to combinatorial AFM.



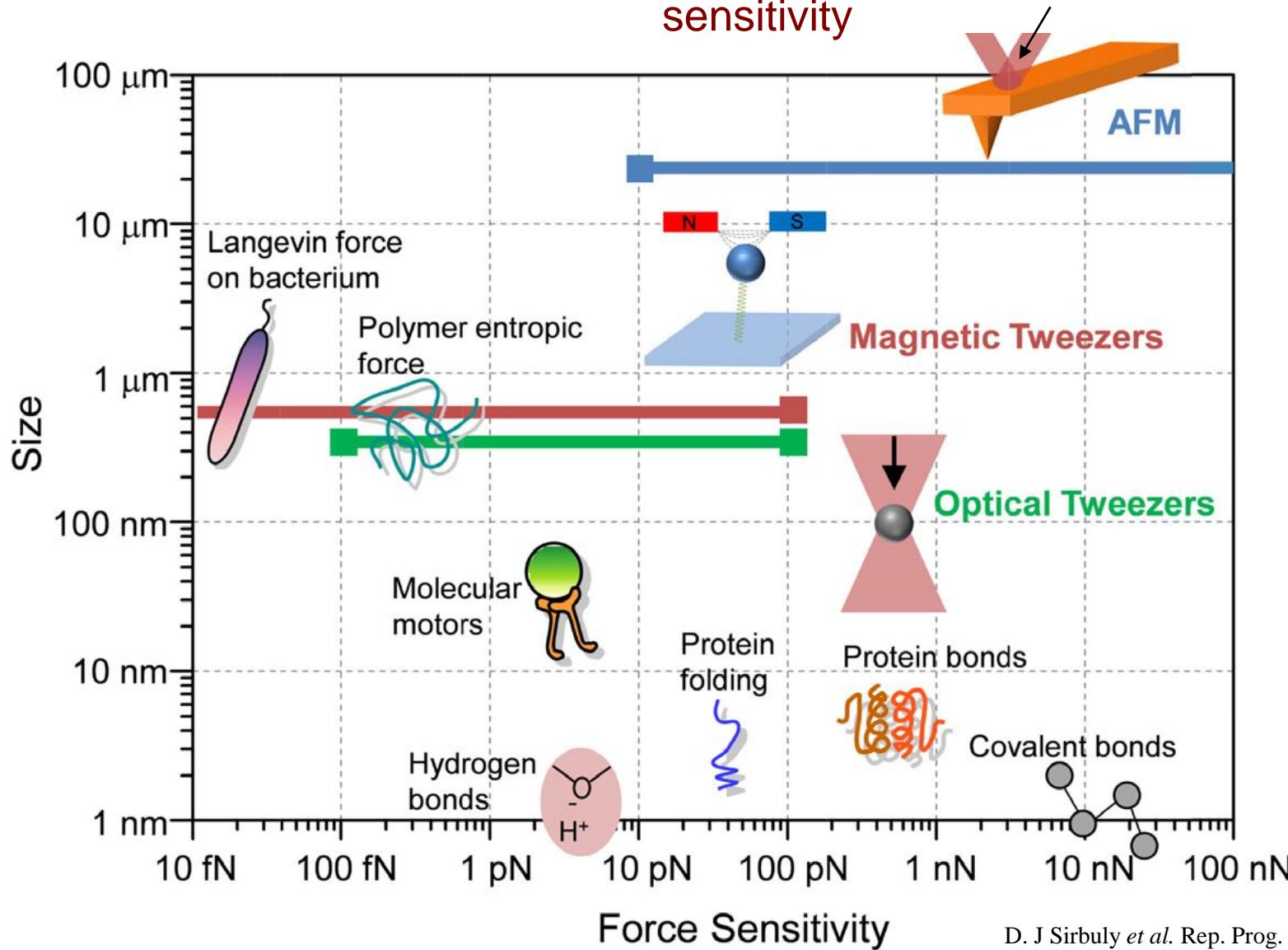
# Nano-Optical Imaging : AFM + Laser

P. Sahoo *et al.* Opt. Mat Exp. 2019



# Technical Limitations: Force Sensitivity

Various molecular systems and nanomechanical transducers ~ Force sensitivity

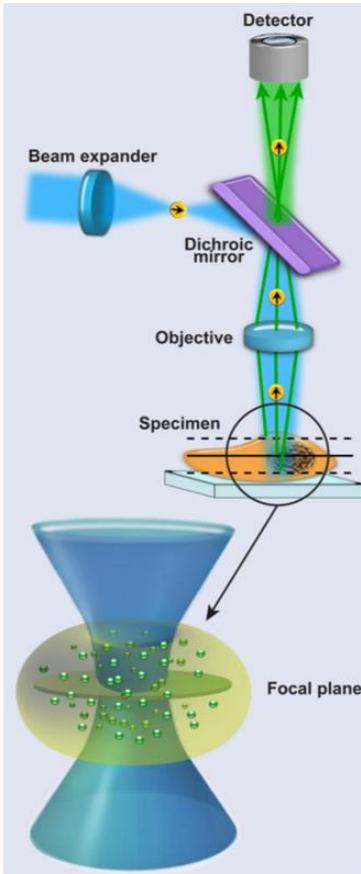


# Real Time Tracking of Cellular Adhesion Forces

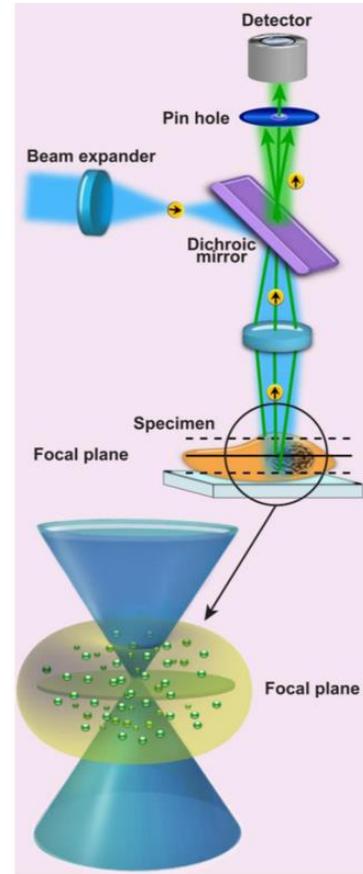
P. Sahoo et al. Nano Letter 2016, 16, 4656

1. Confocal Laser Scanning Microscope (CLSM)
2. Semiconducting Nanowire Arrays

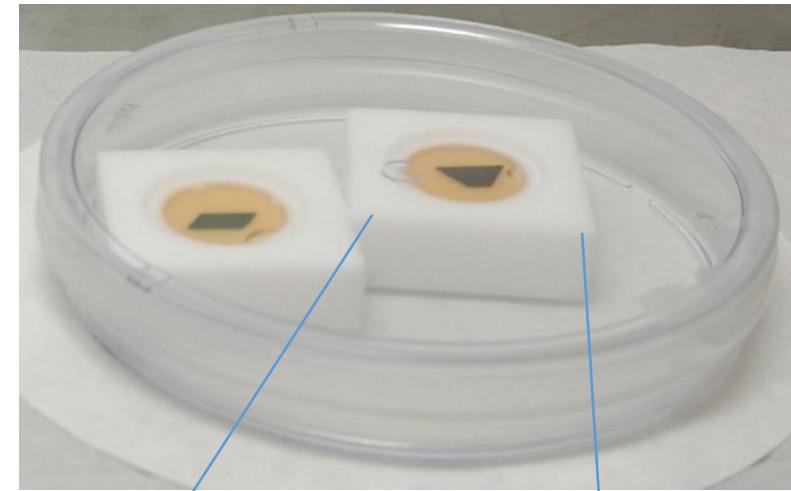
Wide Field



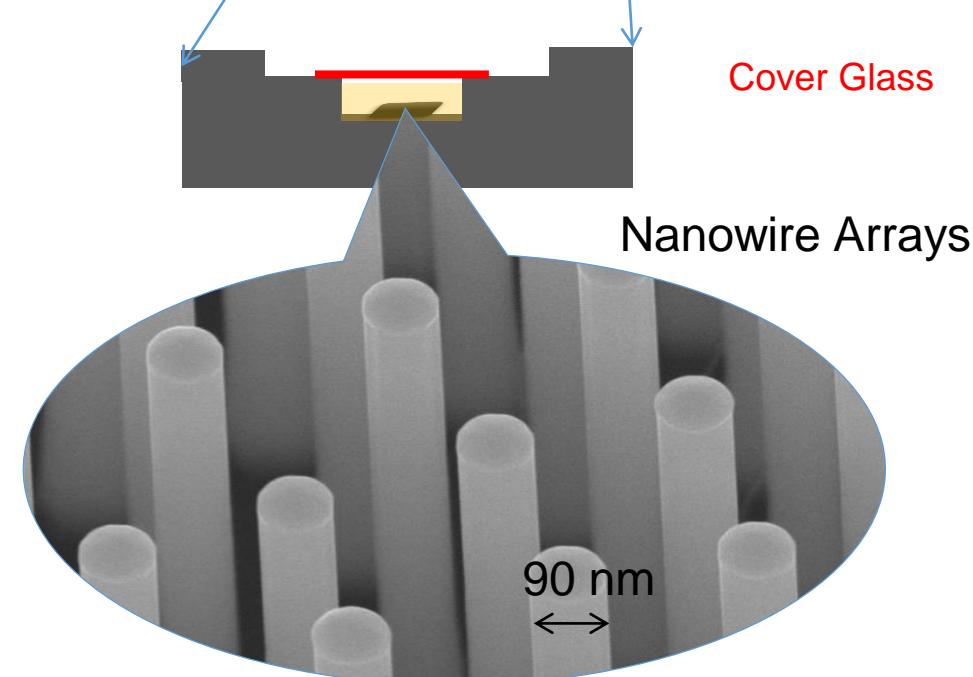
Confocal Microscope



Teflon Sample Holder: Live Imaging



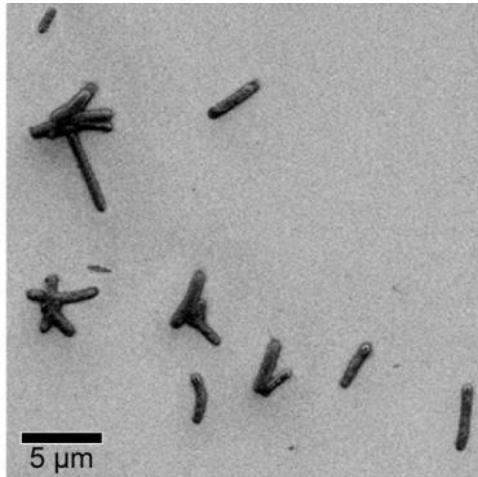
Cover Glass



CLSM Microscope (Zeiss LSM780-NLO )  
(100x & 63x Oil objective; NA. 1.4, Laser= 488 nm)

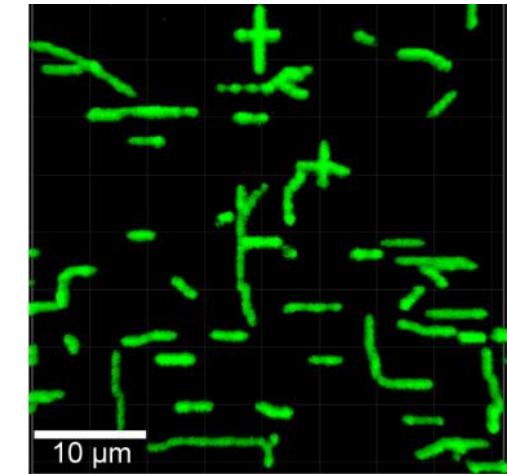
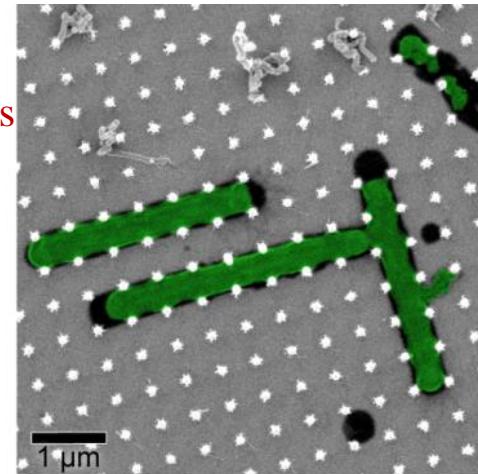
# Bacterial Adhesion on Nanowire Arrays

XF on InP Planar Substrate

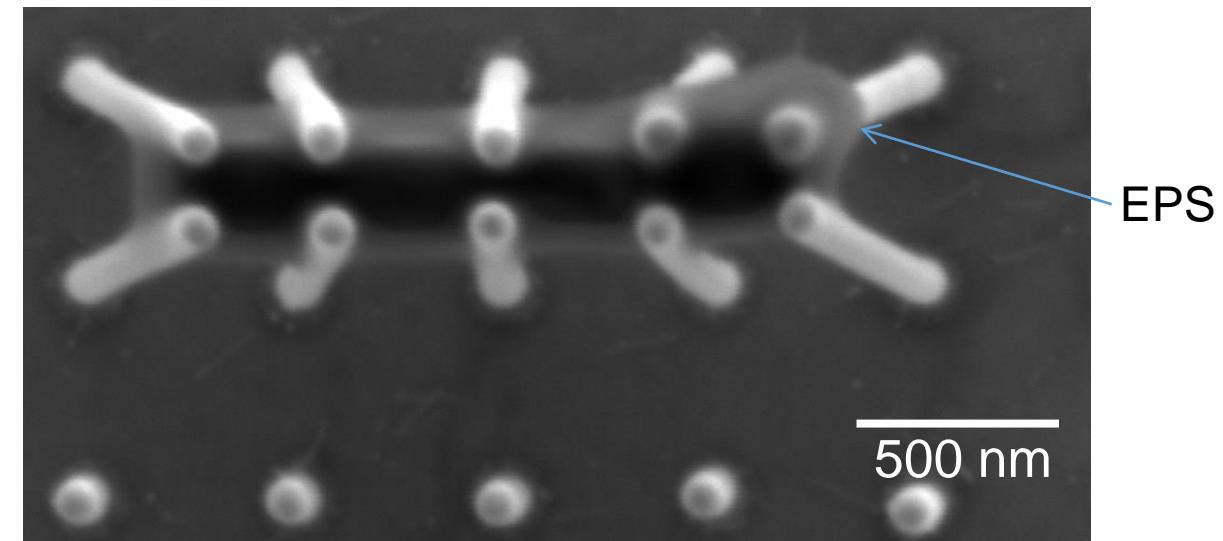
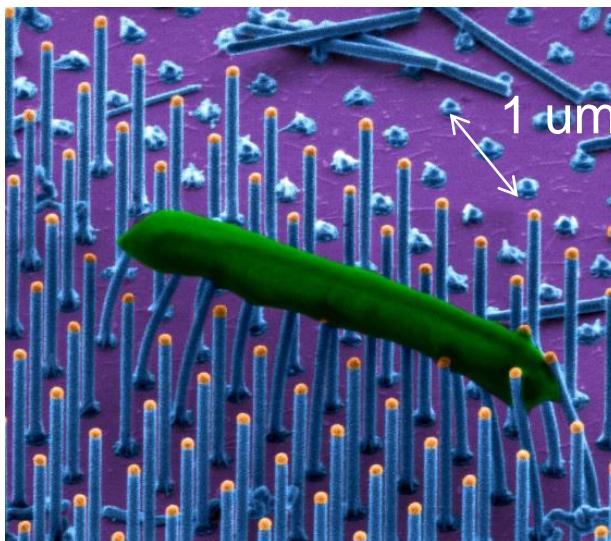


SEM images

XF Bacteria on InP Nanowire Arrays

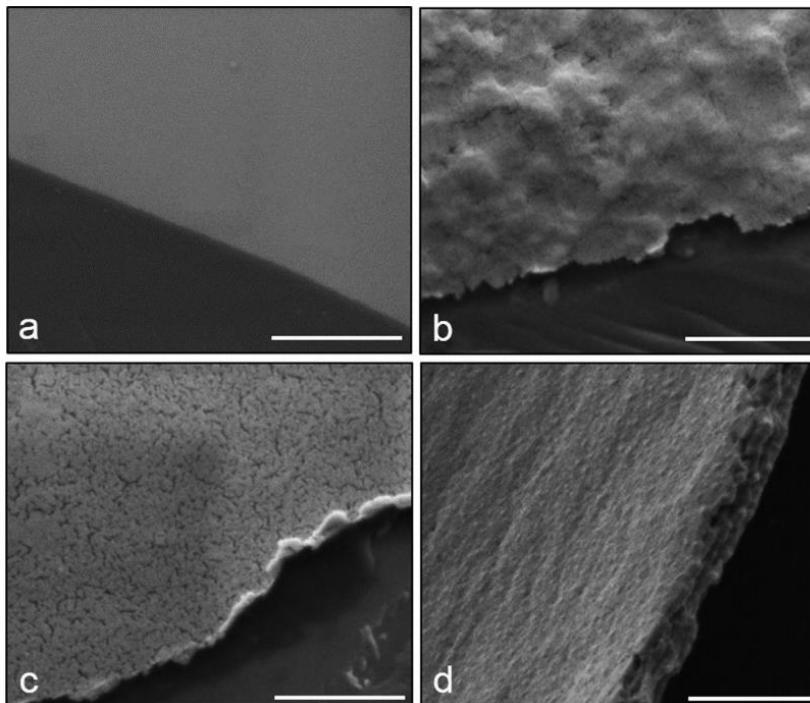


Transition from Motile to Sessile stage : (> 6h growth)

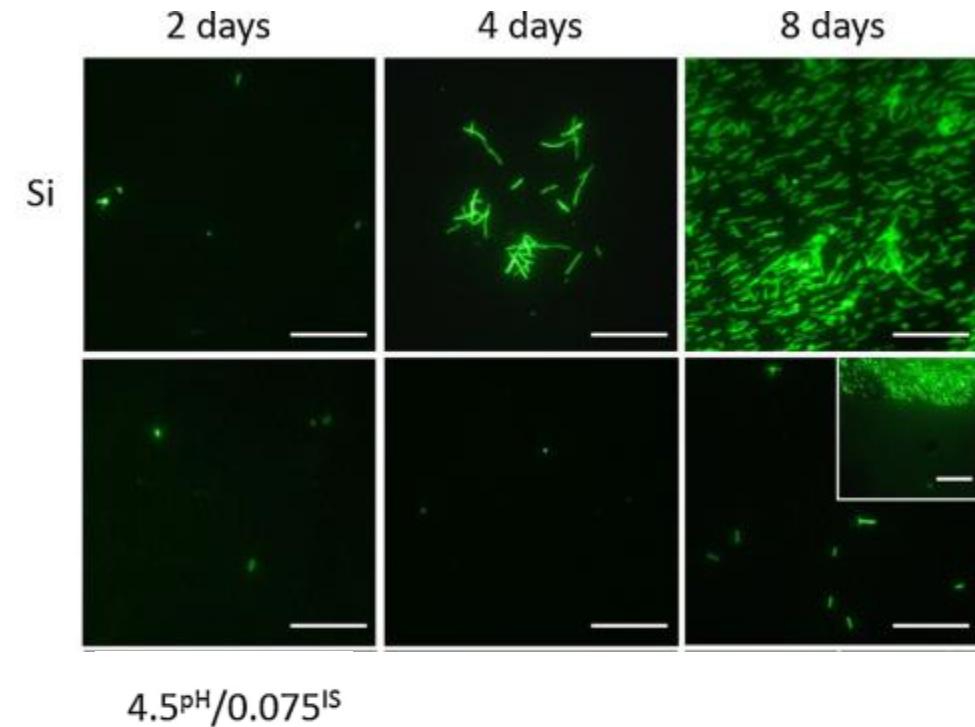


# Nanofilms of hyaluronan/chitosan assembled layer-by-layer: An antibacterial surface for *Xylella fastidiosa*

Jacobo Hernández-Montelongo<sup>a,\*</sup>, Vicente F. Nascimento<sup>b</sup>, Duber Murillo<sup>a</sup>,  
Thiago B. Taketa<sup>b</sup>, Prasana Sahoo<sup>a</sup>, Alessandra A. de Souza<sup>c</sup>, Marisa M. Beppu<sup>b</sup>,  
Monica A. Cotta<sup>a</sup>

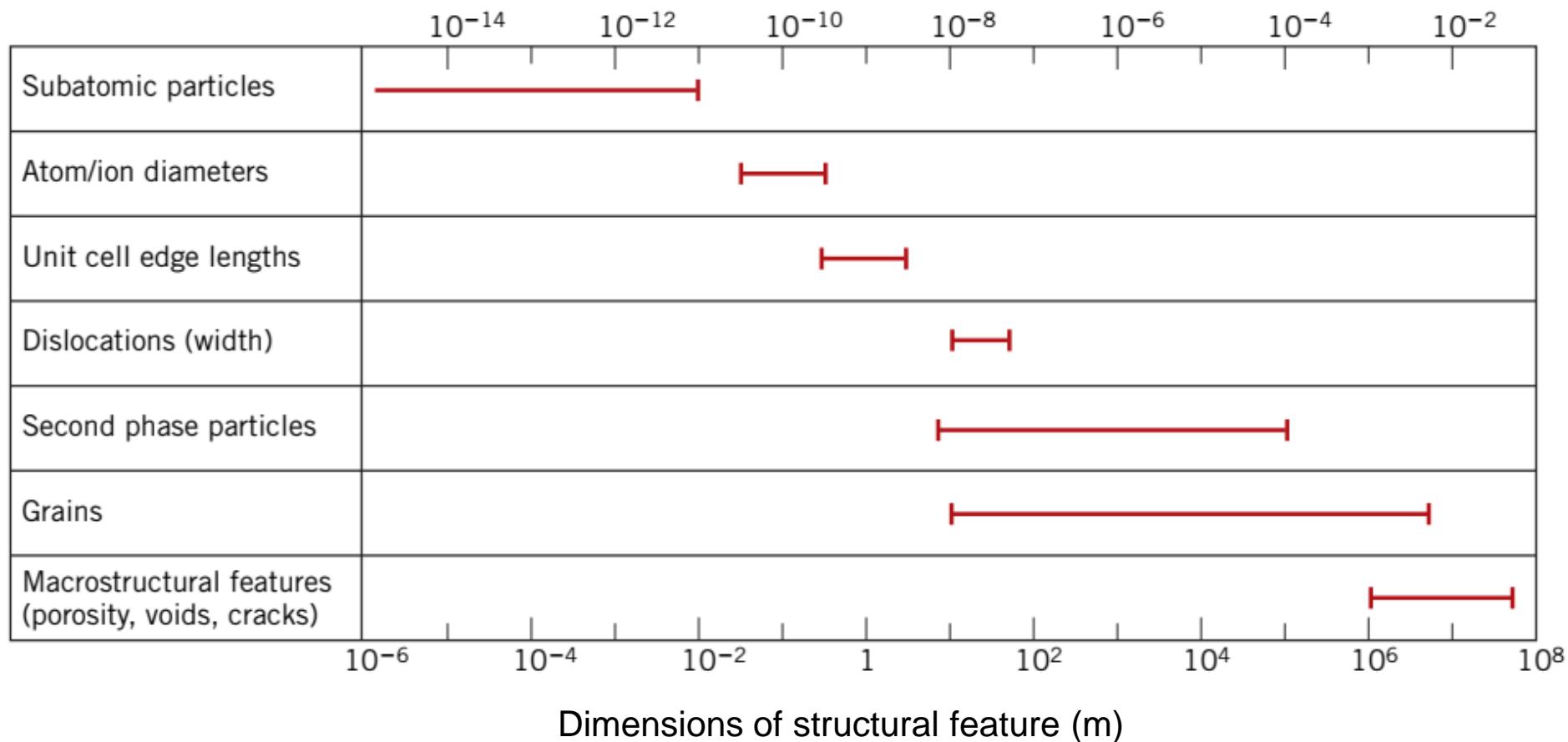


FESEM images of  
hyaluronan/chitosan  
assembled layer-by-layer

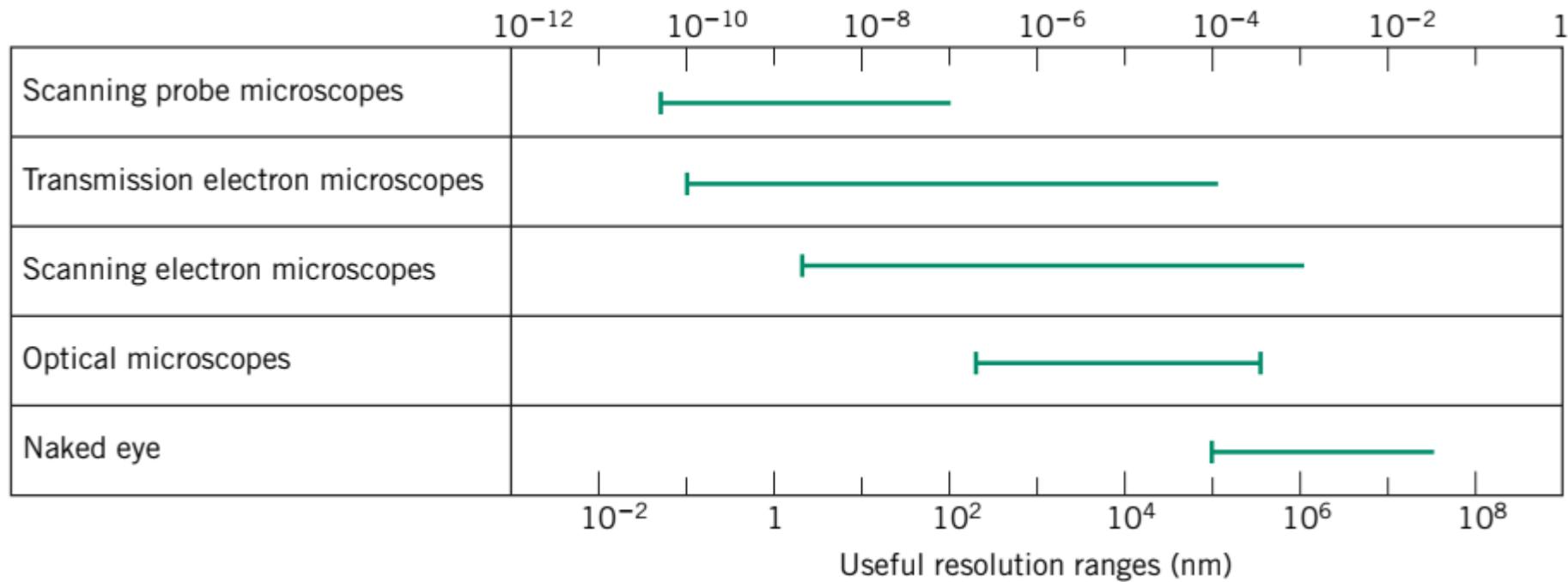


Widefield fluorescence microscopy images of *X. fastidiosa* grown on nanofilm and Si samples for 2, 4, and 8 days. The inset images show the exposed Si surface, with larger number of adhered cells, on the corresponding PEM sample.

# Dimensions of structural feature



# Useful resolution ranges





# Summary

- Two types of solid solutions and provide a brief written definition and/or schematic sketch of each.
- Describe both vacancy and self-interstitial crystalline defects.
- Calculate the equilibrium number of vacancies in a material at some specified temperature, given the relevant constants.
- Name and describe eight different ionic point defects that are found in ceramic compounds (including Schottky and Frenkel defects).
- Given the masses and atomic weights of two or more elements in a metal alloy, calculate the weight percent and atom percent for each element.
- For each of edge, screw, and mixed dislocations:
  - (a) describe and make a drawing of the dislocation,
  - (b) note the location of the dislocation line, and
  - (c) indicate the direction along which the dislocation line extends.
- Describe the atomic structure within the vicinity of
  - (a) a grain boundary and (b) a twin boundary
- Different characterization tools for analyzing , imaging and quantitatively evaluating different types of materials; Optical microscope, Electron microscope (SEM, TEM, STM) and Scanning probe microscope



# Core-Shell $\text{Ga}_2\text{O}_3$ @ GaN Belts

Interface study by

Focused Ion Beam (FIB) cross-sectioning

P. Sahoo et al. Journal of Material Science, 47 (2012) 3447.

P. Sahoo et al. Int. J. Hydrogen Energy 2012

