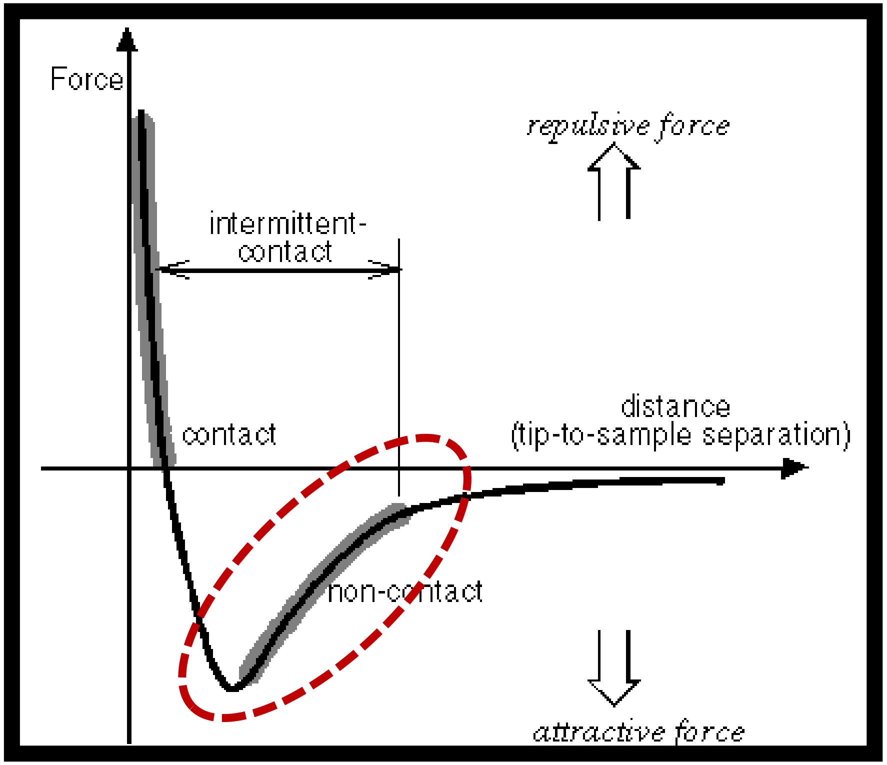
上次课程知识点回顾

- 紫外光电子能谱
- 俄歇电子能谱
- 电子能谱仪构造
  - 激发源（X射线源、紫外光源、电子枪）
  - 单色器原理（石英晶体、铝箔）
  - 电子能量分析器
  - 真空系统（增大自由程、减缓气体分子吸附）
- 扫描隧道显微镜（STM）
  - 研发历史、工作原理
  - 工作模式（恒流模式、恒高模式）
  - 仪器装置（振动隔绝、机械传感、电子控制、探针、计算机）
  - 用途（原子级空间分辨率表面观测、表面化学反应研究、原子级纳米结构加工）
- 原子力显微镜
  - Motivation
  - 工作原理（范德瓦尔斯力、胡克定律、激光放大）
  - 操作模式（接触模式-排斥力、非接触模式-吸引力）

Non-Contact Mode

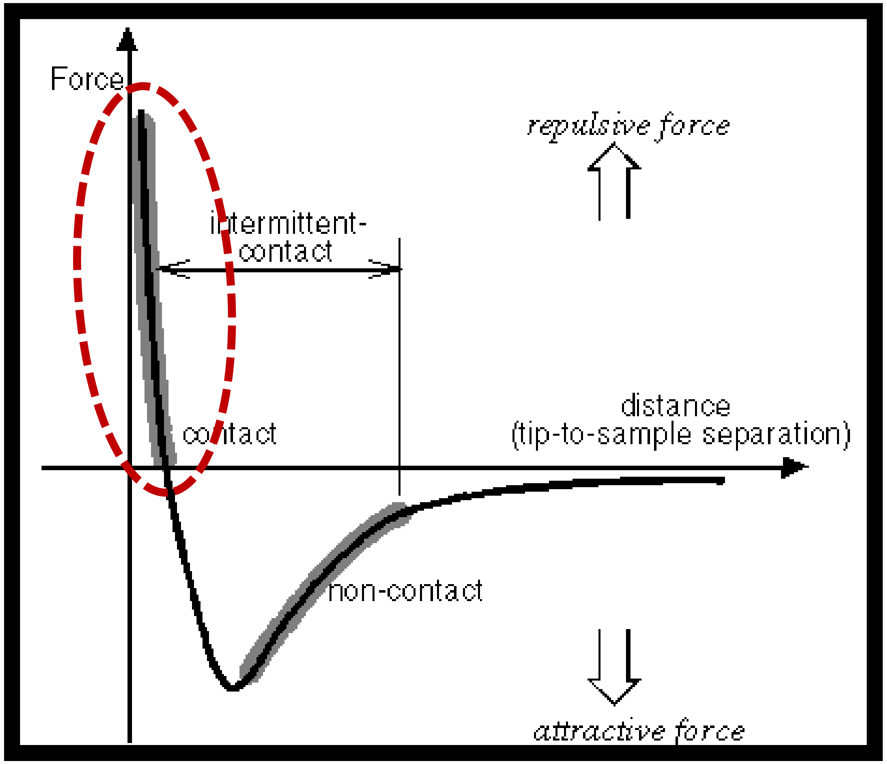
- **Uses attractive forces to interact surface with tip**
- **Operates within the van der Waal radii of the atoms**
- **Oscillates cantilever near its resonant frequency (~200 kHz) to improve sensitivity**
- **Advantages over contact:**
    - **no lateral forces**
    - **non-destructive/no contamination to sample, etc.**



van der Waals force curve

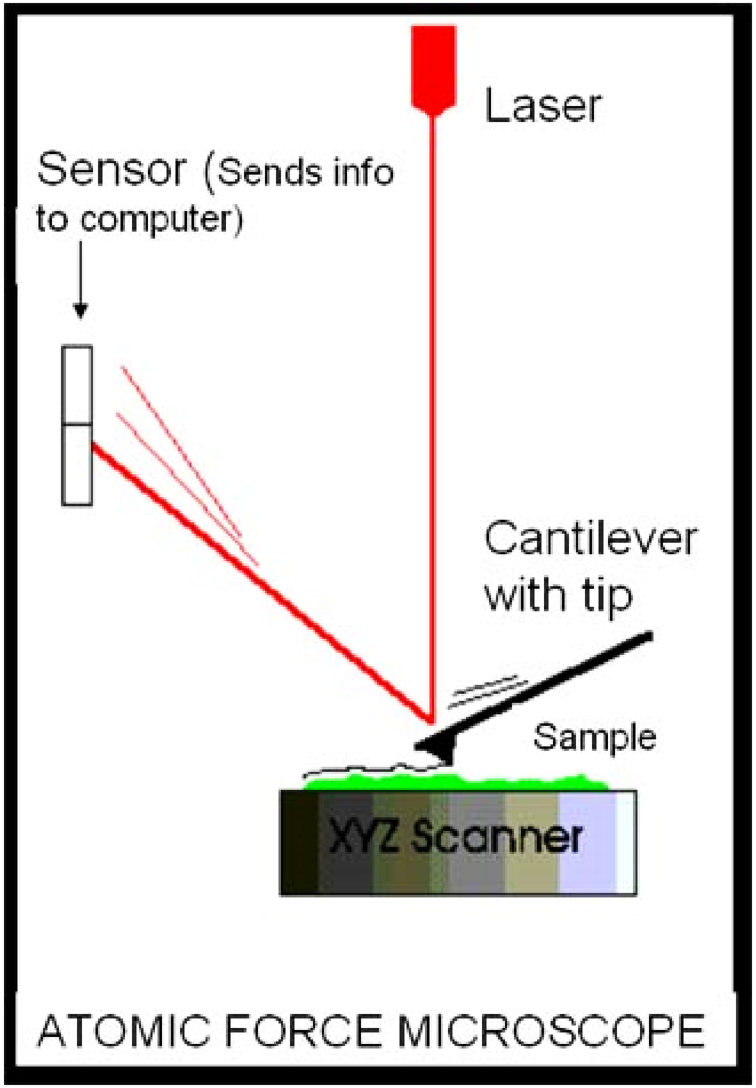
Contact Mode

- Contact mode operates in the repulsive regime of the van der Waals curve
- Tip attached to cantilever with low spring constant (lower than effective spring constant binding the atoms of the sample together).
- In ambient conditions there is also a capillary force exerted by the thin water layer present (2-50 nm thick).



van der Waals force curve

Force Measurement



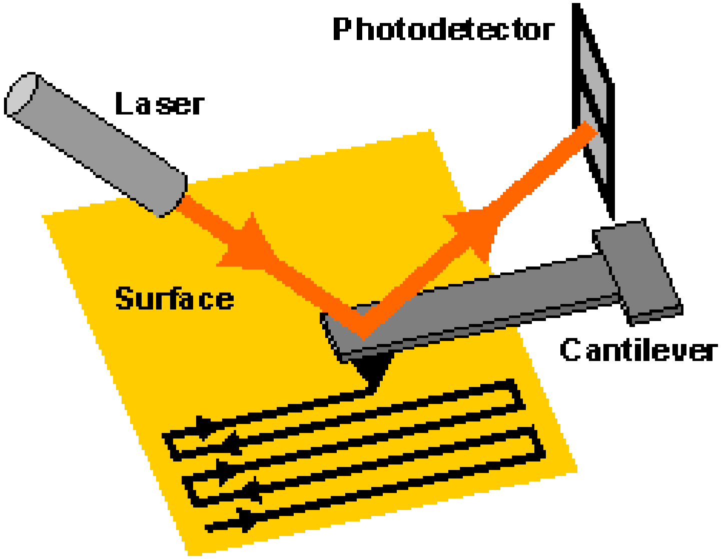
- **The cantilever is designed with a very low spring constant (easy to bend) so it is very sensitive to force.**
- **The laser is focused to reflect off the cantilever and onto the sensor**
- **The position of the beam in the sensor measures the deflection of the cantilever, and in turn the force between the tip and the sample.**

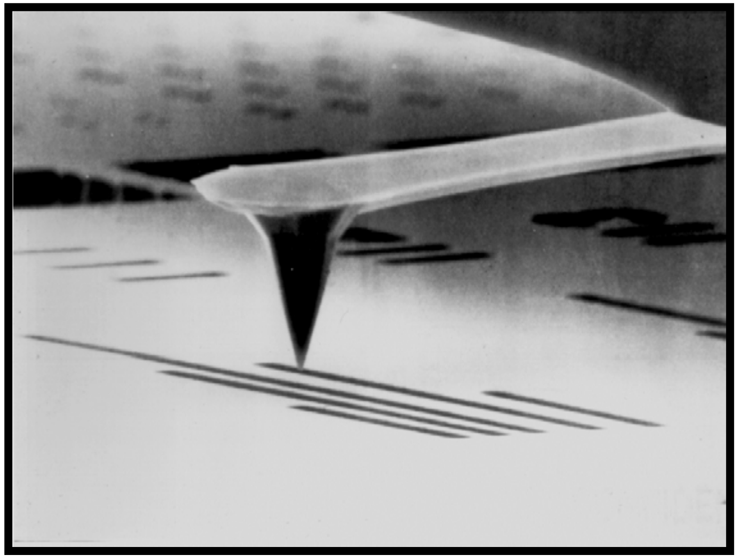
Force Measurement

- 针尖与样品之间的作用力与距离有强烈的依赖关系。一束激光经微悬臂背面反射到光电检测器，可精确测量微悬臂的微小变形。

- 如小于0.01nm的变形，用激光束将之反射到光电检测器后就变成了3～10nm激光点位移，测量精确度比较高，当激光的波长为670nm时极限的分辨率可以达到0.003nm。

Raster the Tip: Generating an Image



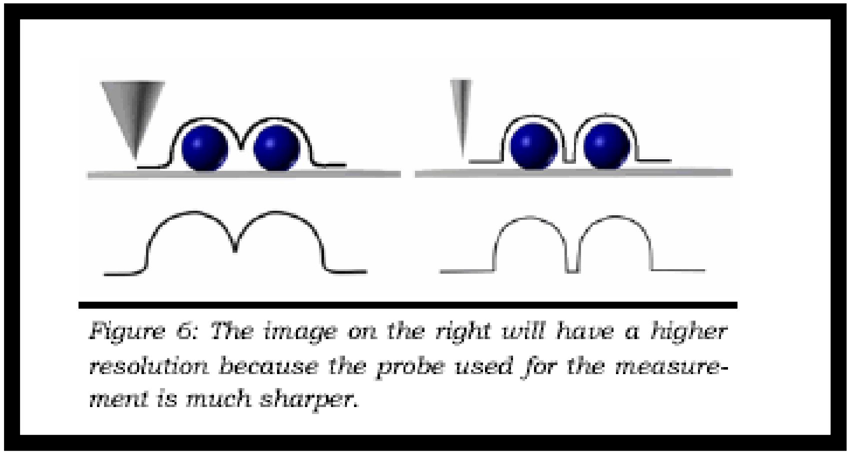


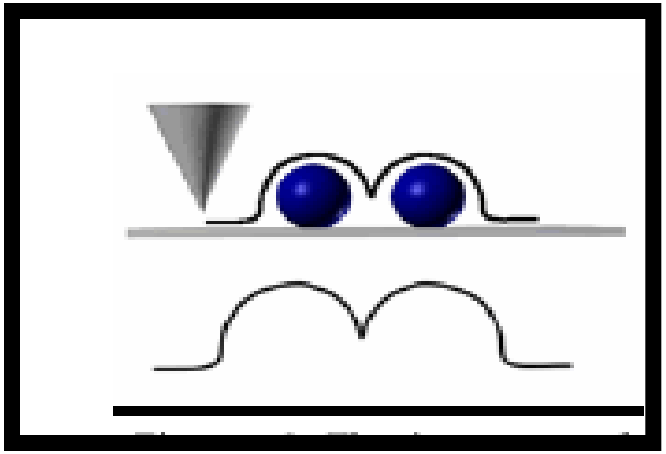
Raster Motion

- The tip passes back and forth in a straight line across the sample (think old typewriter or CRT)
- In the typical imaging mode, the tip-sample force is held constant by adjusting the vertical position of the tip (feedback).
- A topographic image is built up by the computer by recording the vertical position as the tip is rastered across the sample.

Scanning the Sample

- Tip brought within nanometers of the sample (van der Waals)
- Radius of tip limits the accuracy of analysis/ resolution





工作模式

检测方式:

恒力模式
恒高模式

- **恒力模式**：通过反馈系统使探针、样品表面作用力保持恒定，当探针在xy平面内扫描时，探针的z向运动就可反映样品表面形貌及其它表面结构，这种检测方式为恒力模式
- **恒高模式**：在xy平面内扫描时，不使用反馈回路，保持针尖绝对高度恒定，直接检测微悬臂Z方向的变量来成像。这种检测方式为恒高模式。**对于表面起伏较大的样品不适合**

微悬臂形变的检测方法

- 我们讲的测量微悬臂形变的检测方法为**光束偏转法**
- 除光束偏转法外还有其他微悬臂形变的检测方法：

①隧道电流检测法

②电容检测法

③光束干涉法

④压敏电阻检测法

具体操作模式

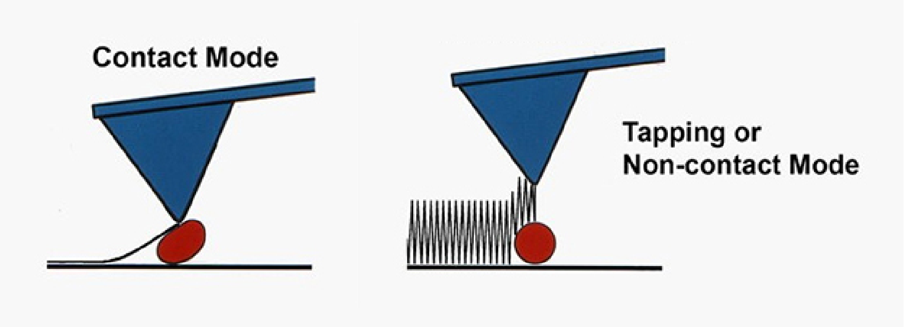
- 由于针尖与样品之间的作用力为**微悬臂的力常数和形变量的乘积**，所以上述所有方法都不应影响微悬臂的力常数。
- 对形变量的检测须达到纳米级以上精度。
- 由于光束偏转法比较简单，而且技术上容易实现，所以目前AFM仪器中应用最为普遍。

AFM的操作模式，主要有三种：

①接触模式

②非接触模式

③轻敲模式



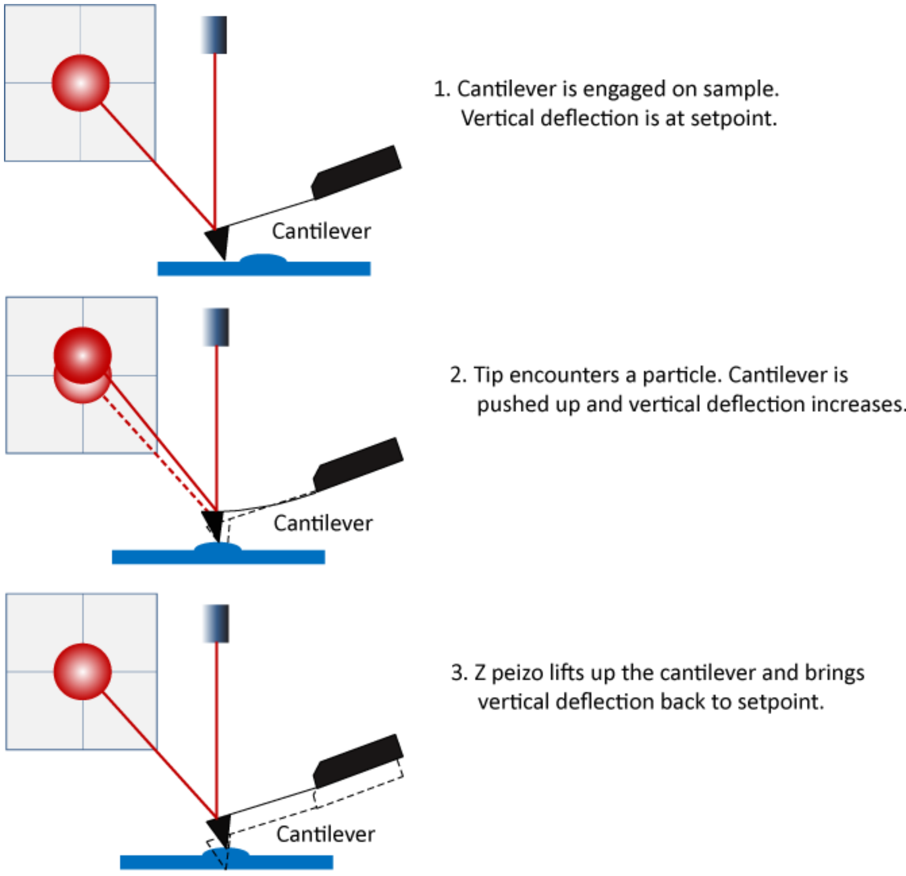
接触模式

①接触模式中，针尖始终和样品接触，以恒高或恒力的模式进行扫描。扫描过程中，针尖在样品表面滑动。

The force is calculated from
Hooker’s Law: F = -kx

F: Force
k: Spring constant
x: Deflection of cantilever

Operation can take place in ambient and liquid environments.



Feedback Loop Maintains Constant Cantilever Deflection

Advantages and Disadvantages

Advantages

• Compared with tapping mode under same experimental conditions, the contact mode has higher scan speeds (throughput)

• Rough samples with extreme changes in vertical topography can sometimes be scanned more easily

• Some special applications, such as lithography, SCM, scratch, must be done under contact mode

• Compared with tapping mode, contact mode is a “static” mode, no need to deal with dynamics of cantilever (no tuning needed), feedback control is easier

Disadvantages

• Lateral (shear) forces can distort features in the image

• Forces normal to the tip-sample interaction can be high in air due to capillary forces from the adsorbed fluid layer on the sample surface

• Combination of lateral forces and high normal forces can result in reduced spatial resolution and may damage soft samples (i.e., biological samples, polymers, silicon) due to scraping between the tip and sample

非接触模式

②非接触模式：是指探针离样品表面上面并有一定距离，始终不与样品接触，这时微悬臂压电陶瓷器件产生高频振动，频率接近其固有振动，针尖与样品间的相互作用力对其距离的变化将会直接影响到微悬臂的振动频率及振幅，用光学方法测量振幅的变化就可得知探针与样品表面作用力的变化，即可测得样品形貌等。

- 但由于针尖和样品之间的距离较长，分辨率较接触式低，而且操作也相对较难，所以非接触模式目前基础上未被采用。

轻敲模式

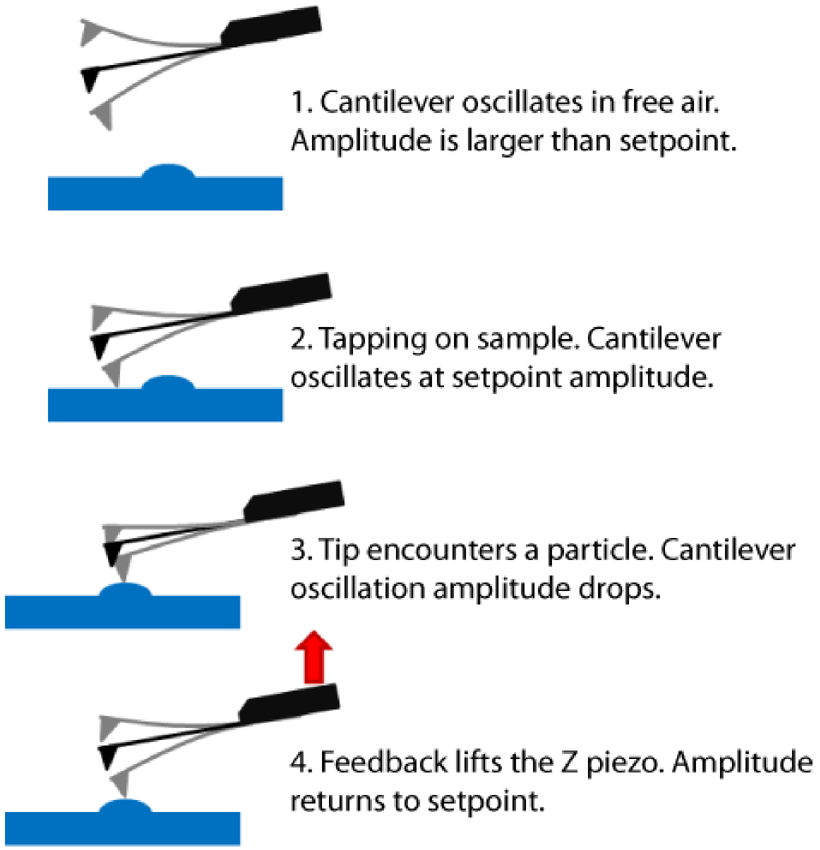
- ③轻敲模式中，探针在样品表面上以接近微悬臂固有频率振动，振荡的针尖交替地与样品表面接触和抬高，这种交替通常每秒钟$5\times10^4\sim5\times10^5$次。
- 针尖与样品接触可以提高分辨率，针尖抬高离开样品时，可避免在表面形成拖刮。这一模式也是利用压电陶瓷通过微悬臂振动实现的。

Tapping Mode AFM

The vertical position of the scanner at each (x,y) data point in order to maintain a constant “setpoint” amplitude stored by the computer to form the topographic image of the sample surface.

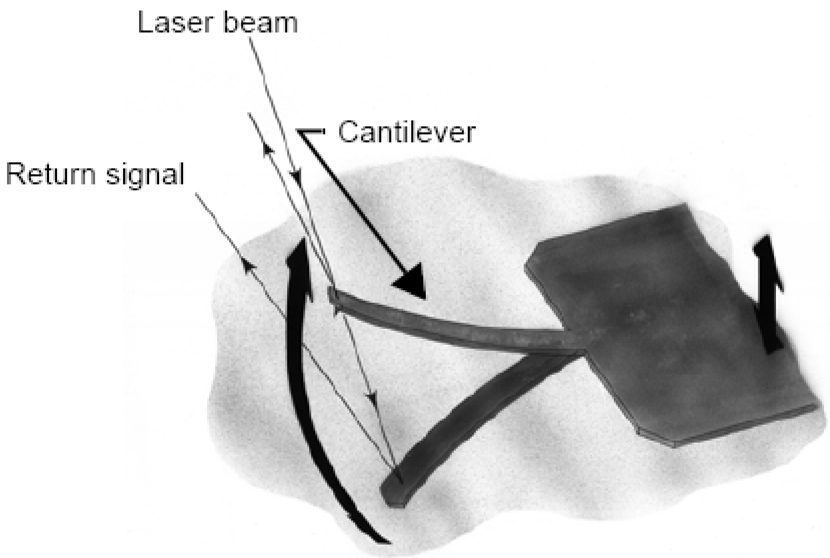
By maintaining a constant **oscillation amplitude**, a constant tip-sample interaction is maintained during imaging.

Operation can take place in ambient and liquid environments. In liquid, the oscillation do not need to be at the cantilever resonance.

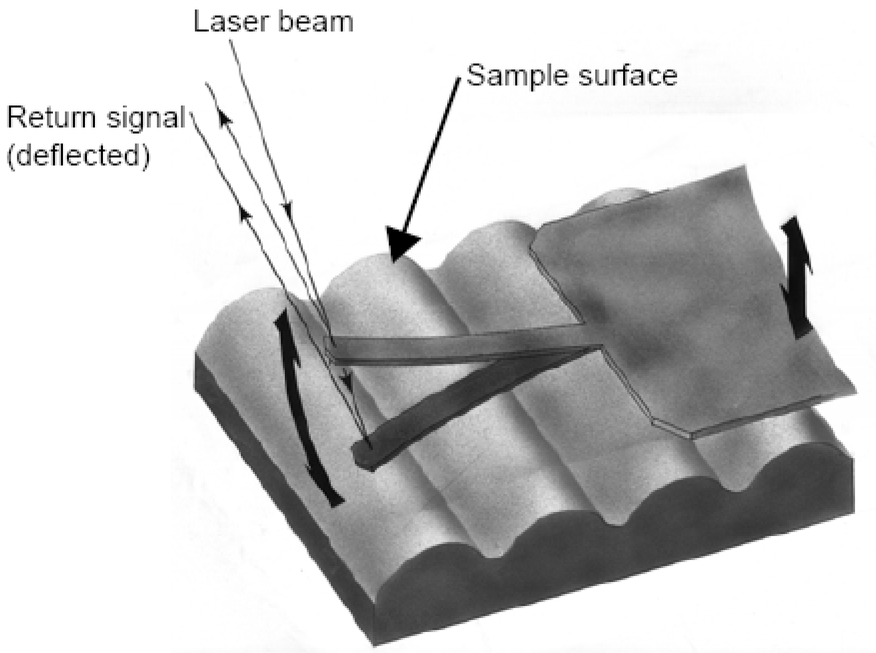


Feedback loop maintains a constant oscillation amplitude

Tapping Mode AFM



Tapping Cantilever in Free Air



Tapping cantilever on sample surface. Note deflection of cantilever and return signal.

Advantages and Disadvantages

Advantages

• Compared with contact mode, tapping mode has lower forces and less damage to soft samples imaged in air

• Compared with contact mode in air, tapping mode can achieve higher lateral resolution on most samples (1nm to 5nm)

• Lateral forces are virtually eliminated, so there is no scratching

Disadvantages

• Slightly slower scan speed than contact mode AFM

• Need to deal with dynamics of cantilever, feedback loop is harder to adjust

• Cannot be easily operated in vacuum environment

• Fluid operation is difficult

• Tip-sample interaction force is not directly controlled (PeakForce)

仪器组成

原子力显微镜的装置

和STM一样，AFM也由：

振动隔绝系统

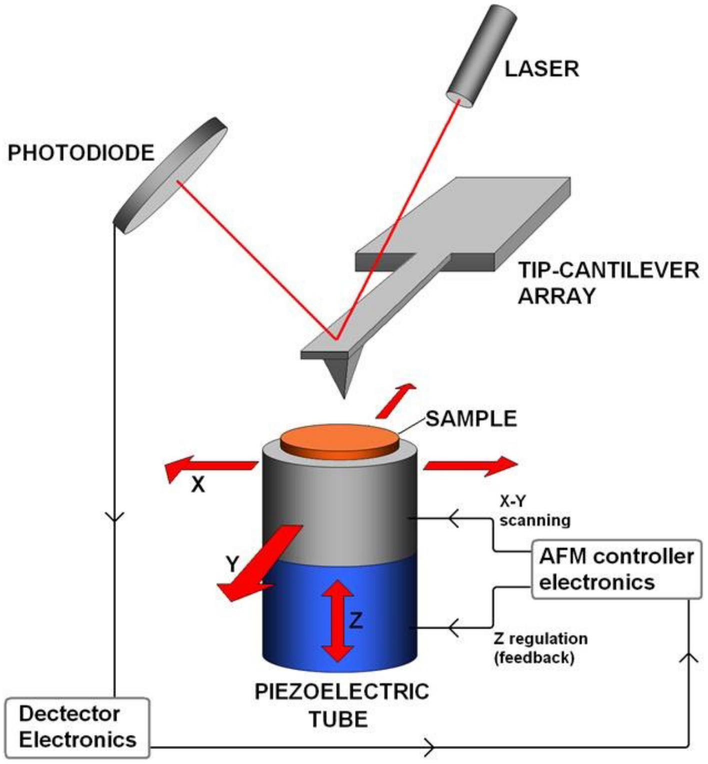
机械系统

针尖系统

电子系统

计算机系统

几个大的部分组成。



装置

- 其关键部分仍是针尖系统。

　　这里，针尖感受的不是隧道电流，而是原子间的相互作用力，因此它由带针尖的力敏感元件和力敏感元件运动检测系统构成，其反馈电路也用于临控力敏感元件的运动。

- AFM对于隔绝振动、样品逼近、扫描和反馈控制、计算机图像存储和处理以及显示系统等方面，可利用STM技术稍加改进。
- 但微悬臂及其针尖是AFM所特有的，并且是技术成败的关键之处，所以我们主要介绍AFM力传感器上的微悬臂及其针尖

微悬臂

AFM微悬臂要求：

①**相对低的力常数**，即受到很小的力就能产生可检测到的位移。（K = F/ΔZ）

②为了得到与STM相当的数据采集速度和成像带宽，要求微悬臂的**共振频率应大于10kHz**

③对微悬臂横向刚性的要求是减小横向力的影响，以防止图像失真，故通常将**微悬臂制成V字形，以提高横向刚性**。

④如果采用隧道电流方式来检测微悬臂的位移。其背面必须要有金属电极。

若采用光束偏移法时，则要求微悬臂的背面有**尽可能平滑的反光面**。一般SiO_2，Si_3N_4表面。

微悬臂

综上所述，为了准确反映样品的形貌和尽可能提高仪器的刚性，力敏感元件要满足以下要求：

①低的力弹性常数

②高的力学共振频率

③高的横向刚性

④短的微悬臂长度

⑤传感器带有镜子或电极

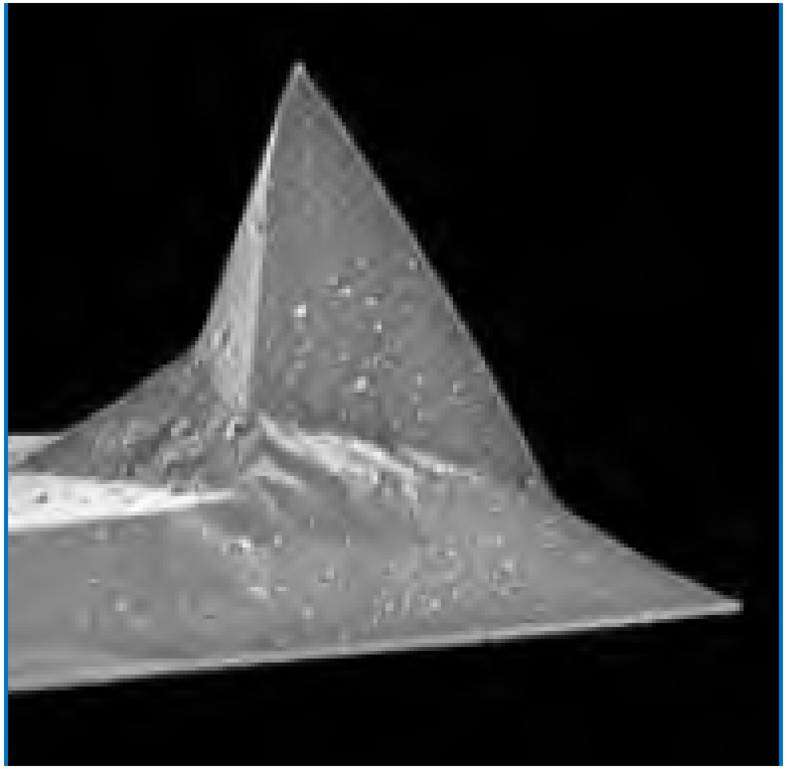
⑥带有一个尽可能尖的针尖

微悬臂

- 1987年，美国斯坦福大学制成了V型SiO_2微悬臂及针尖传感器，这种传感器没有外加针尖，而是利用微悬臂的V字形尖端作为针尖。

微悬臂

- 1989年，美国斯坦福大学又研制成了尖端带有金字塔形针尖的V字形Si_3N_4微悬臂。

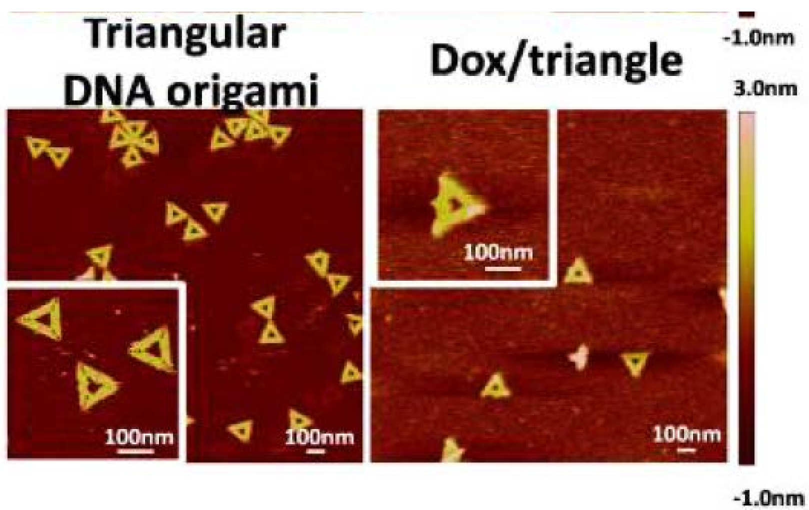


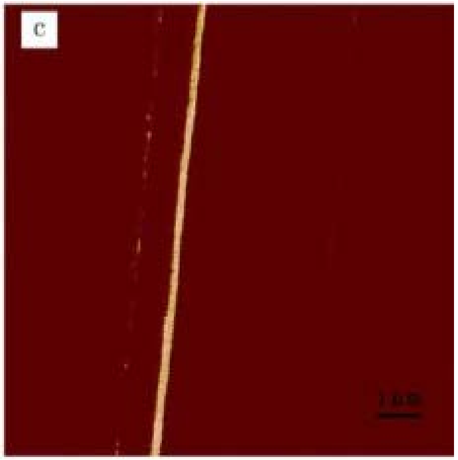
AFM的应用

①纳米材料的形貌测定

AFM不仅可用来直接表征导体、半导体的形貌，还可以直接用于绝缘体样品的研究。

- 人们已经获得了许多材料的原子级分辨图像。





AFM的应用

②纳米尺度的物性测量

对纳米尺度的物性研究有助于人们的进一步认识纳米世界的运动规律，运用这些性质来设计和制备下一代纳米器件。

AFM为研究这些局域现象提供了强有力的技术支持

例如：

利用AFM研究纳米机械性质，可测定表面微区摩擦性质、微区硬度、弹性模量等。

利用AFM可以测量材料的电学特性，人们可测量碳纳米管等电学性质、单分子的导电性等。

AFM的应用

③生物材料的研究

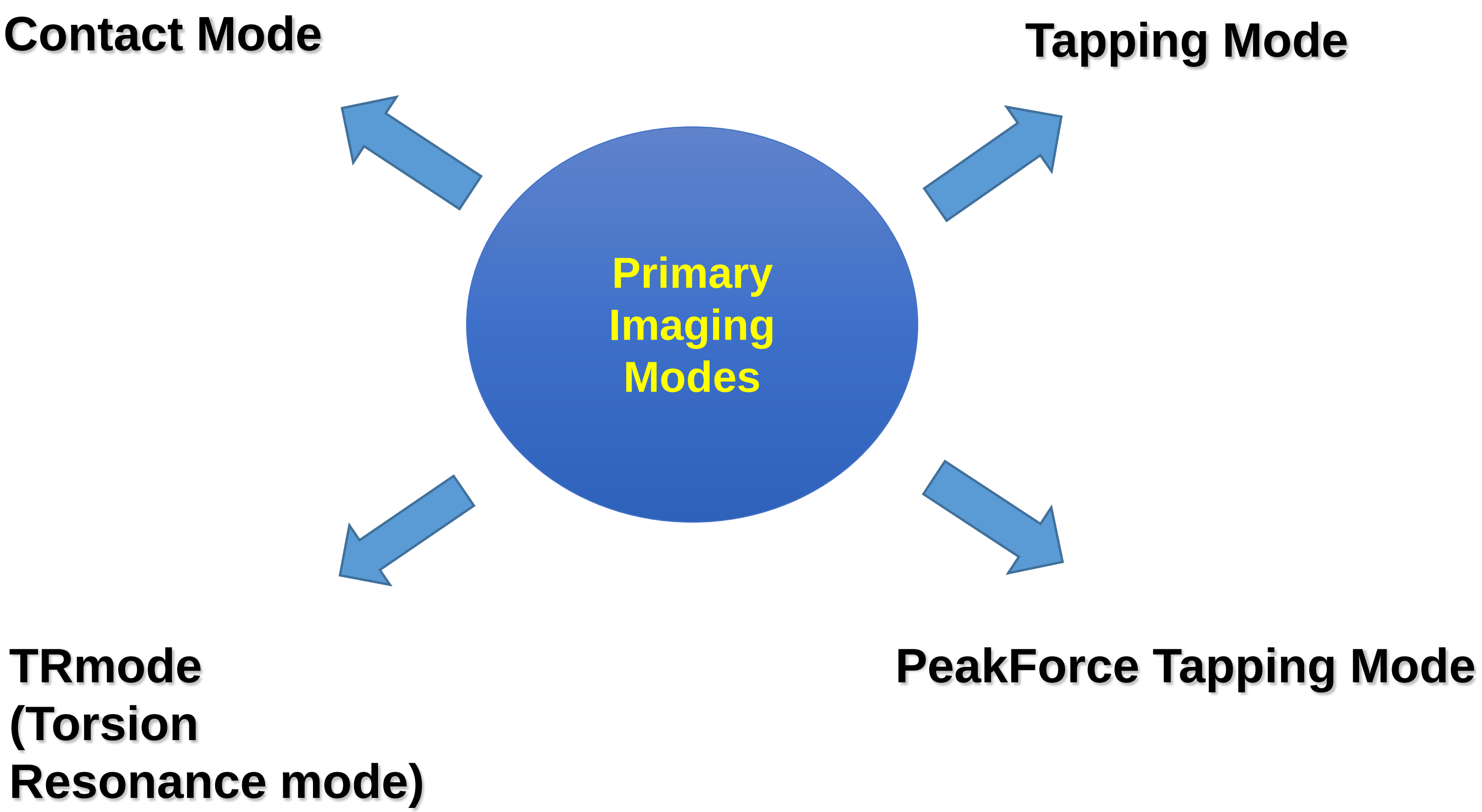
AFM不仅可以对生物分子进行高分辨**成像**，而且还可以对生物分子进行**操纵**

④纳米结构加工

利用AFM针尖与样品之间的相互作用力可以搬动样品表面的原子、分子，而且可利用此作用力改变样品的结构，从而对其性质进行调制

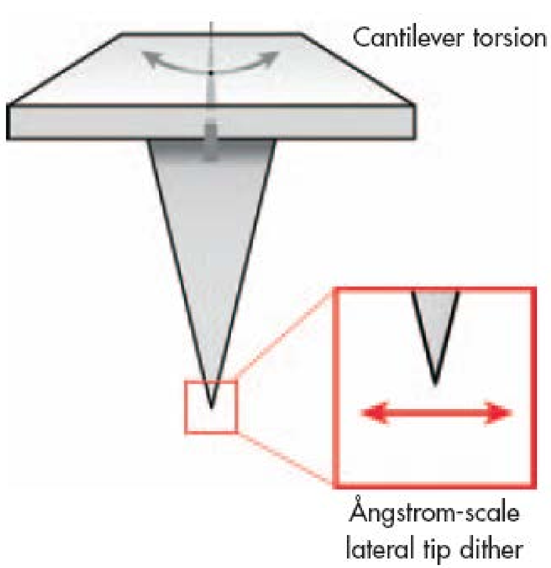
视频展示

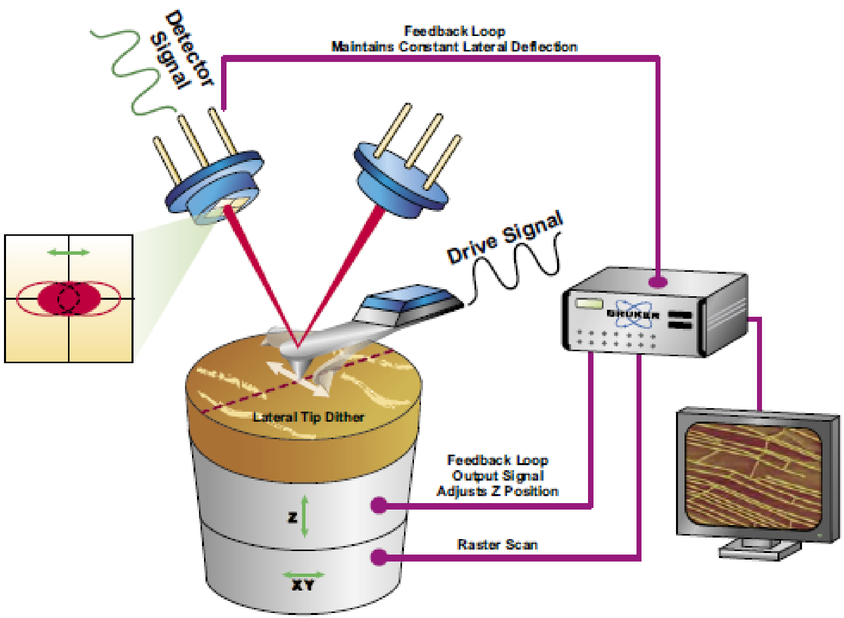
Primary Imaging Modes of AFM



TRmode AFM - torsional resonance mode

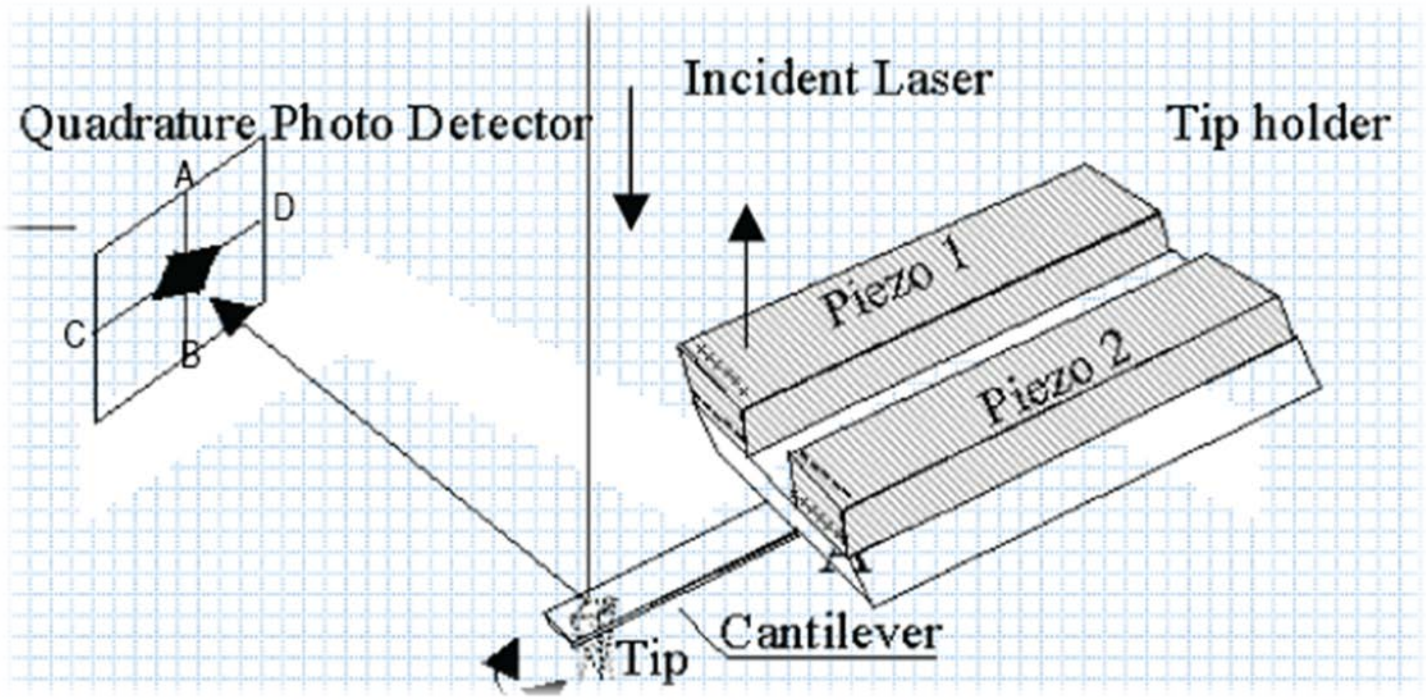
- TRmode is an exciting new imaging technique that measures tip-sample interactions through **torsional resonance** of the SPM cantilever.
- This new, unique imaging mode is complementary to Tapping Mode, allows for faster scanning, better tracking and is able to detect **longitudinal force gradients**.
- The optical leverage of TRmode is several times larger than that of Tapping Mode resulting in greater sensitivity which allows for Angstrom-scale dithering.
- Unlike TappingMode, TRmode operates with the probe tip in constant, close proximity to the sample surface.





Feedback loop maintains a constant oscillation TR amplitude

TRmode Probe Holder

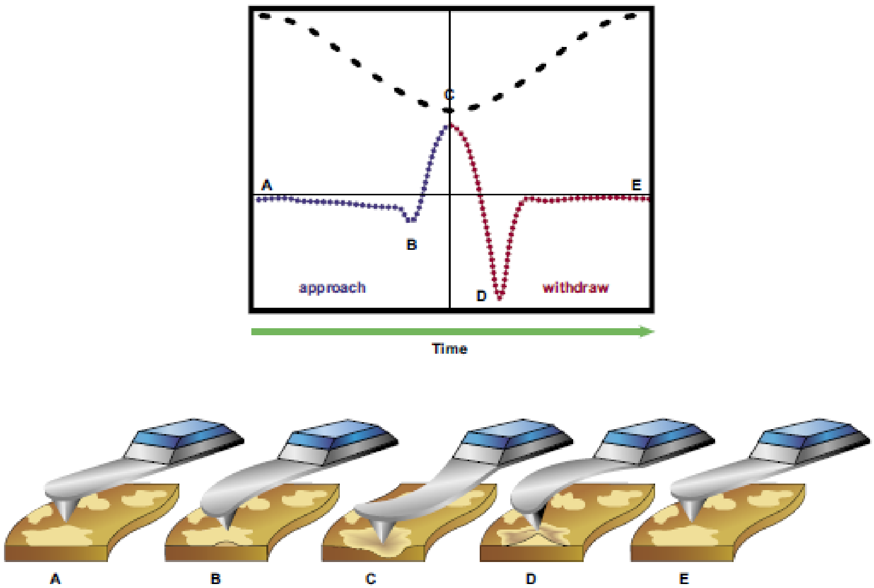


Torsional Resonance mode drive and detection

PeakForce Tapping AFM

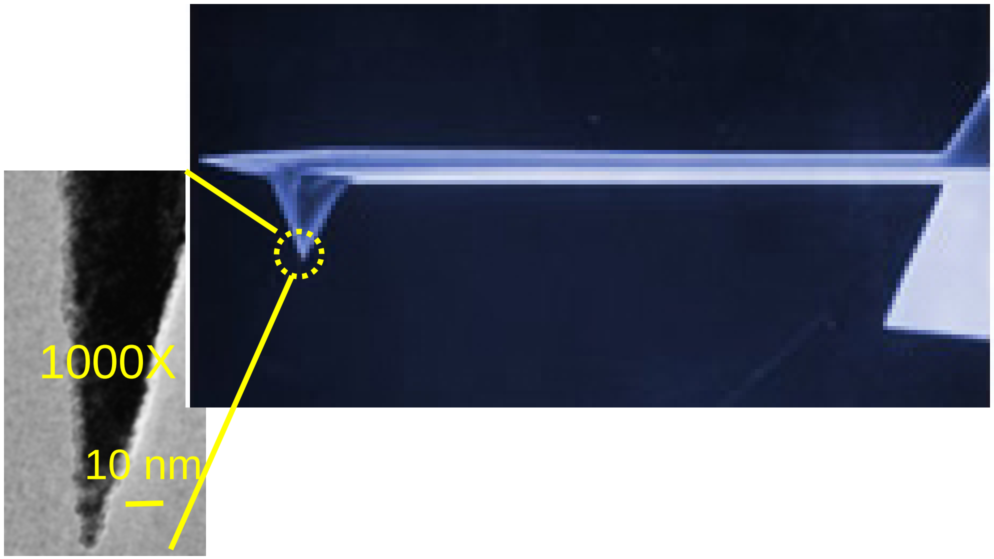
AFM limitations:

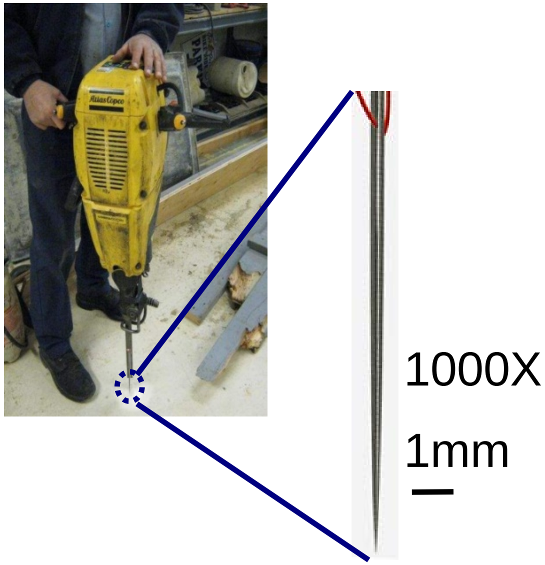
- AFM is too difficult to use. It takes a long time to become proficient at operating one, even for basic imaging.
- It can be very difficult to interpret AFM images because there is not enough information to distinguish or identify different materials.
- Most AFMs are more or less equivalent.



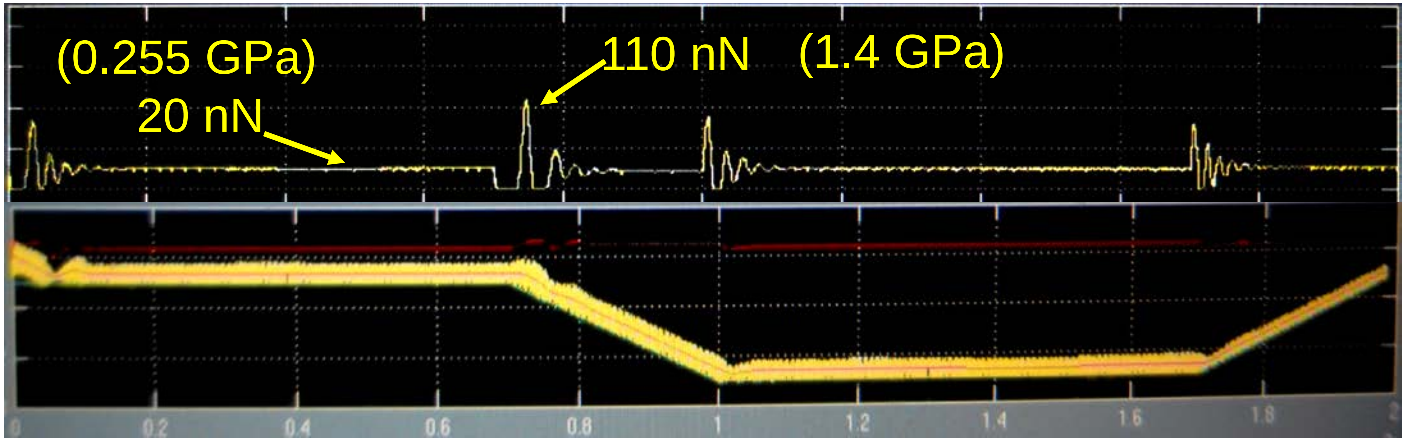
Feedback loop maintains a constant Peak Force

Challenge: High Resolution

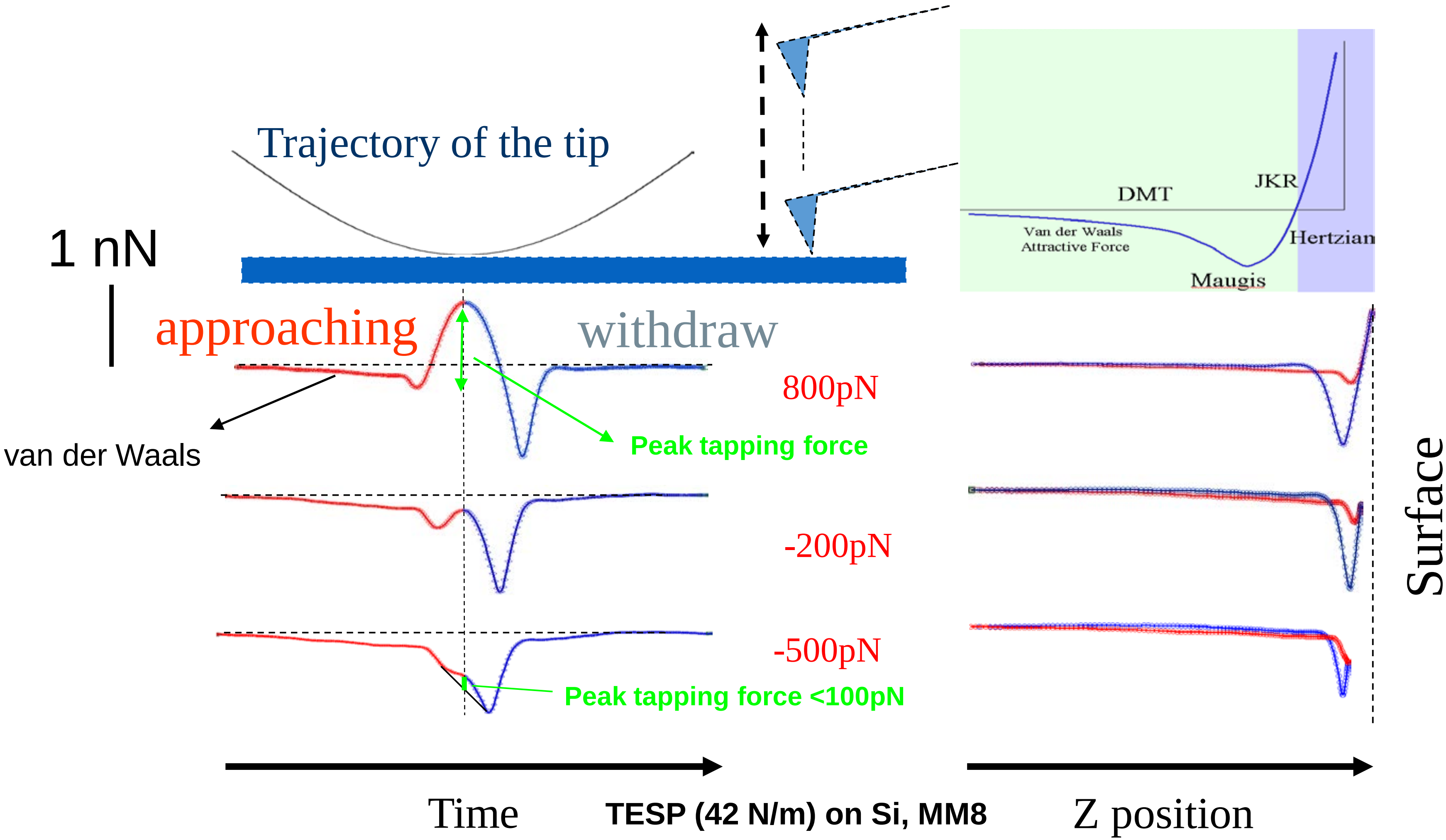




Tip end radius 5 nm,
40N/m Si Probe,
Asp/A0: 80%
A0: 40nm

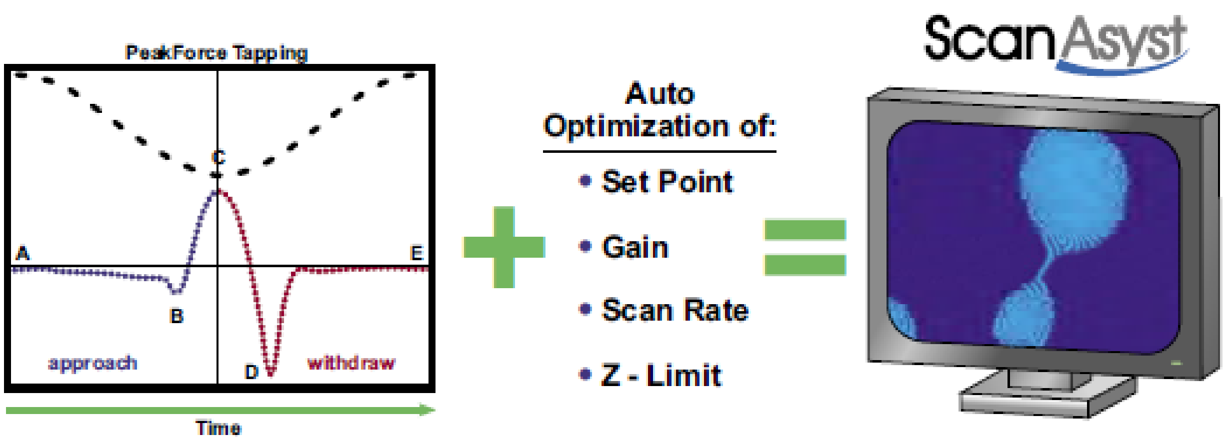


Peak Force Tapping Control

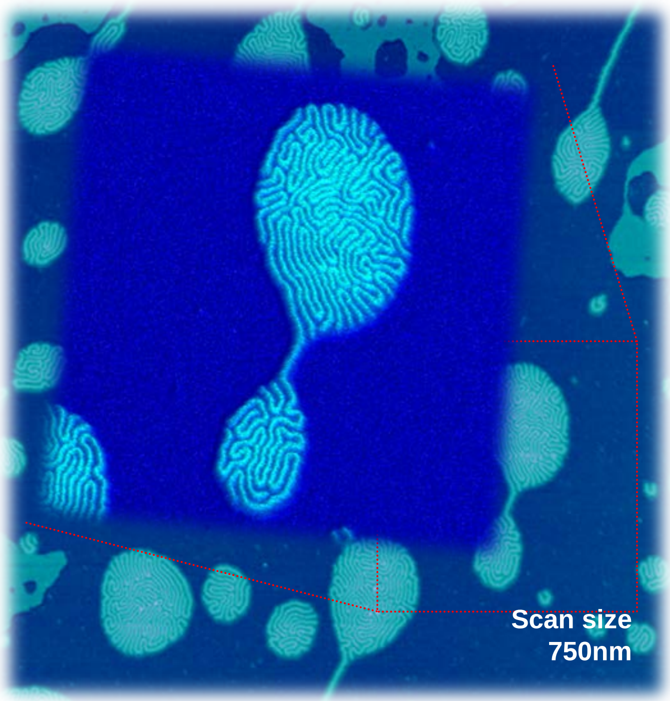


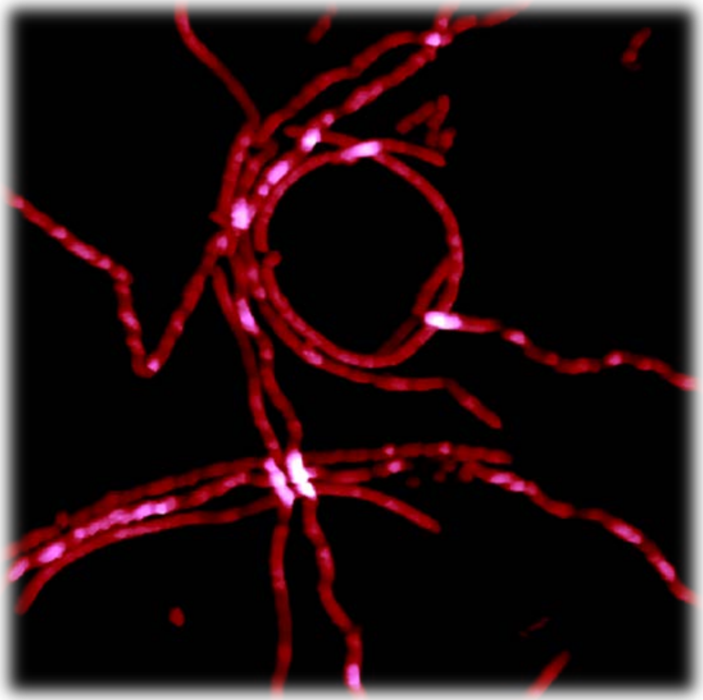
Peak Force Tapping Control

- **Automatic image optimization results in faster, more consistent results, regardless of user skill level**
- **Direct force control at ultra-low forces helps protect delicate samples and tips from damage**
- **Elimination of cantilever tuning, setpoint adjustment, and gain optimization makes fluid imaging simple**



Examples





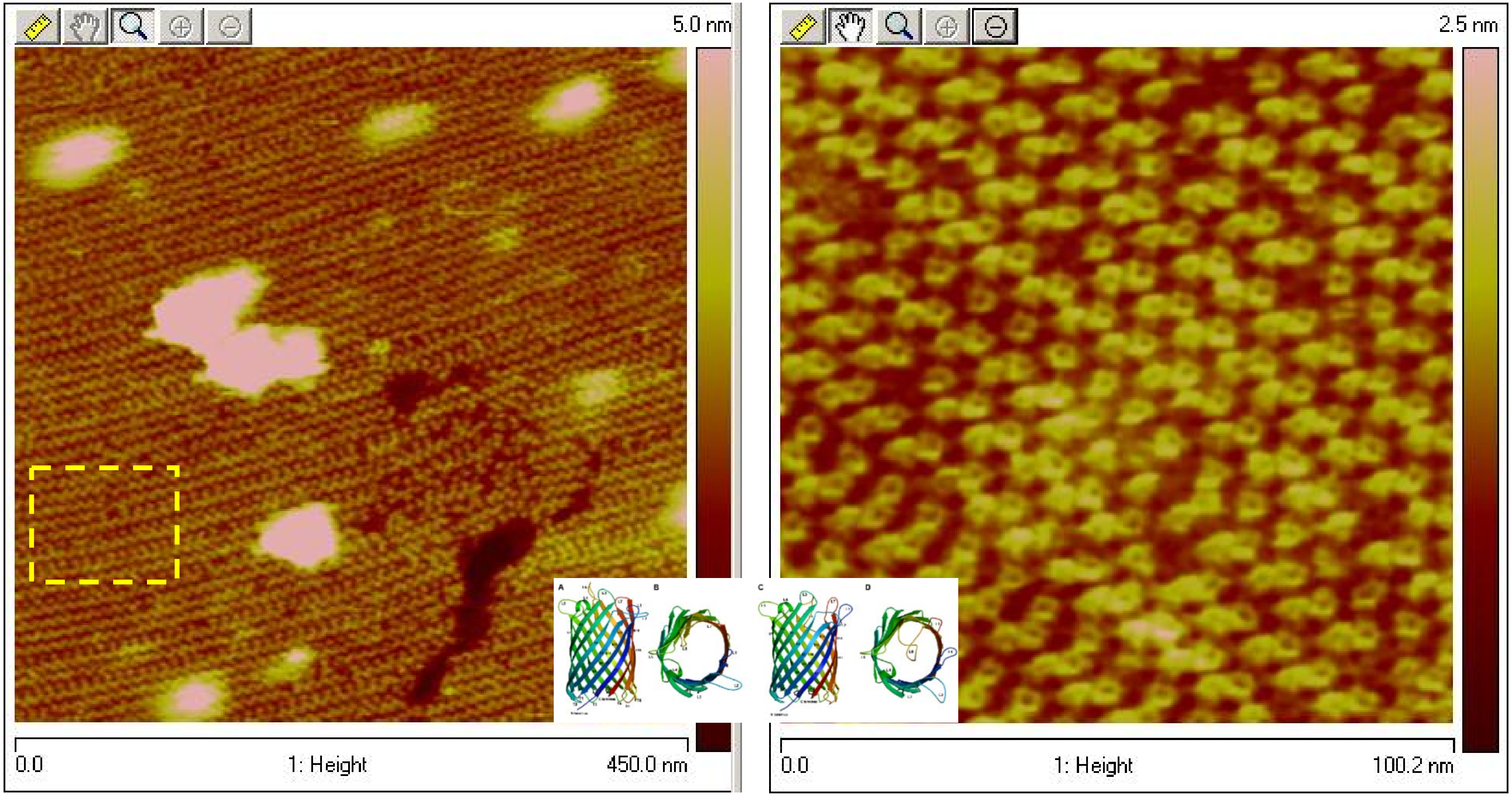
Polymer brush sample imaged on a MultiMode 8 using ScanAsyst. Scan size 2 µm.

Hyperphosphorylated tau filaments, also known as paired helical filaments (PHF-tau), imaged in fluid on a MultiMode 8 at a force of only 50 pN. Scan size 1.5 µm.

- Direct force control allows operation at very low forces (**<100 pN**), which results in higher resolution, because both sample and tip are protected from damage

- image in liquids
  - The imaging force can be precisely controlled at ultra-low setpoints, here just 50 pN

Membrane Protein Imaging in Fluid

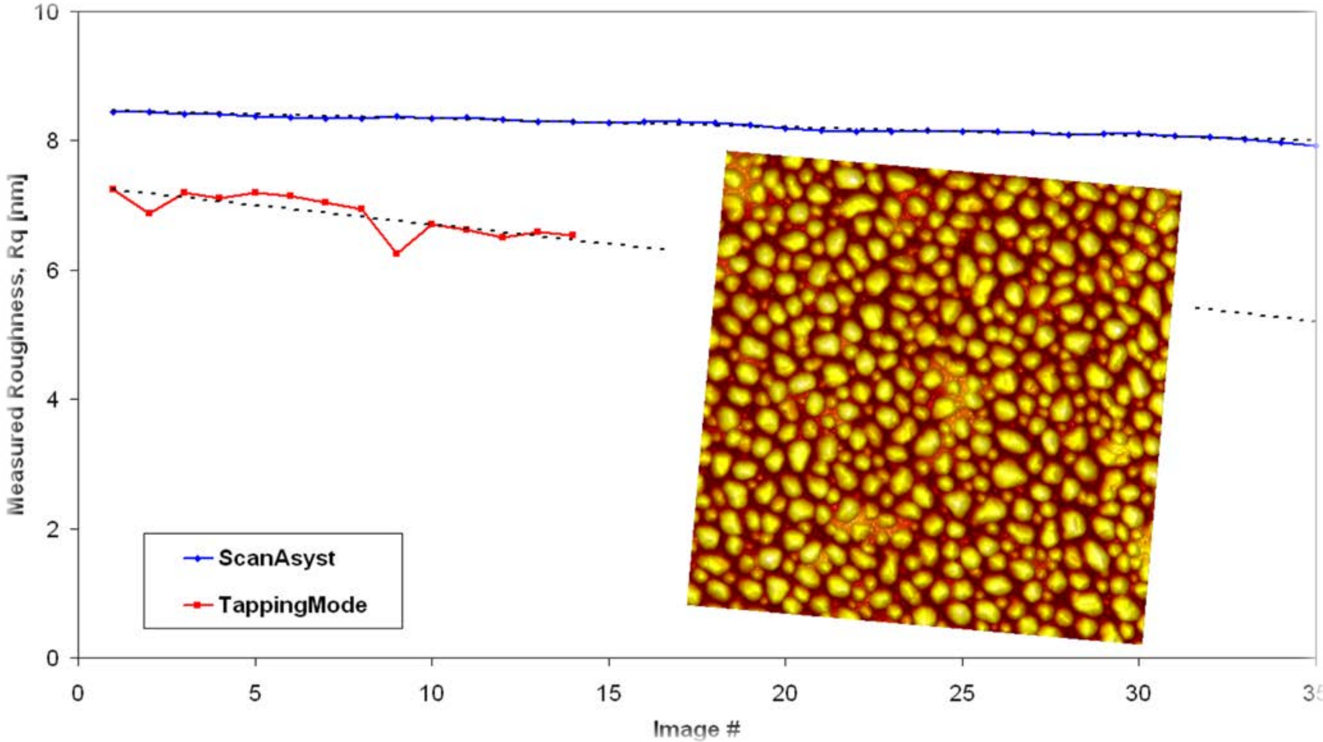


Fluid Imaging at 50 pN Peak Force

OmpG Membrane Pore

Advantage

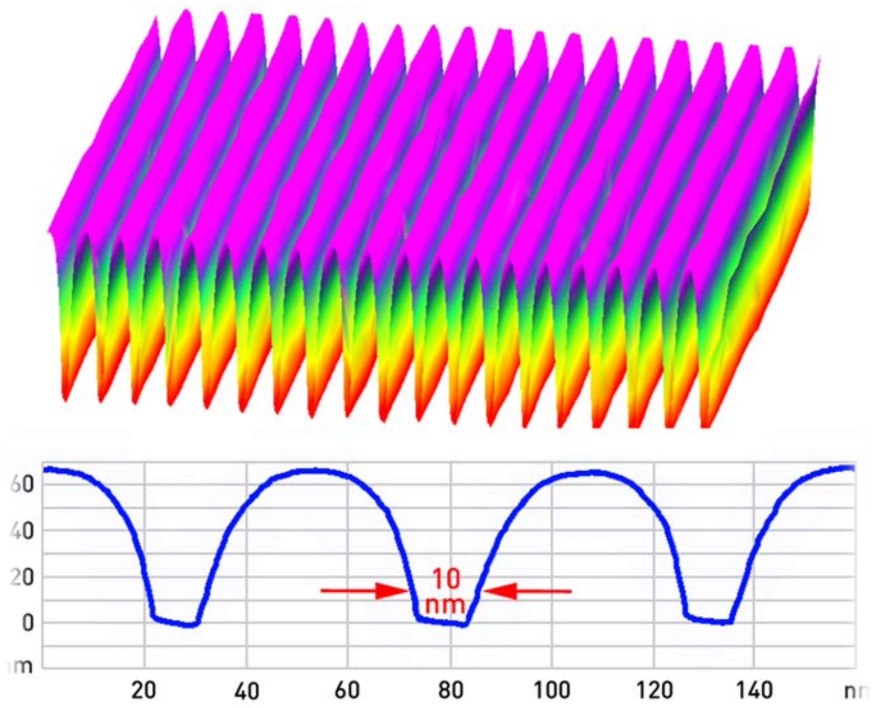
- Direct force control helps protect the tip from damage, even on very rough samples



Inset: Polysilicon imaged using ScanAsyst on a MultiMode 8 at 5 Hz. Scan size 1.5 µm.

Plot: The measured roughness is a sensitive measure of tip sharpness, with sharper probes yielding larger roughness values. Note that the PeakForce Tapping probe starts sharper and stays sharper much longer than the TappingMode probe.

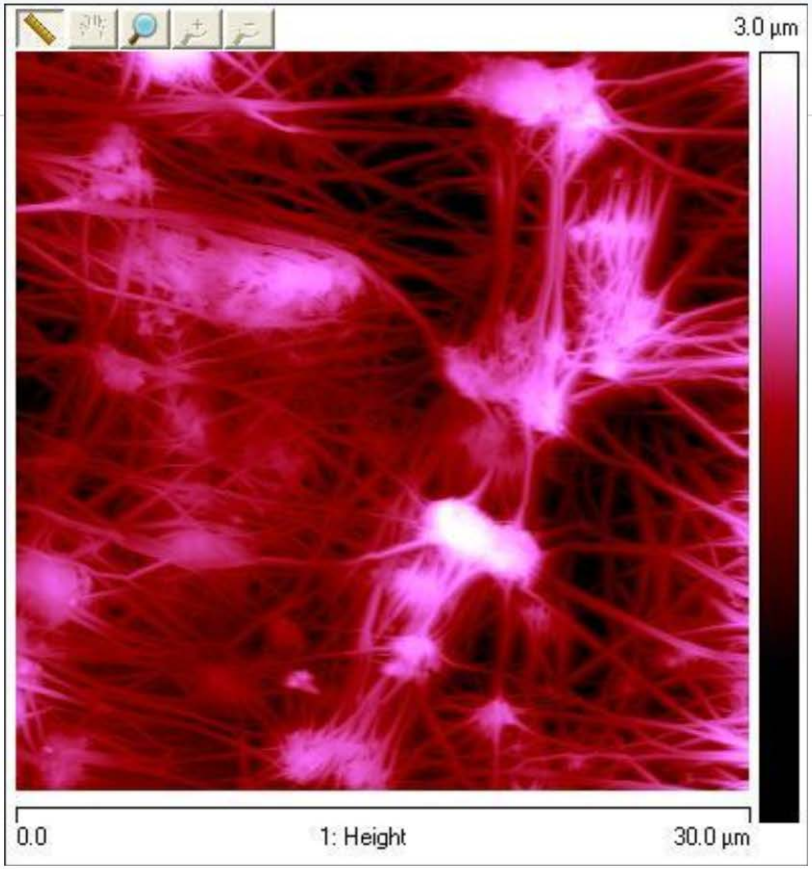
Advantage



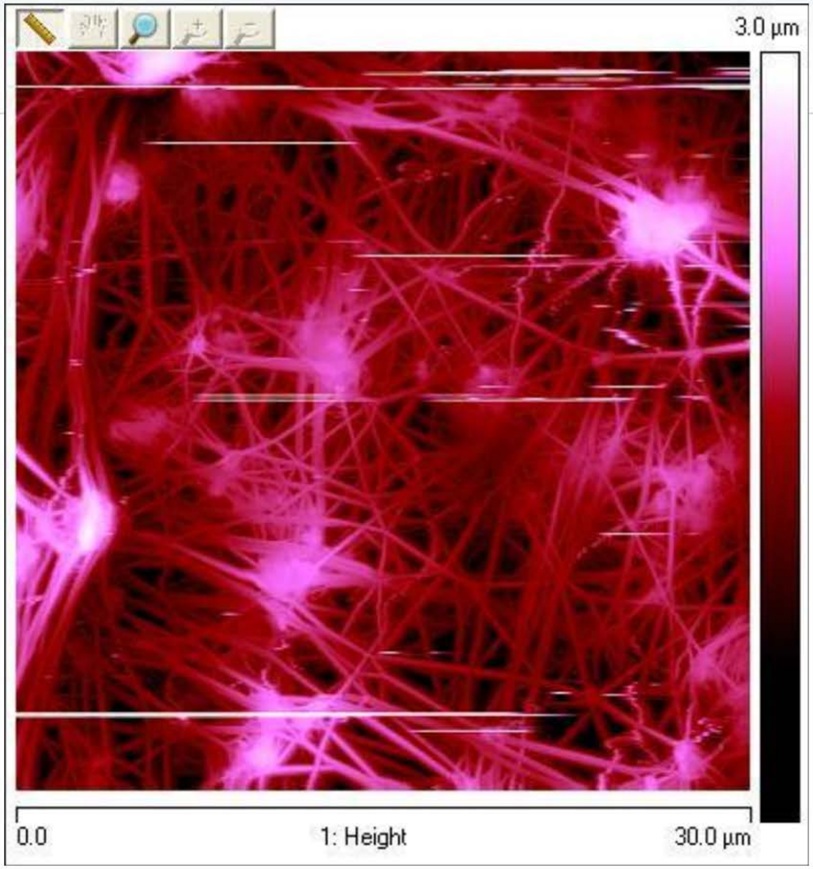
Deep (~65 nm), narrow (~10 nm) trenches are difficult to image with TappingMode due to excessive damping of the probe oscillation. But here PeakForce Tapping easily reaches the bottom of the trenches. Scan size 1 µm on a Dimension Icon.

- PeakForce Tapping can image samples that are extremely challenging or impossible with conventional Tapping Mode
- Deep, narrow trenches and pits are very difficult for Tapping Mode because the geometry excessively damps the tapping oscillation, preventing the tip from reaching the bottom.
- PeakForce Tapping is based on direct imaging force control, it is immune to these effects.

Challenging Geometries

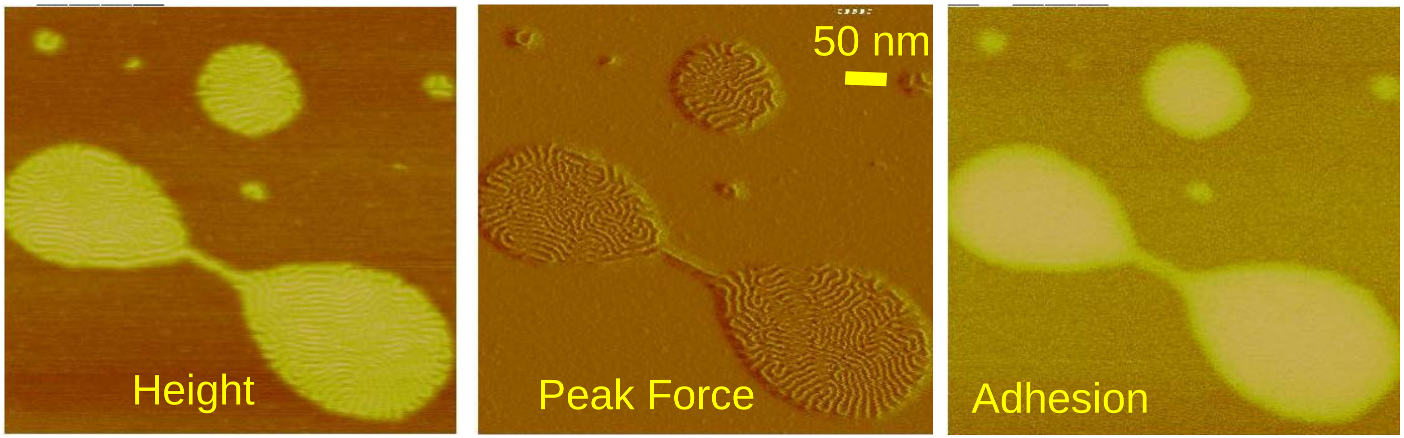


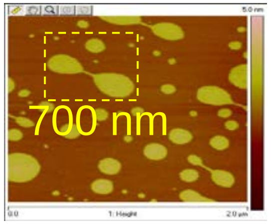
PeakForce



Conventional
TappingMode

Tapping Mode vs. PeakForce Tapping

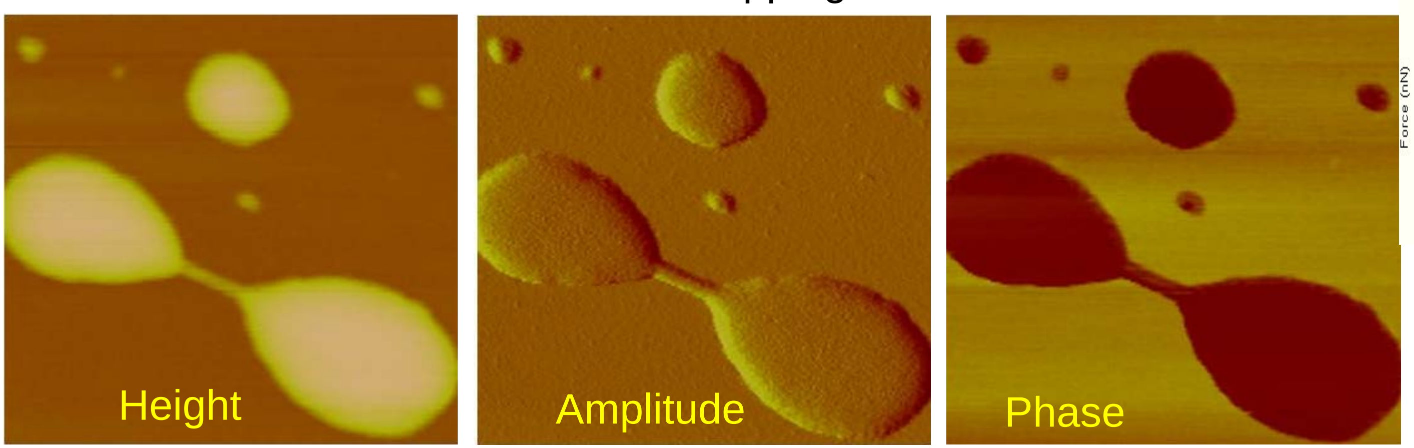


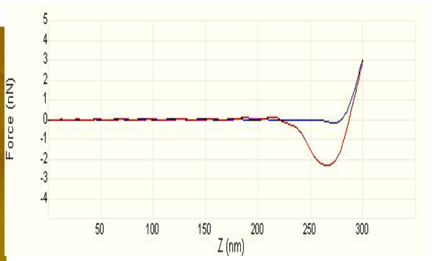


(Peak Force Tapping 4 nN)

Tapping Lever 40 N/m

Hard Tapping





Peakforce Advantages

- **Provides data quality often better than conventional Tapping Mode**
- **Works in any environment**
- **Enables automation of the critical part of the imaging process**
- **Creates a platform to extract quantifiable information on the nanometer scale**

Secondary Imaging Modes

Derivation of Contact Mode

LFM
cAFM
TUNA
SCM
SSRM
PFM
SThM

Derivation of Tapping Mode

Phase Imaging
EFM
MFM
KPFM

Derivation of TRmode

TR cAFM
TR TUNA

Derivation of PeakForce Tapping

ScanAsyst
PeakForce QNM
PeakForce TUNA
PeakForce KPFM

Properties Mapping

Electromagnetic Properties

MFM
EFM
KFM
PFM
SCM
cAFM/TUNA
SSRM

Mechanical Properties

LFM
FMM
Force Curve
Force Volume
Phase Imaging
HarmoniX
PeakForce QNM

Thermal Properties

SThM
VITA

Others

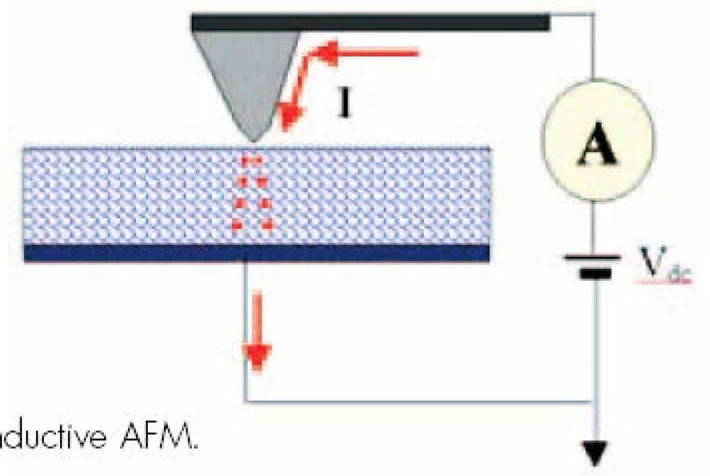
ECAFM/ECSTM/SECPM
AFM-Raman

Applications-Electromagnetic Properties

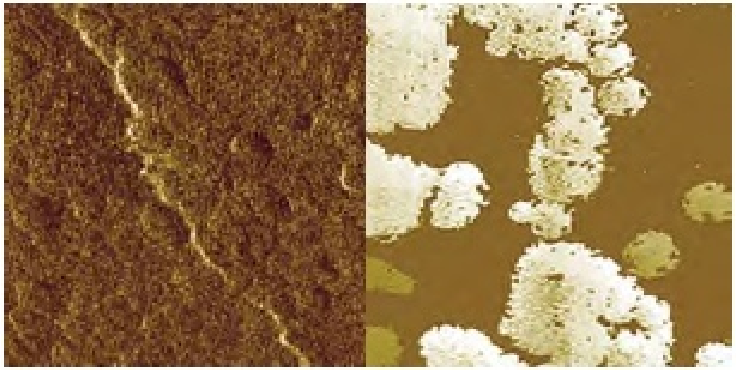
- **cAFM-conductive AFM/Tunnelling AFM**
- **EFM-Electrostatic Force Microscopy**
- **KPFM-Kelvin Probe Force Microscopy**
- **PFM-Piezoelectric Force Microscopy**
- **SCM-Scanning Capacitance Microscopy**
- **MFM-Magnetic Force Microscopy**
- **SSRM-Scanning Spreading Resistance Microscopy**

Conductive AFM (cAFM)

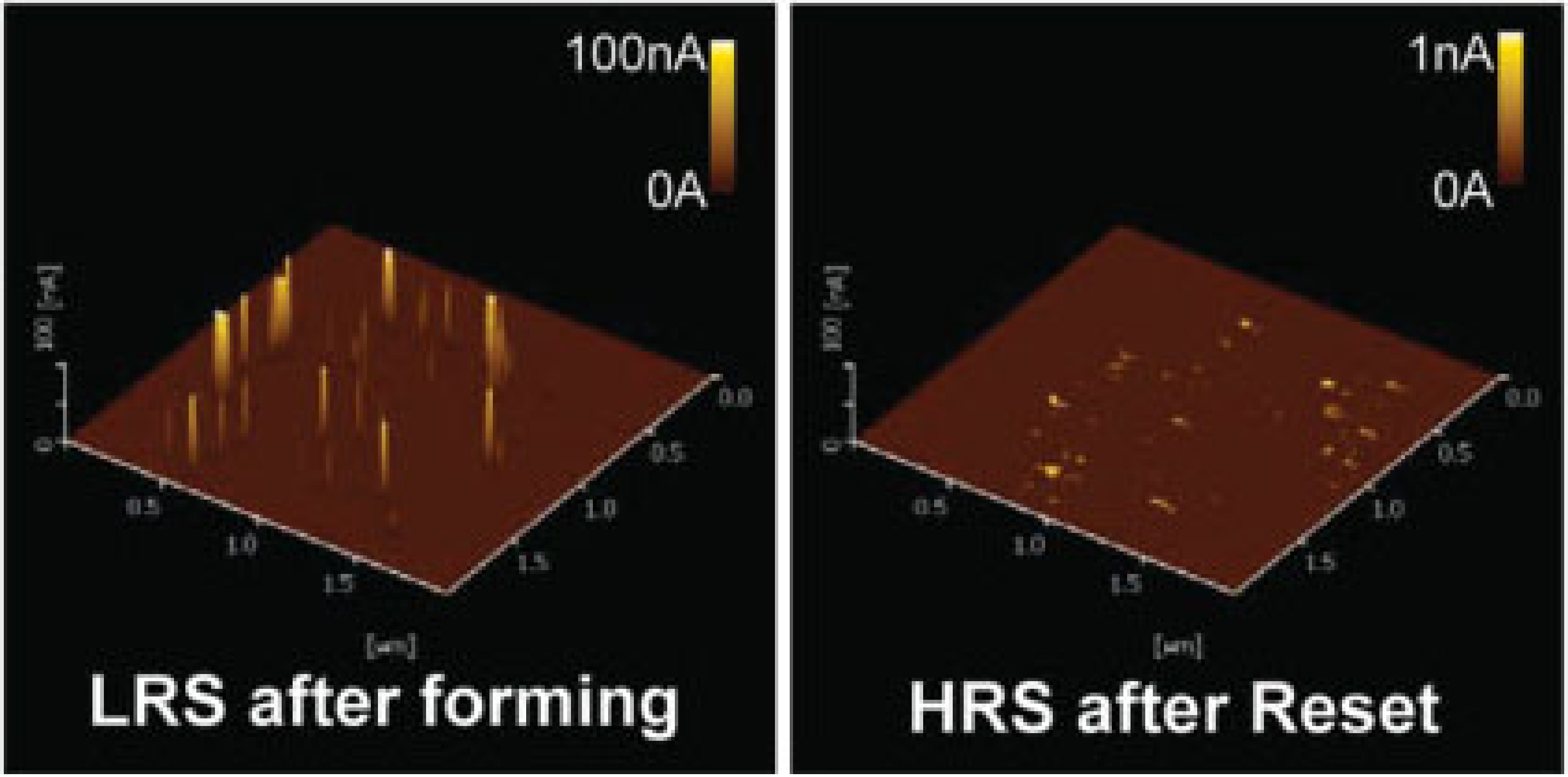
- **Conductive AFM (cAFM)** — Conductive atomic force microscopy (CAFM) is a secondary imaging mode derived from contact AFM that characterizes conductivity variations across **medium- to low-conducting and semiconducting materials**.
- CAFM performs general-purpose measurements and has a current range of **pA to μA**.



Conductive AFM.

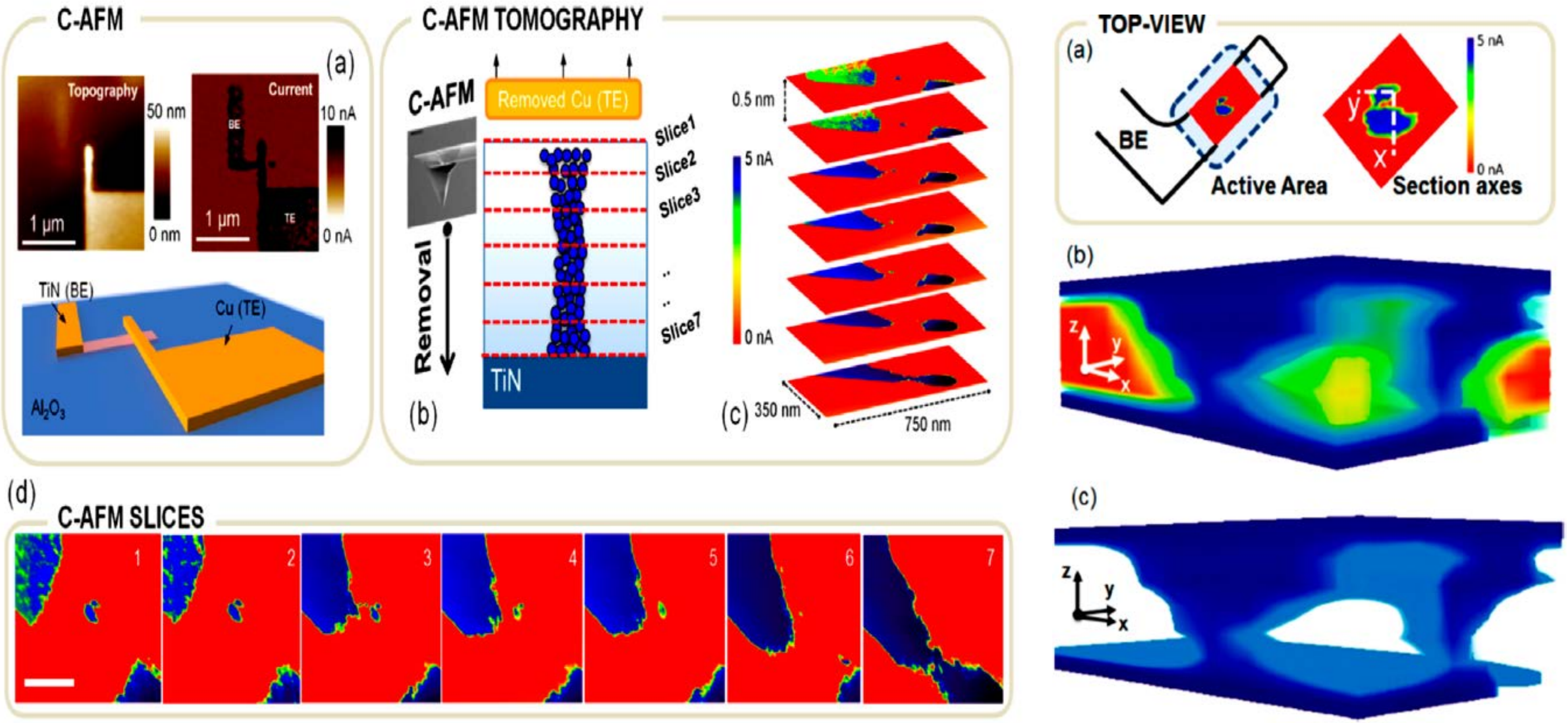

Polyaniline on ITO

cAFM Application Example



CAFM, Chae et al., Adv. Mater. 20, 1154, 2008

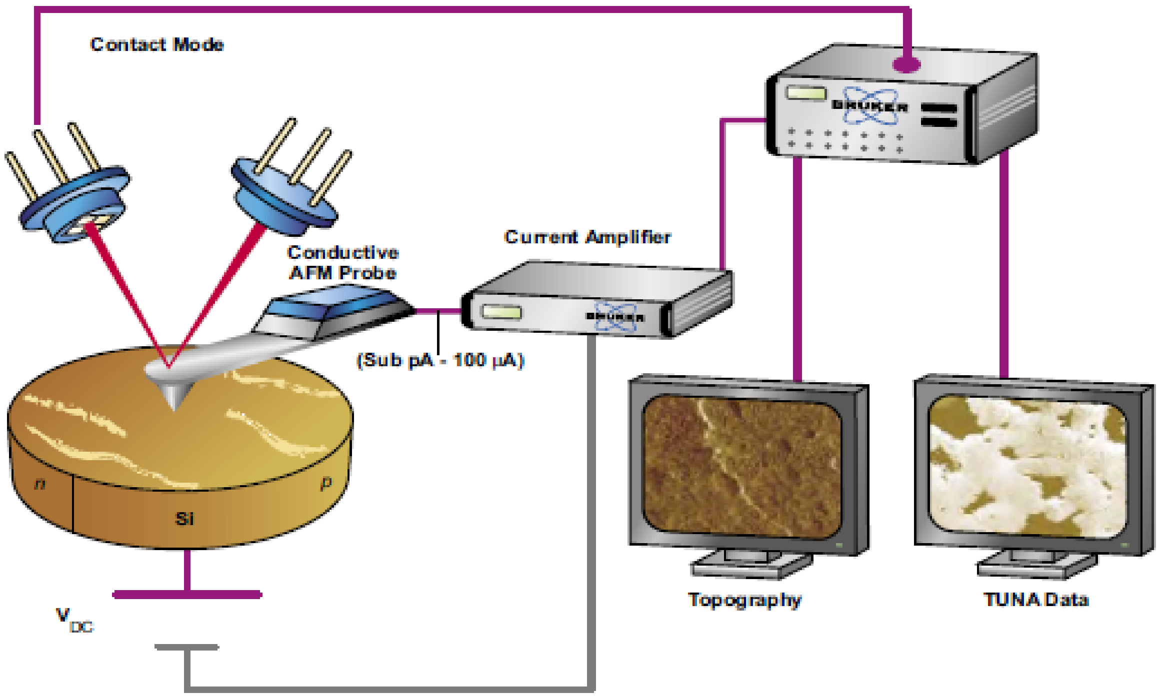
3D cAFM tomography



Celano et al., Nano Letters 14, 2401, 2014

Tunneling AFM

- **Tunneling AFM** — Tunneling AFM works similarly to conductive AFM, but with higher sensitivities. TUNA characterizes ultra-low currents (**between 80fA and 120pA**) through the thickness of thin films. The TUNA application can be operated in **either imaging or spectroscopy mode**. Applications include gate dielectric development in the semiconductor industry.



Application Example

Embedded defects in SiO_2

加上负电压后可以看到二氧化硅中隐藏的缺陷，电压越大，缺陷越明显。