

纳米光学表征方法

分为三大类：

1. 扫描探针技术
2. 光谱技术
3. 成像技术



**We are
here!**

Three categories:

1. SPM:

◆ NSOM

◆ AFM

◆ STM

2. Spectroscopy :

◆ General introduction

◆ Raman Spectrometry

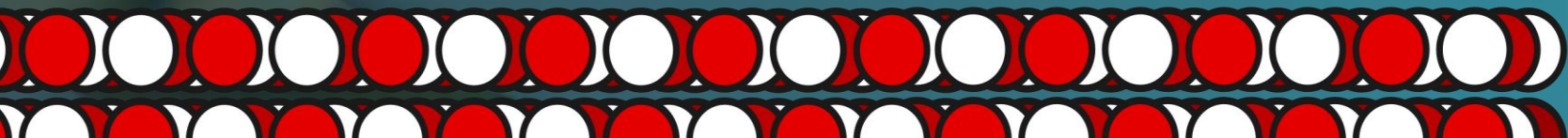
3. Imaging:

◆ Confocal imaging

◆ multi-photon imaging²

SPM

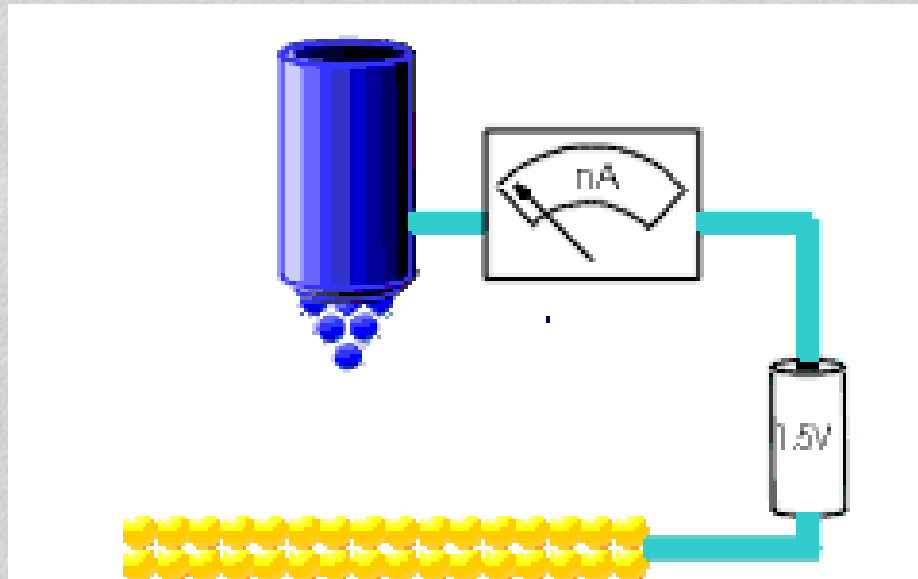
Scanning Probe Microscopy



Scanning Probe Microscopy

- ◆ Scanning Tunneling Microscopy
- ◆ Atomic Force Microscopy
- ◆ Near-field Scanning Optical Microscopy

Scanning Tunneling Microscope



Lecture Plan

1. Introduction

- Comparison with other techniques
- Fundamentals
- Tips

2. Construction

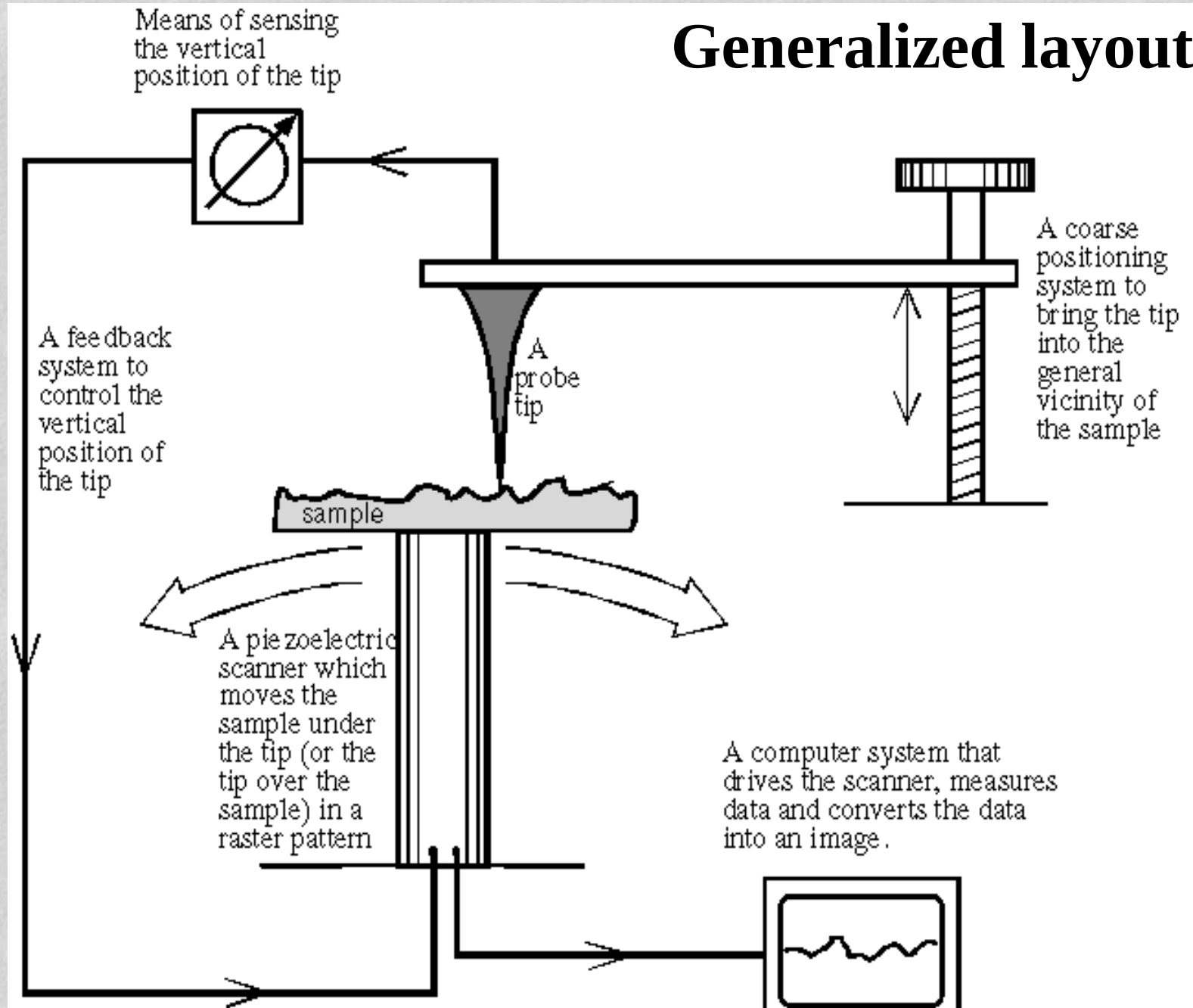
- Scanner
- Vibration
- Electronics

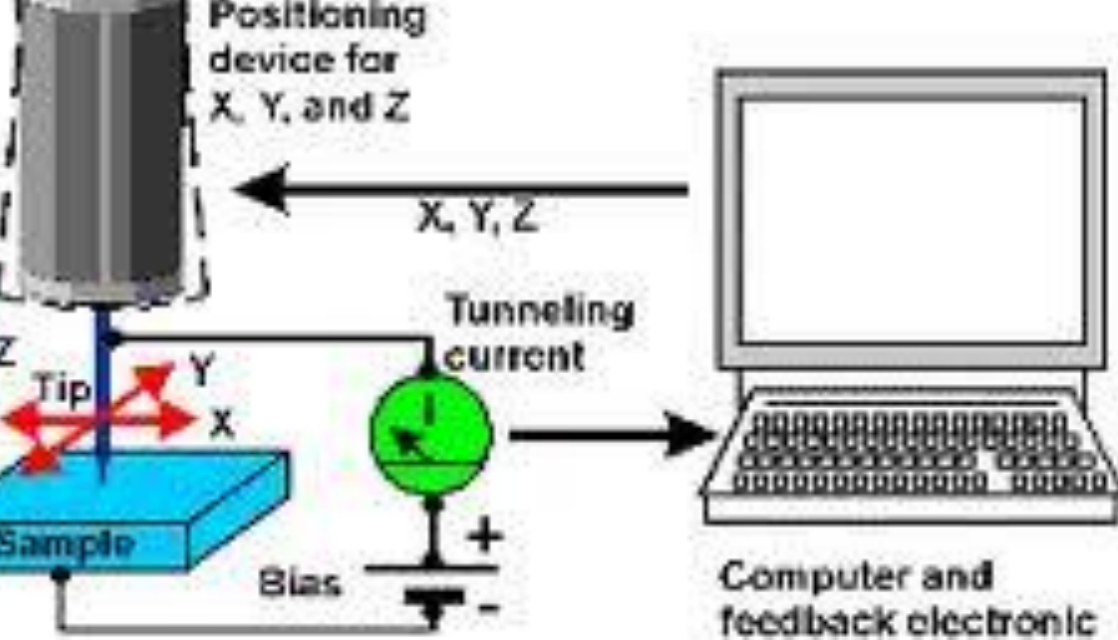
3. Calibration

4. Applications

Scanning Probe Microscope

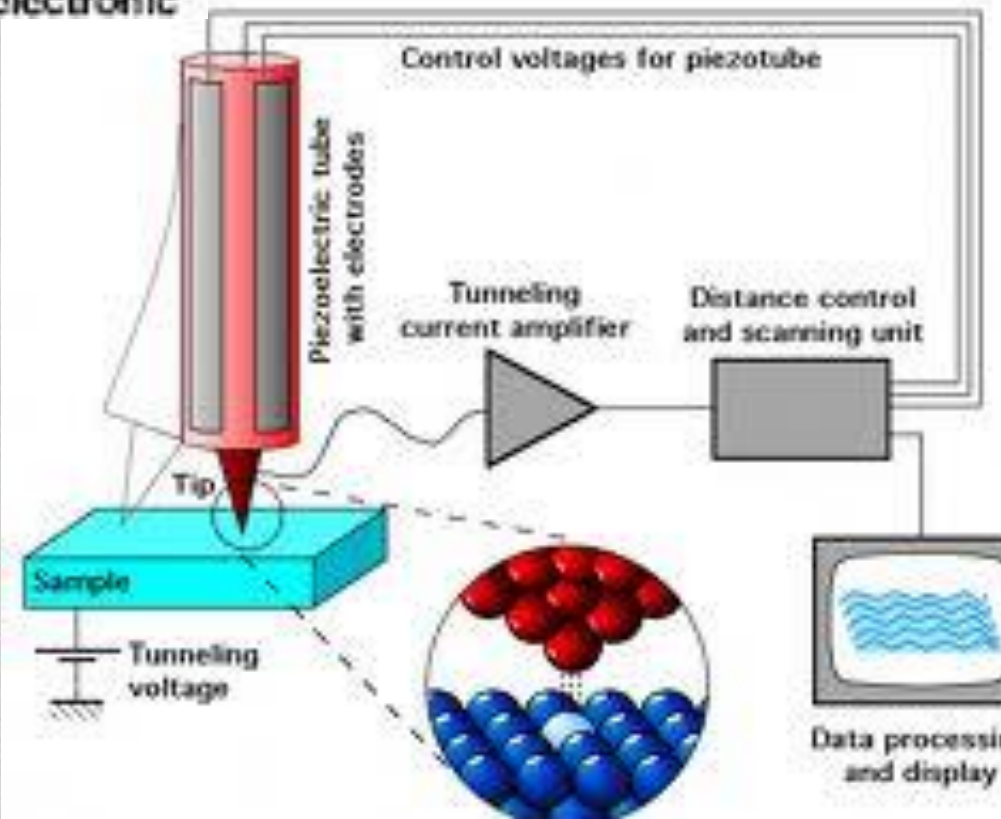
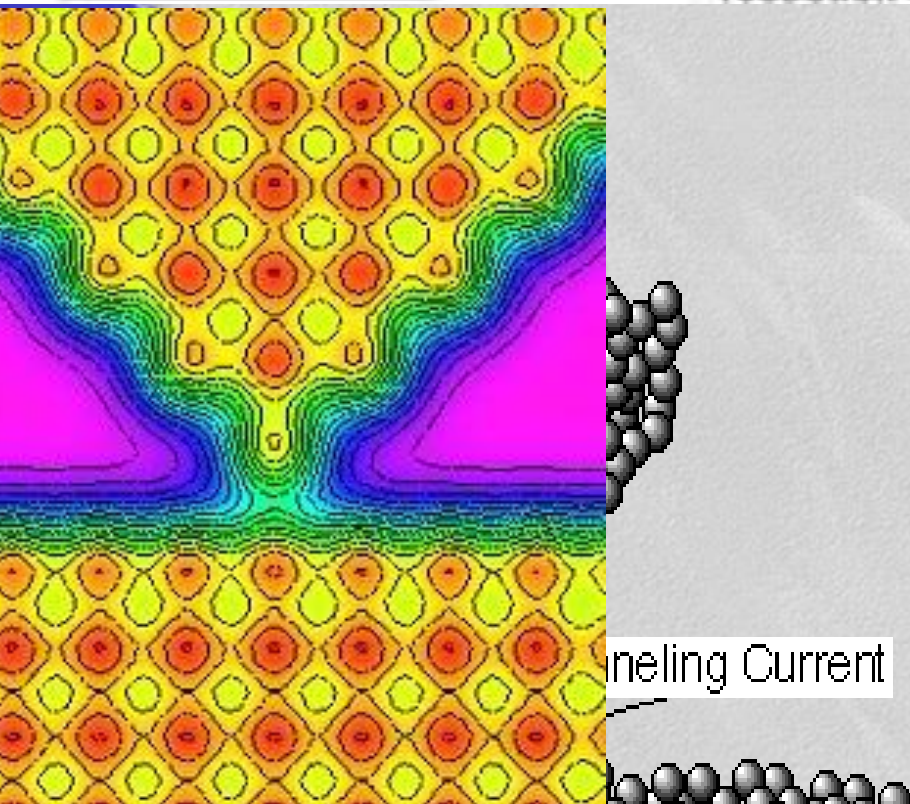
Generalized layout

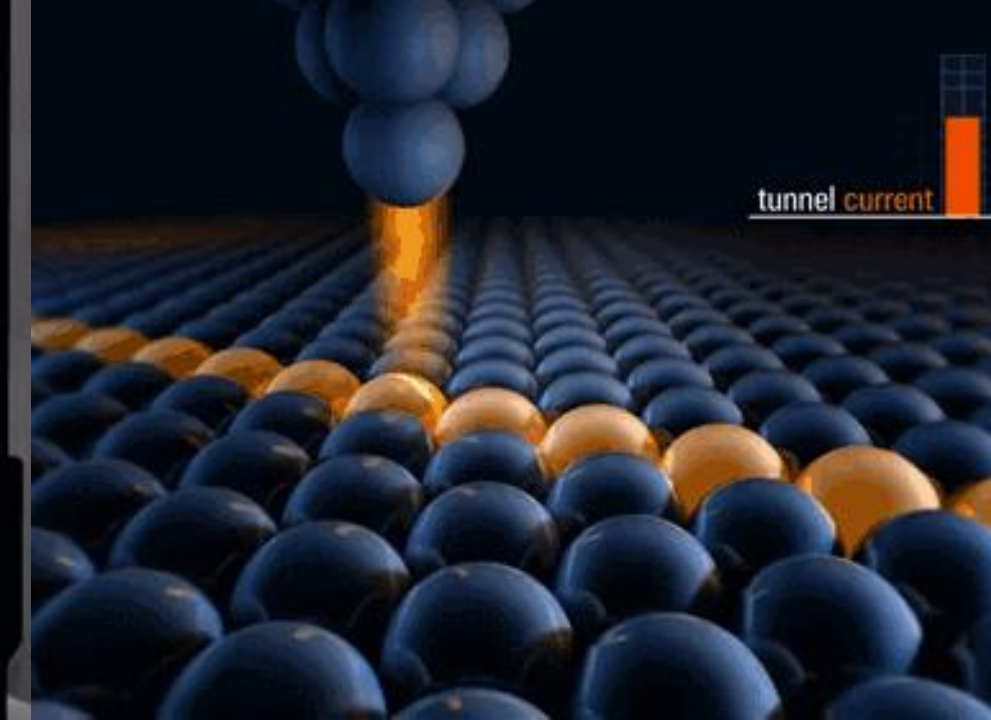
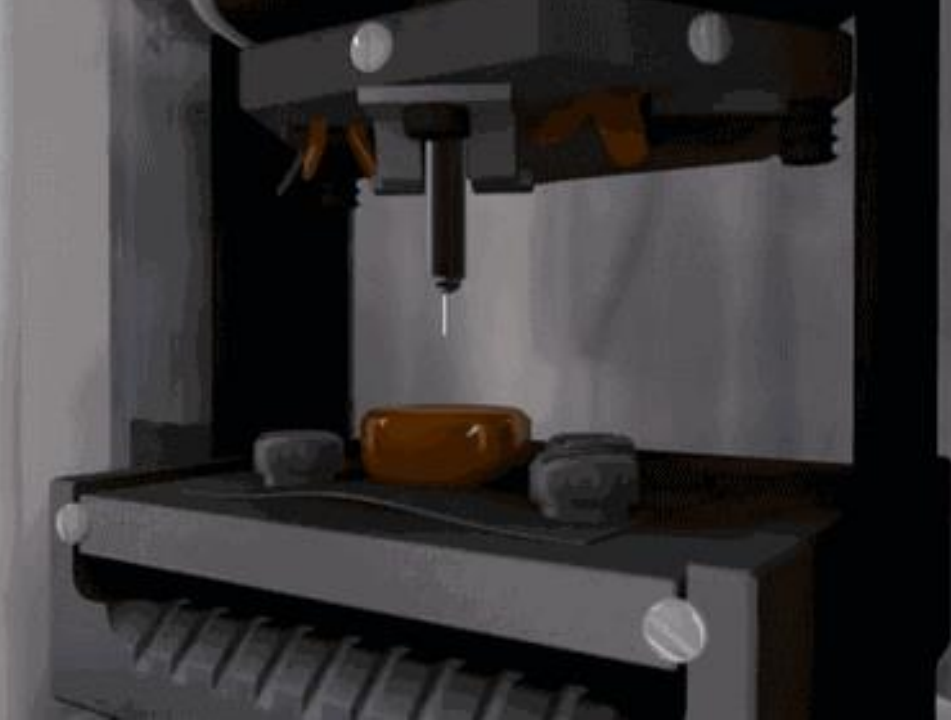




Schematic diagram of STM

- conductive substrate
- form electric circuit





nano ampere

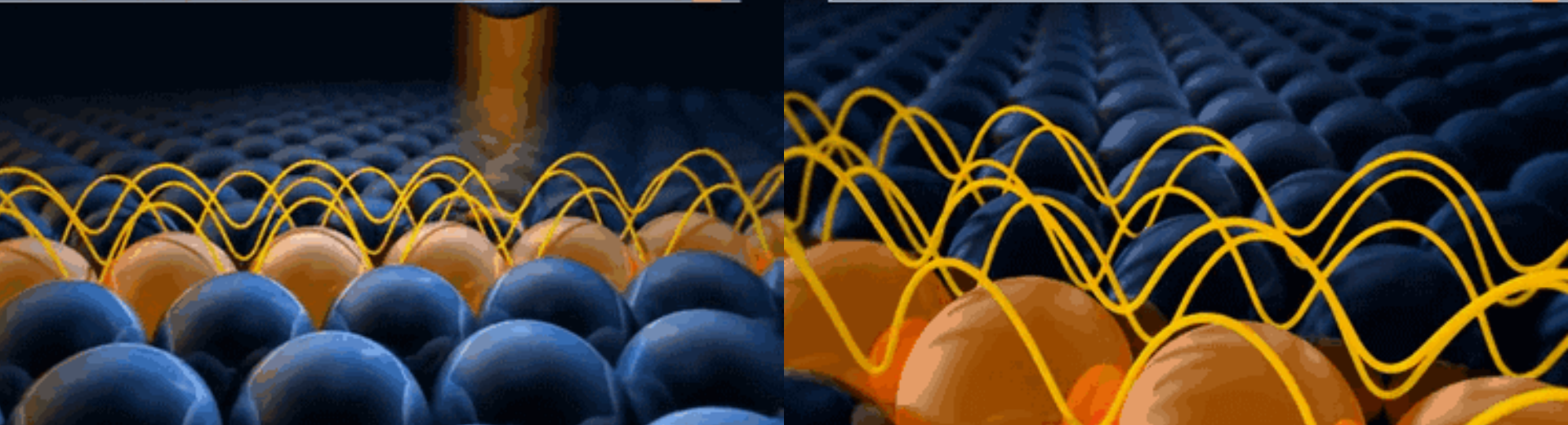


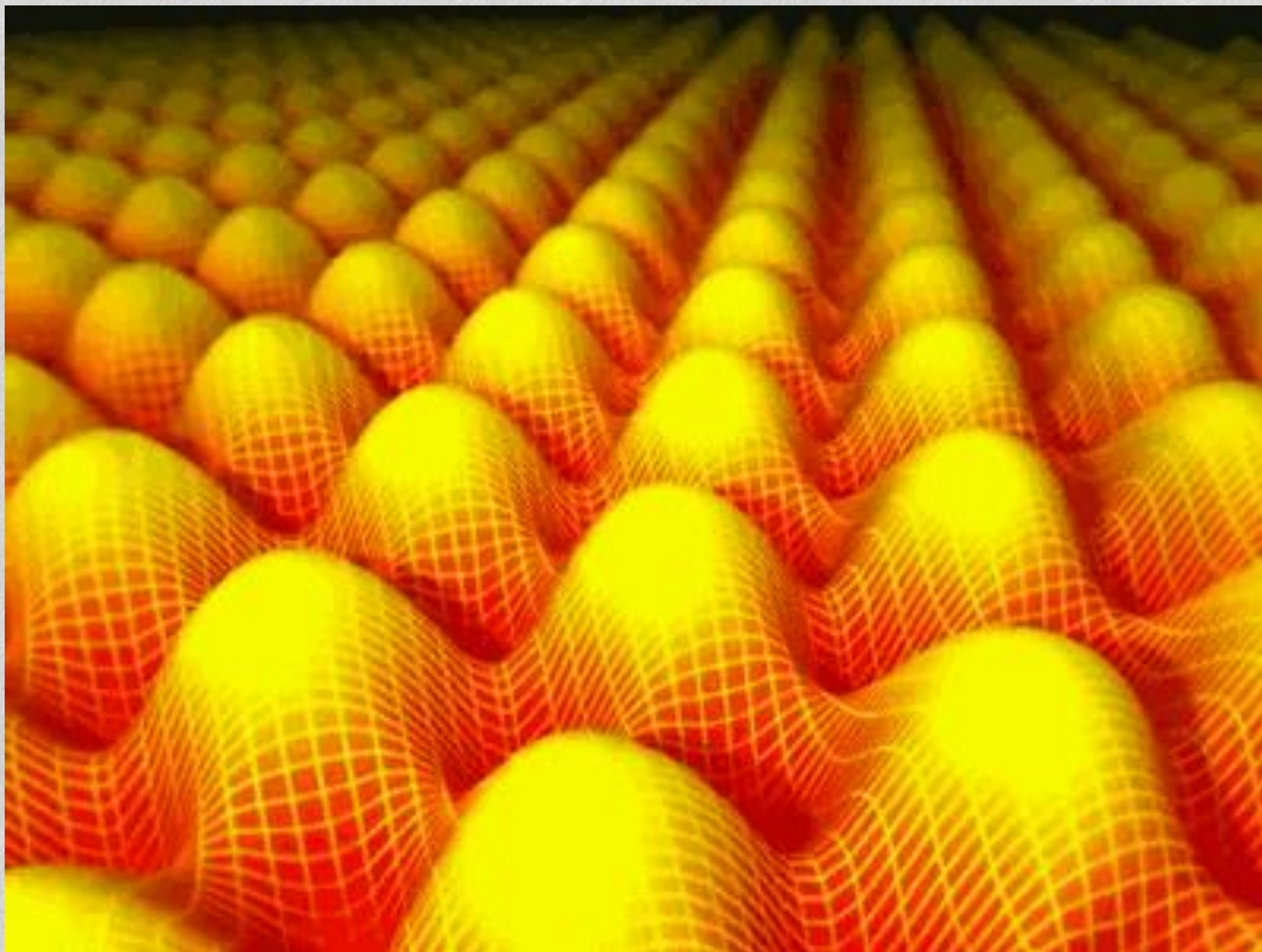
tunnel current

nano ampere



tunnel current



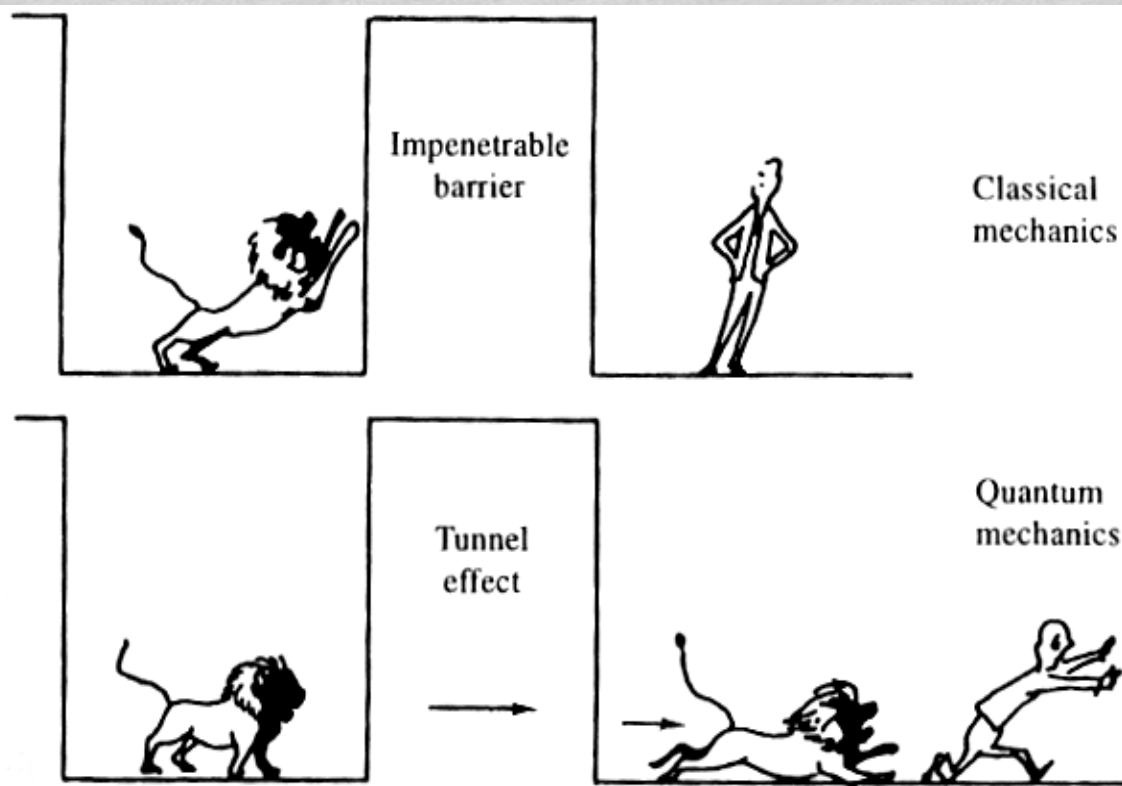
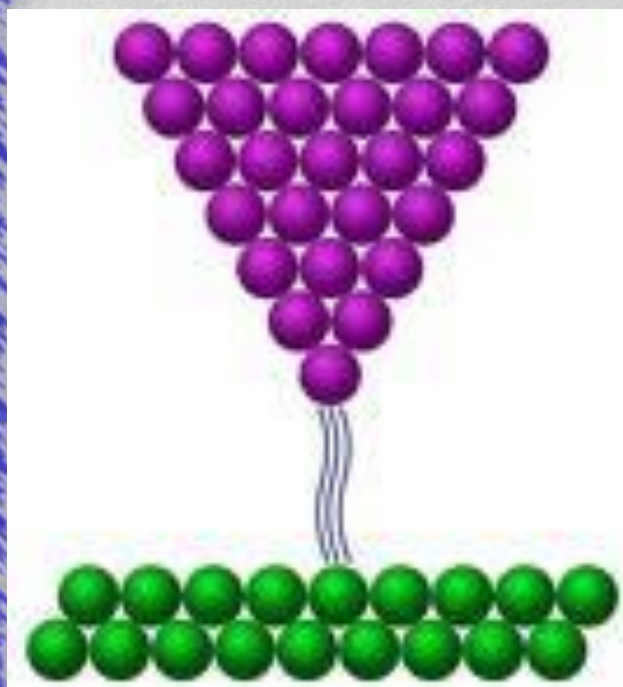




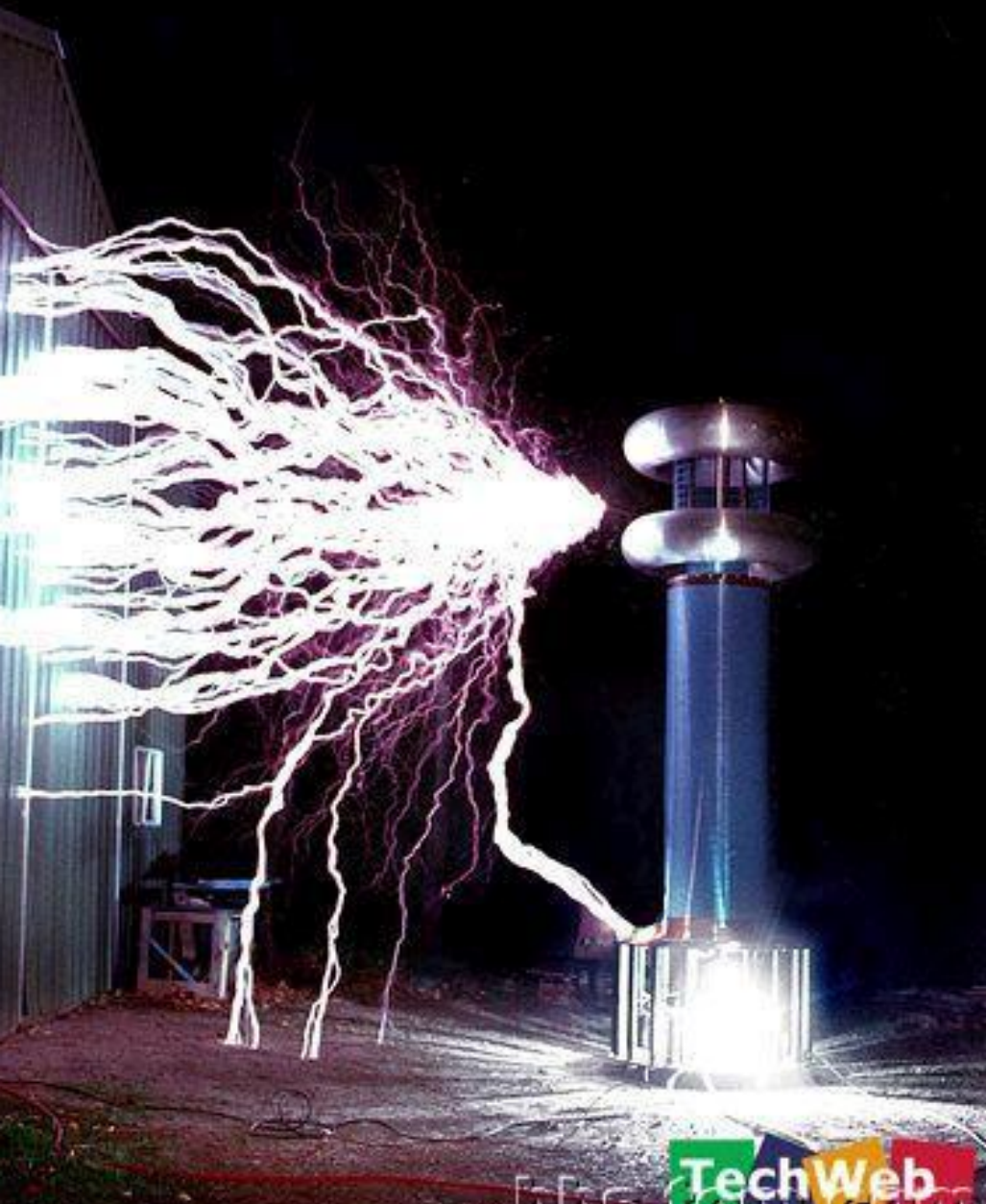
Scanning Tunneling Microscopy systems

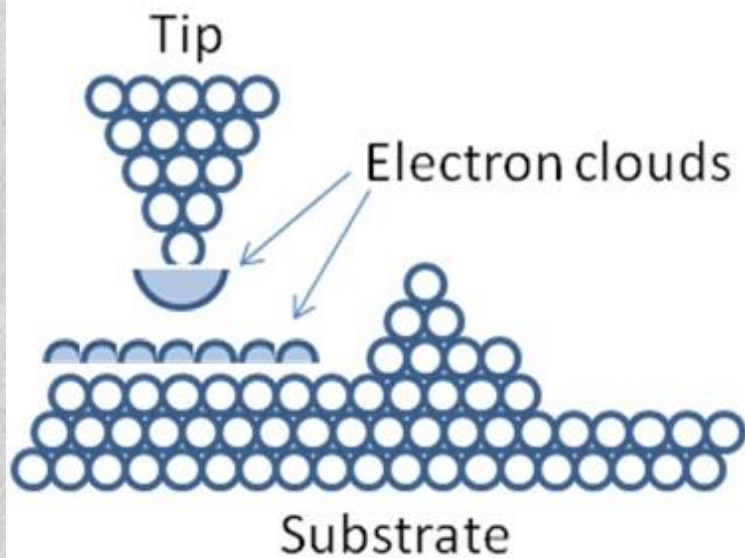
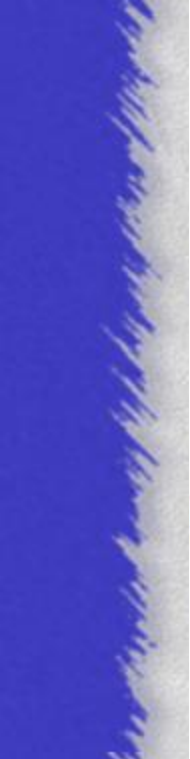
Fundamentals

⌘ 隧道电流来源于粒子（电子）的波动特性及量子特性。当电子入射于真空势垒其势能大于电子的动能时，仍然存在非零的概率使其能够穿越禁带区域出现在势垒的另一侧。

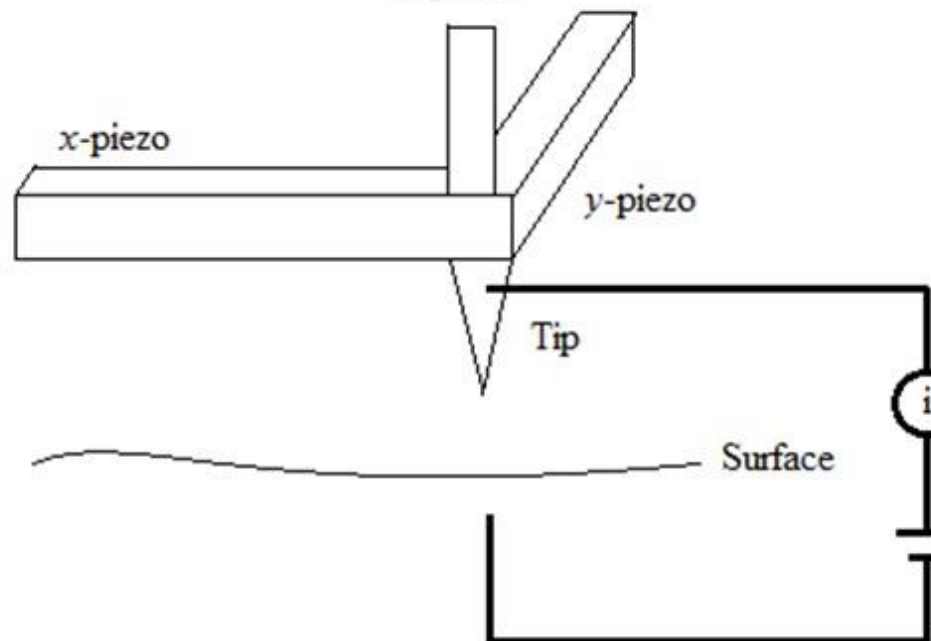


Breakdown under high voltage



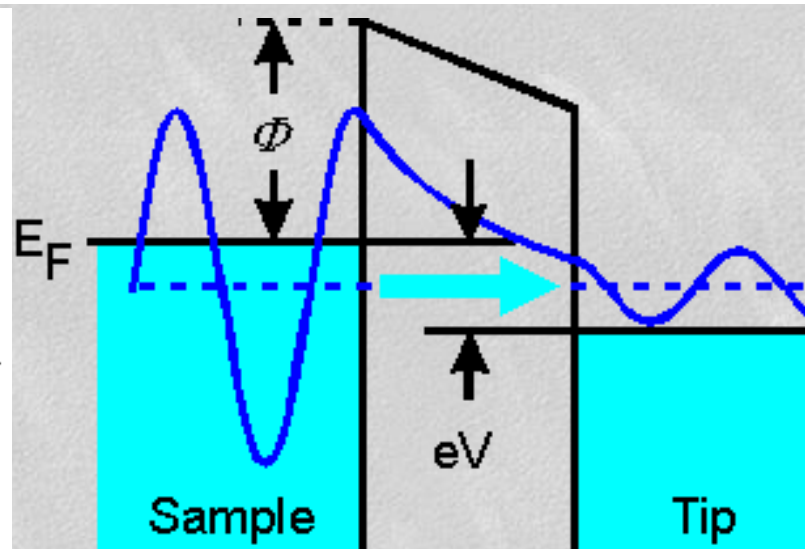
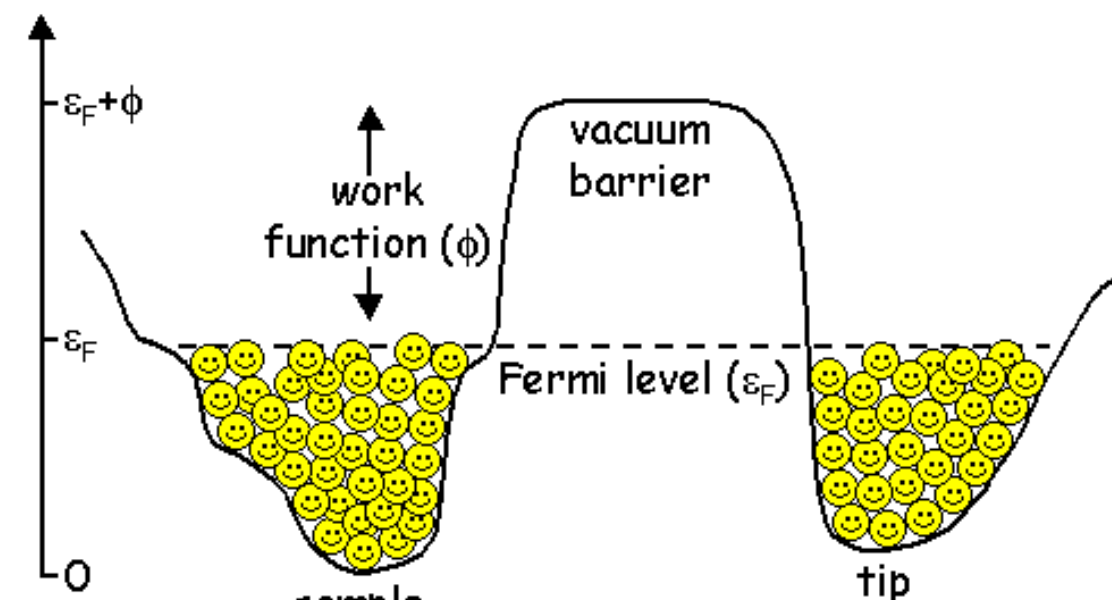


(a)



(b)

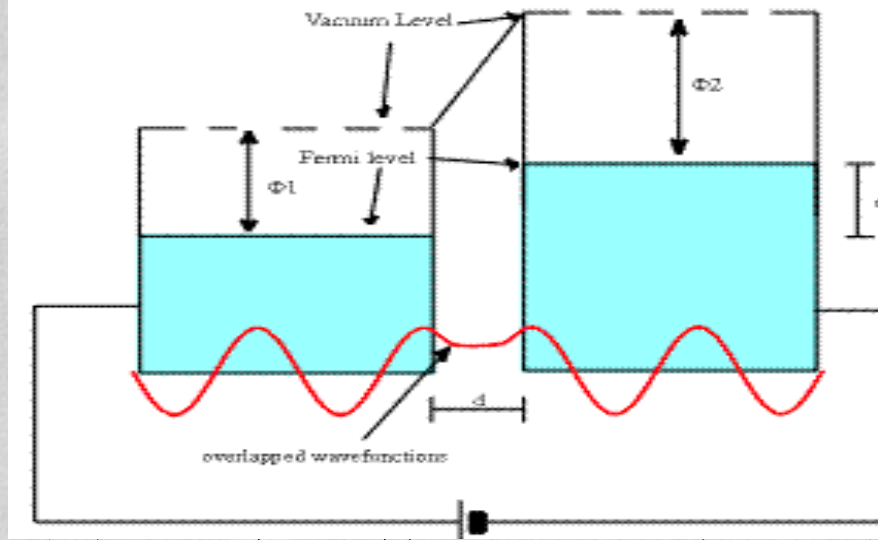
Energy (ϵ)



Fundamentals

⌘ 泄露电子的波函数.

$$I \propto \exp(-2Kd)$$



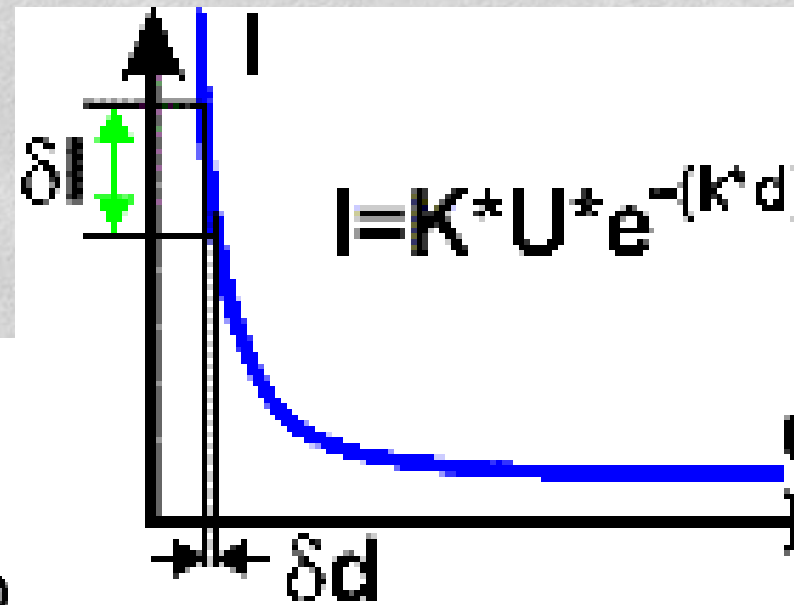
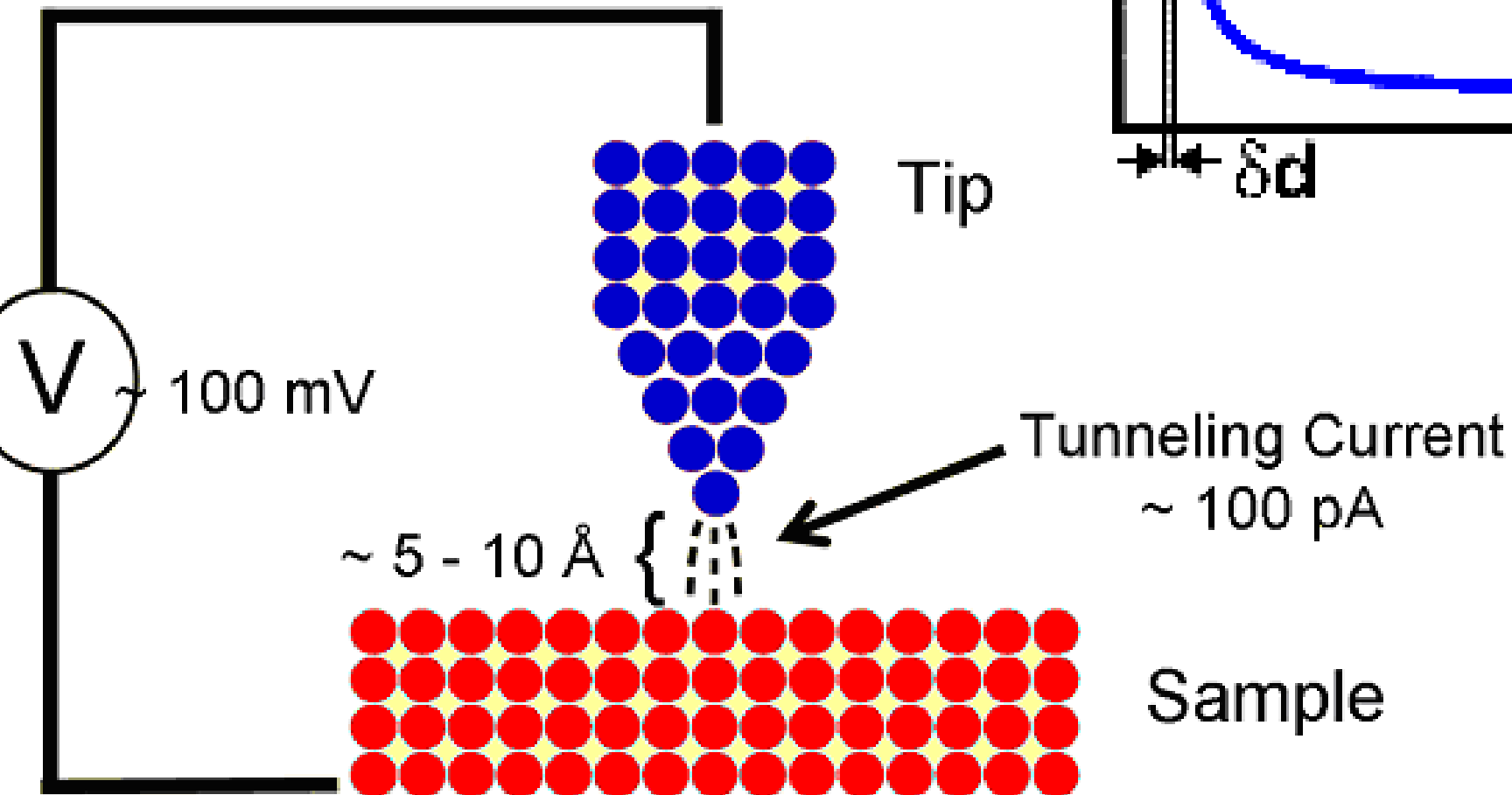
⌘ 如果距离 d 太近则导致泄露电子波函数重叠，该泄露电子波函数在费米能级处的衰减系数 K 可由下式表达

$$K = \frac{\sqrt{2m\Phi}}{\hbar}$$

$$\Phi \propto \frac{d}{V}$$

其中, m 电子质量, Φ 局域隧道势垒高度 或平均波函数。当较小的电压 V 施加于样品与探针之间，叠加的波函数允许量子隧穿效应产生， I 为流过间隙的电流。

Working principle of Scanning Tunneling Microscopy

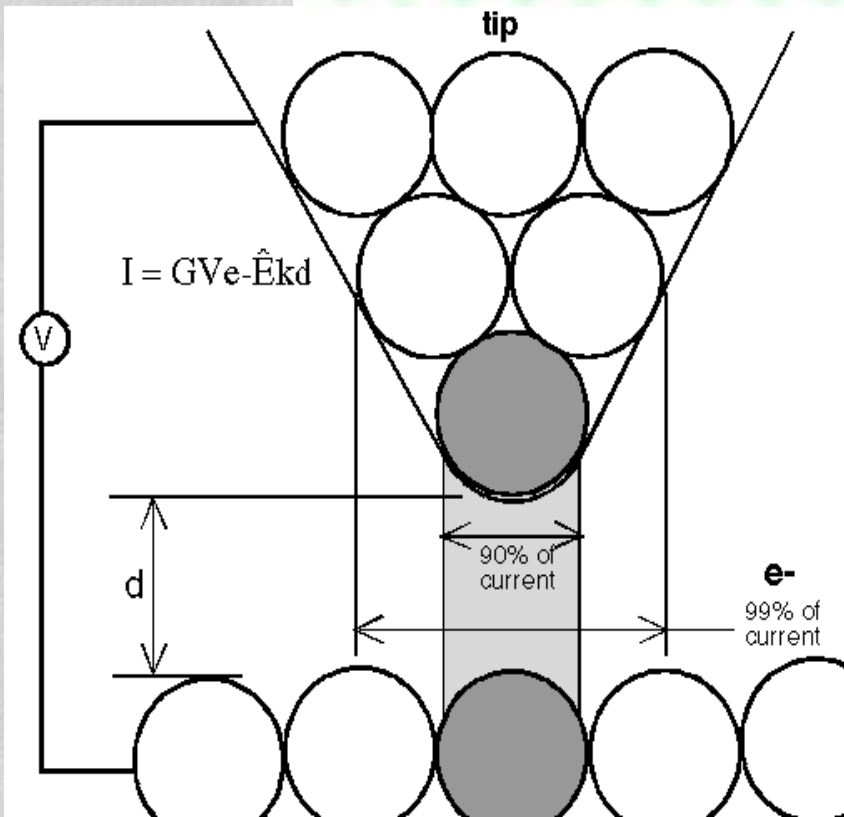
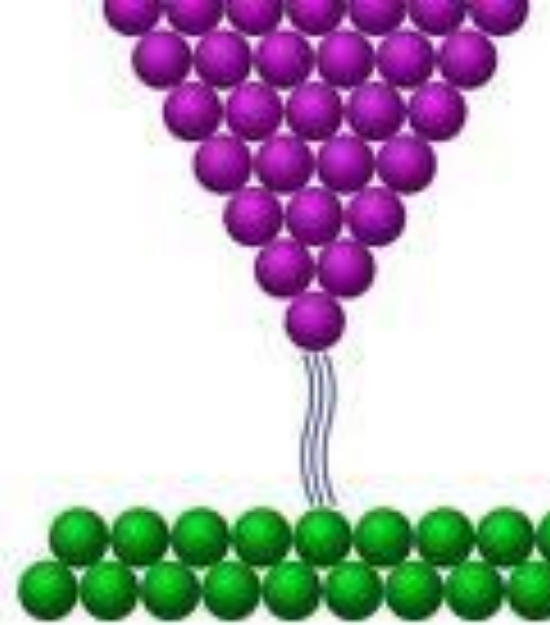


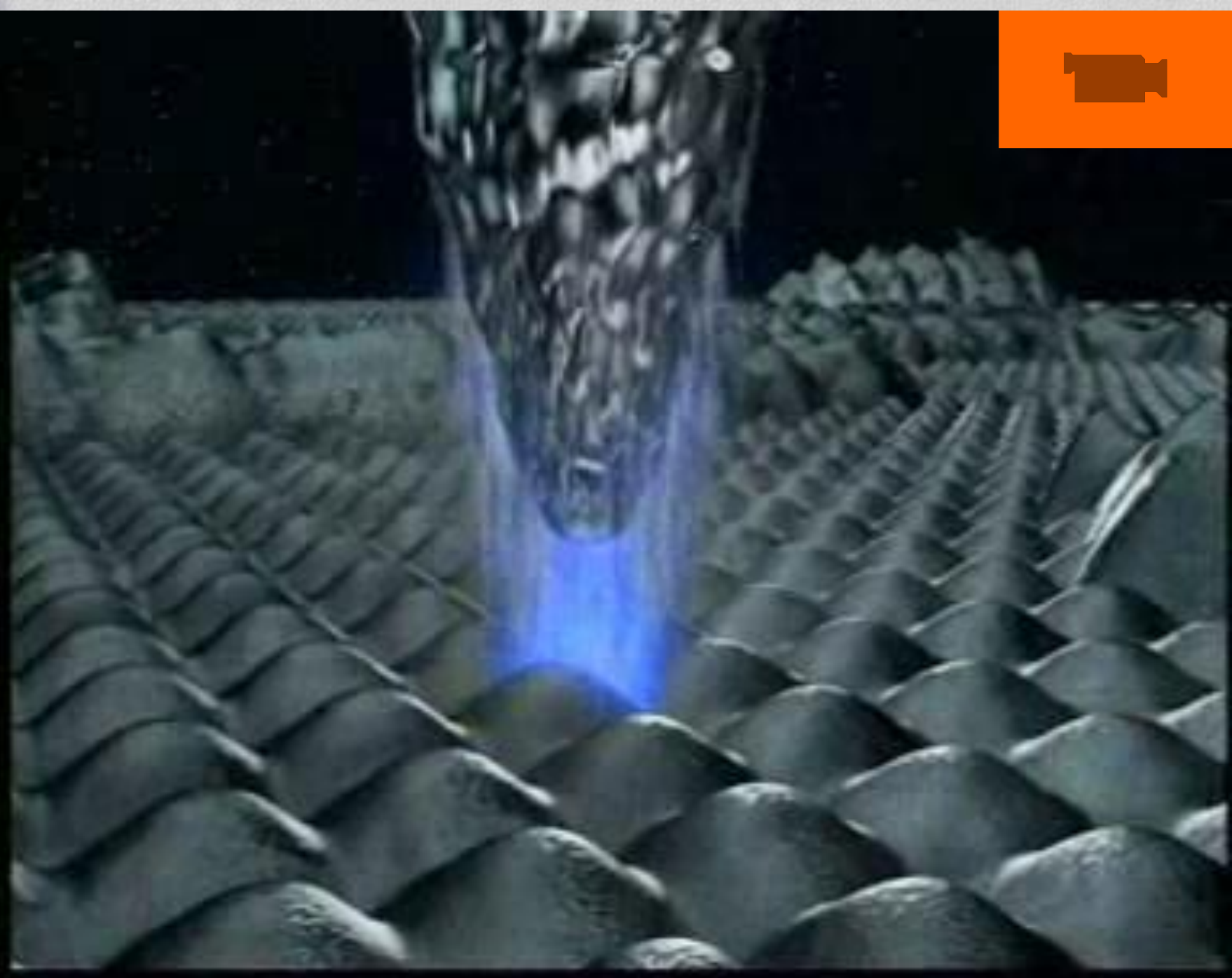
Fundamentals of STM

⌘ 隧穿电流是间隙的指数函数;间隙的变化量为 10% (样品平整光滑)。

⌘ 这种关系保证了高灵敏度测量。

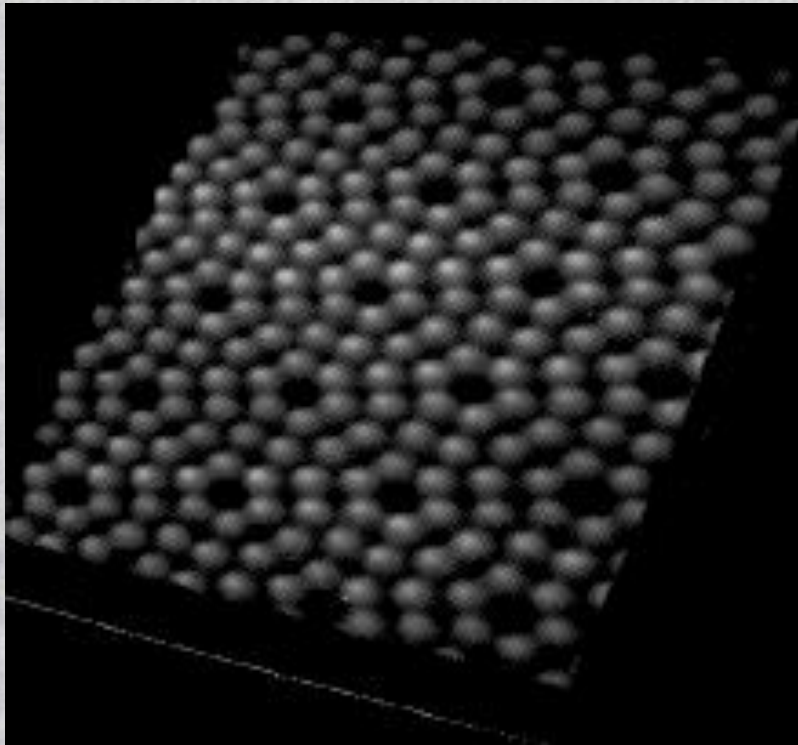
⌘ 垂直分辨率可达到 *sub-angstrom*, 横向分辨率可达到原子水平。





Fundamentals of STM

This is the STM image of Si(111)- 7×7 μm^2 surface, the white spots represents the position of the atoms.

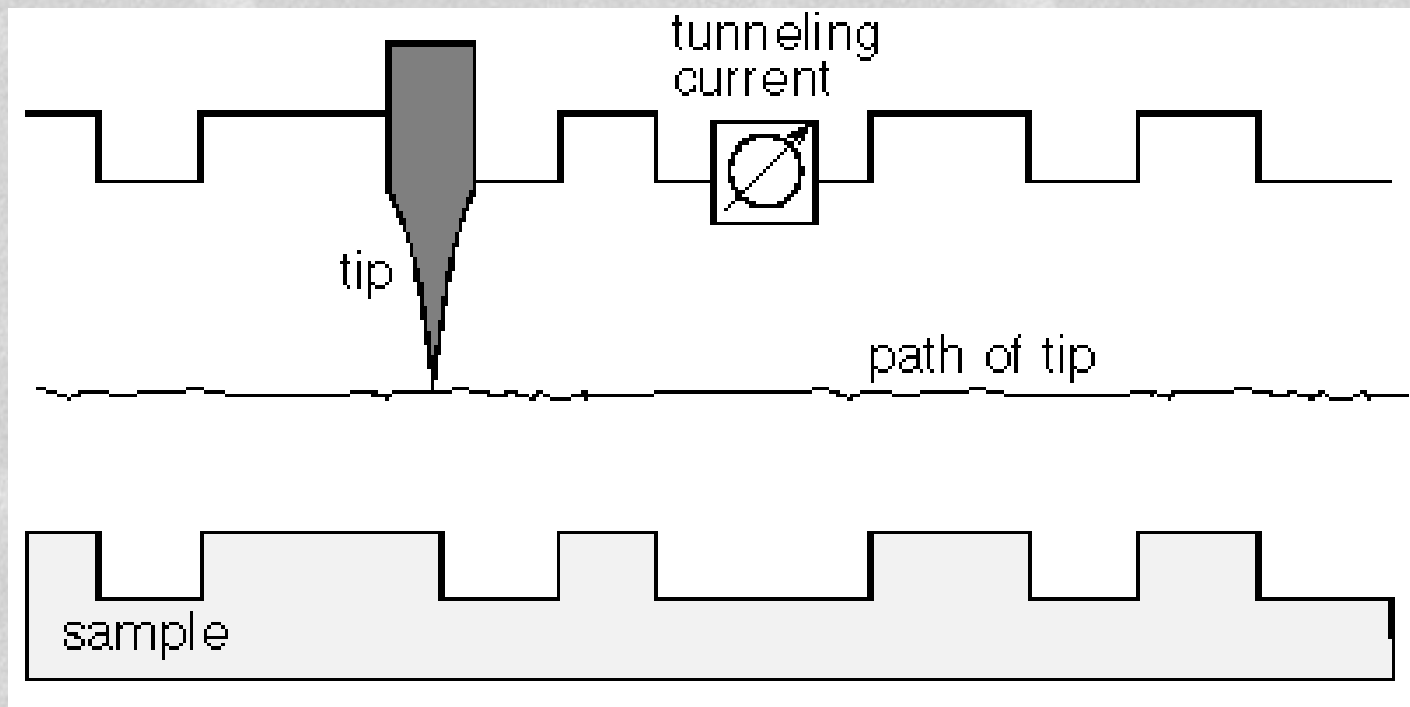


Remember !

STM不是直接探测原子的位置, 而是测量电子密度。所以, STM图像并不总是反映原子的位置, 而是隧道电流变化的幅度。

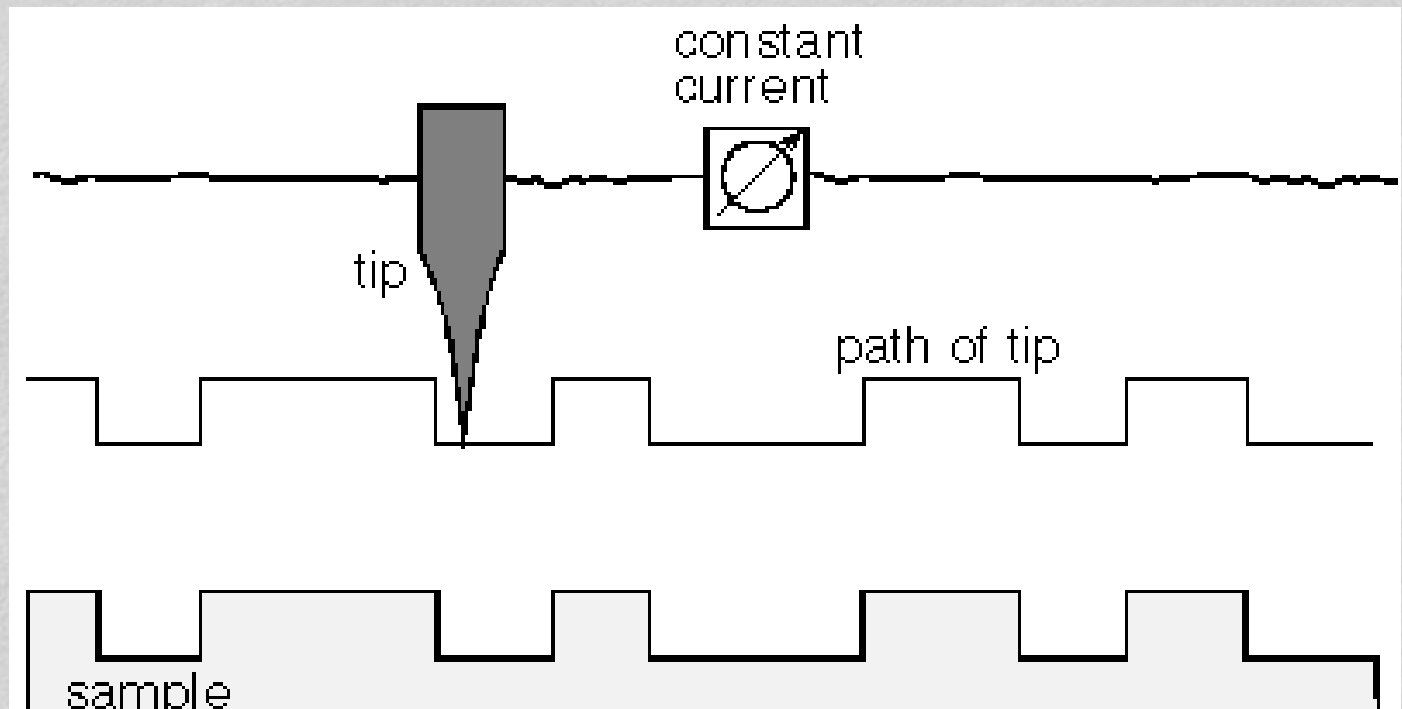
Constant Height

- ⌘ Tip travels in a horizontal plane
- ⌘ Tunneling current will vary
- ⌘ Only suitable for smooth surfaces
- ⌘ Relatively fast



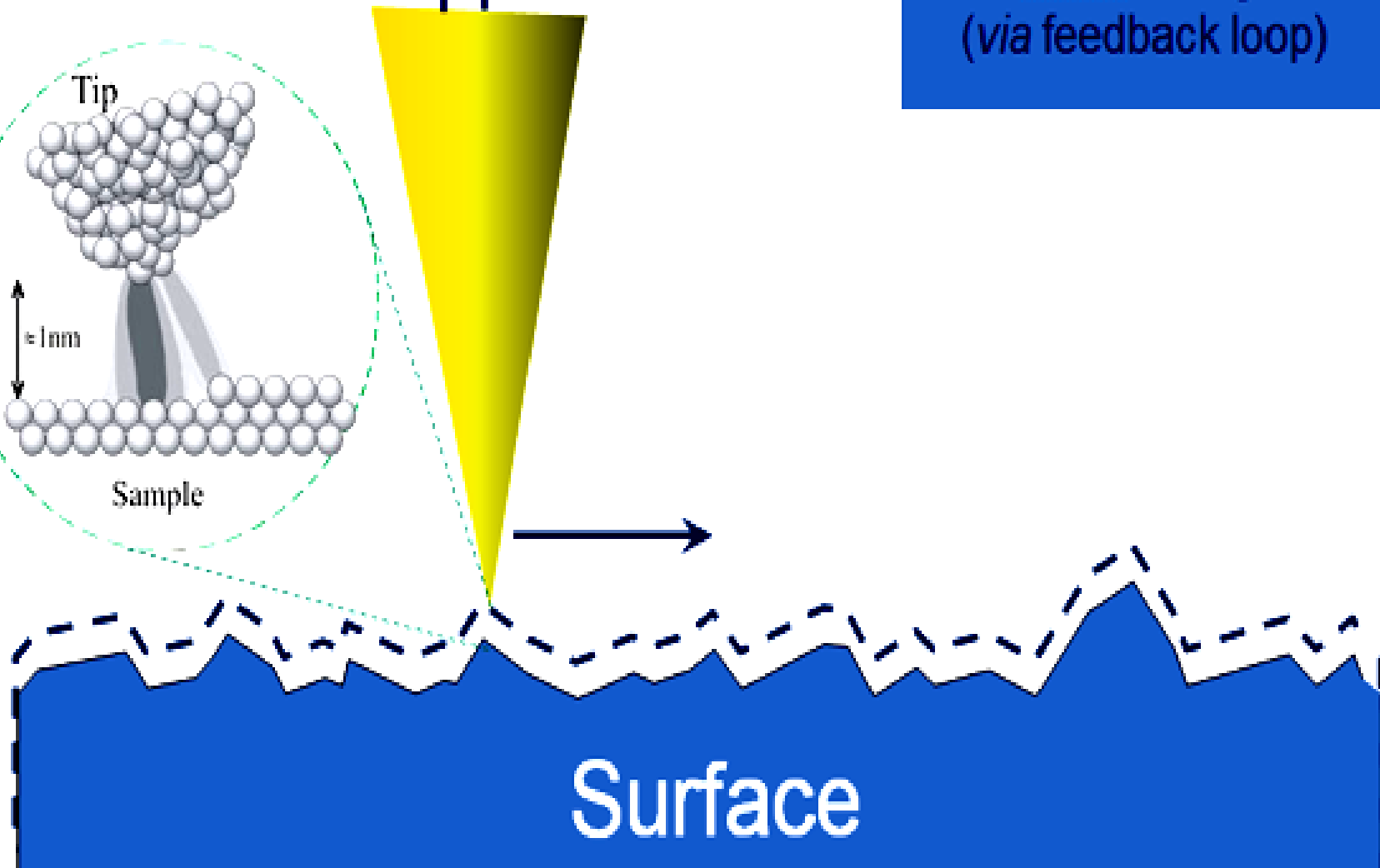
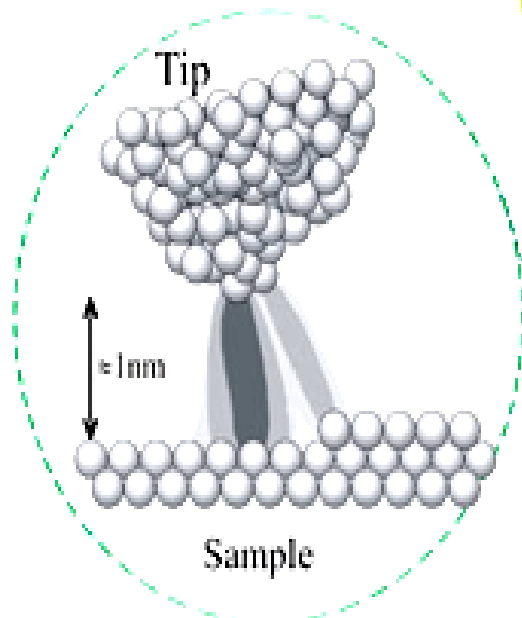
Constant Current

- ⌘ The STM uses feedback to keep the tunneling current constant.
- ⌘ Tip-to-sample distance varies to a few hundredths of an angstrom
- ⌘ Can measure irregular surfaces
- ⌘ Time longer



Constant Current

Tunneling current
Piezo voltage
(via feedback loop)

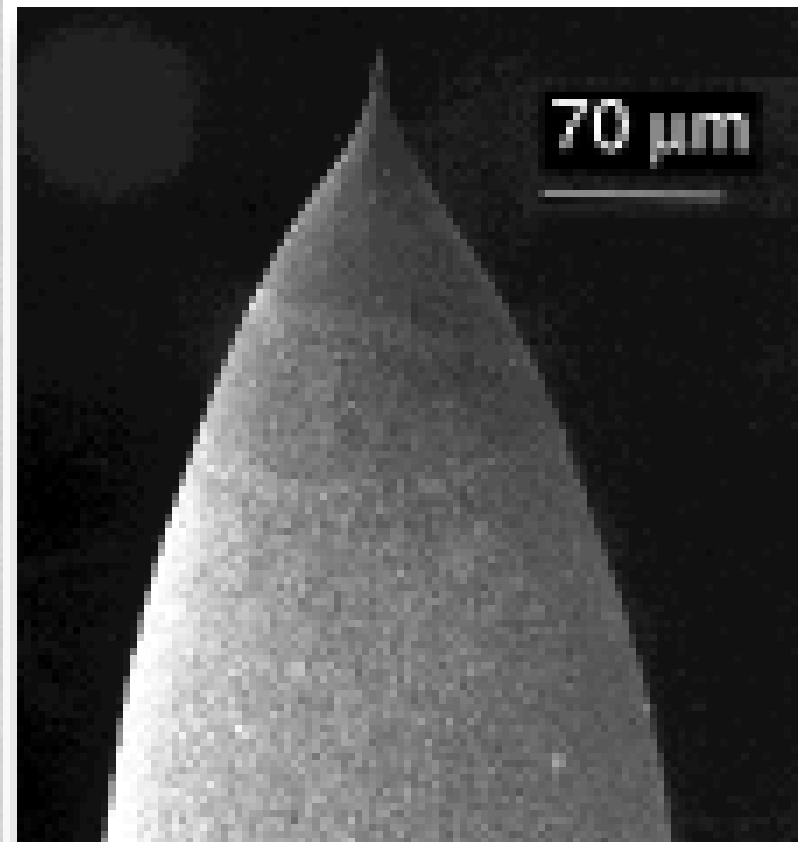
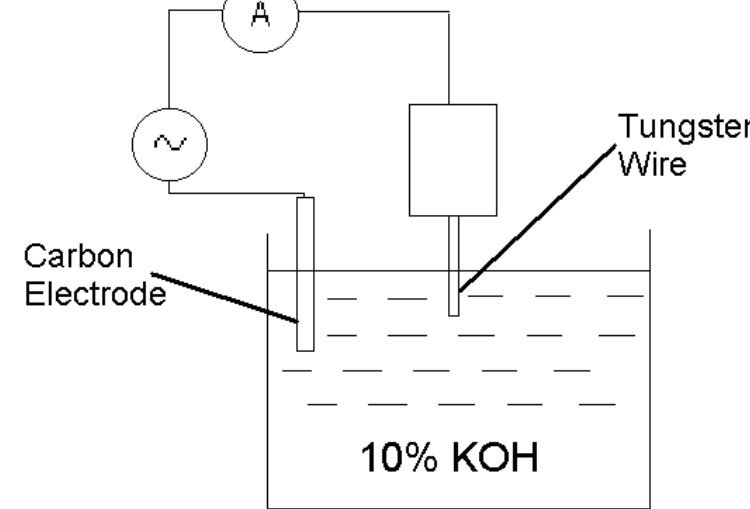


Tips Fabrication

- To ensure atomic resolution, it is essential the tip is of one atom dimension at its end.
- Easy from fabrication!!!!!!
- But hard to verify :)

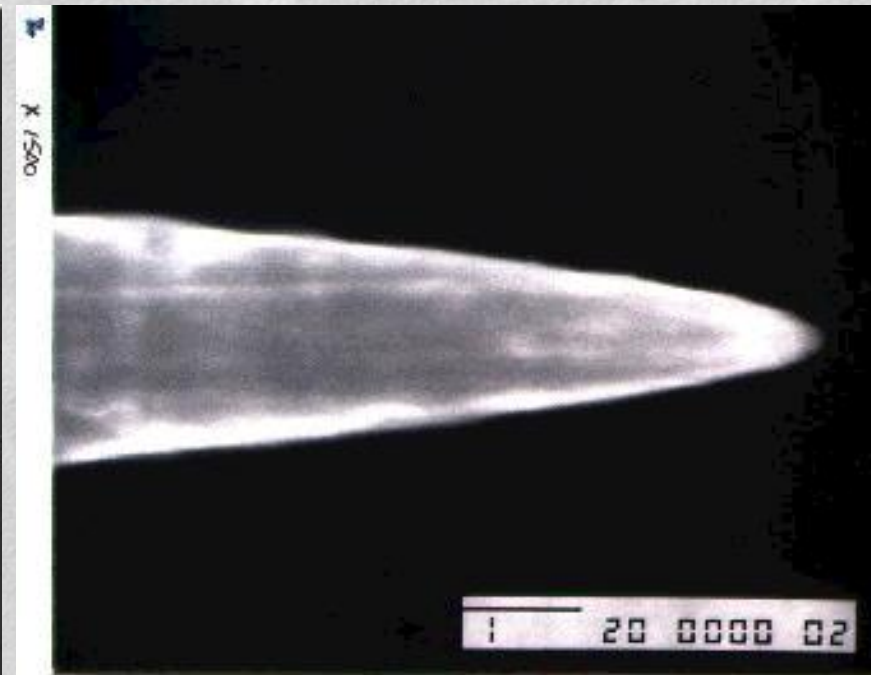
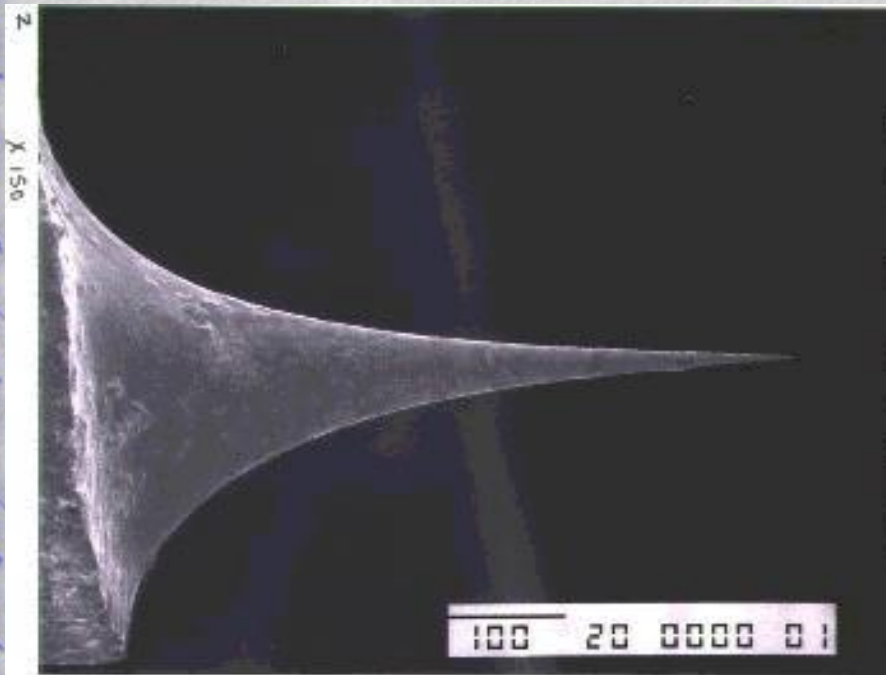
Tip Nanofabrication

- ⌘ The most common types of STM tips are electrochemically etched tungsten wires and cut platinum-iridium wires.
- ⌘ Use of materials that do not oxidize in air such as Pt-Ir or Au might be advantageous as well as the stability of tunneling in air.
- ⌘ However, tungsten is most commonly used in ultra-high vacuum, where oxidation is not a factor.



Tip

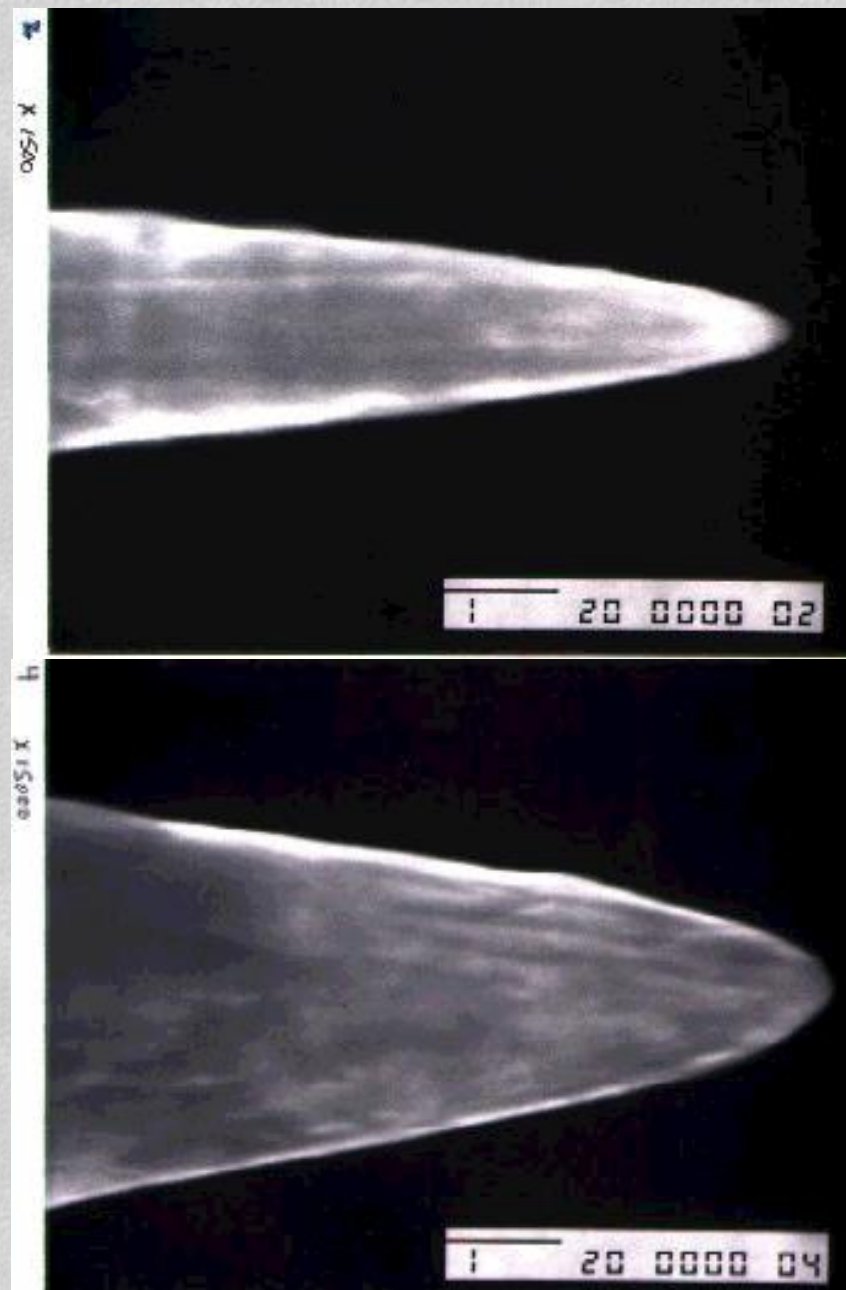
⌘ This tip was made by electro-chemically etching tungsten wire in KOH at 3 Volts and 18 mA for 67 min.



Tips

⌘ KOH at 3 Volts and 18 mA for 67 min.

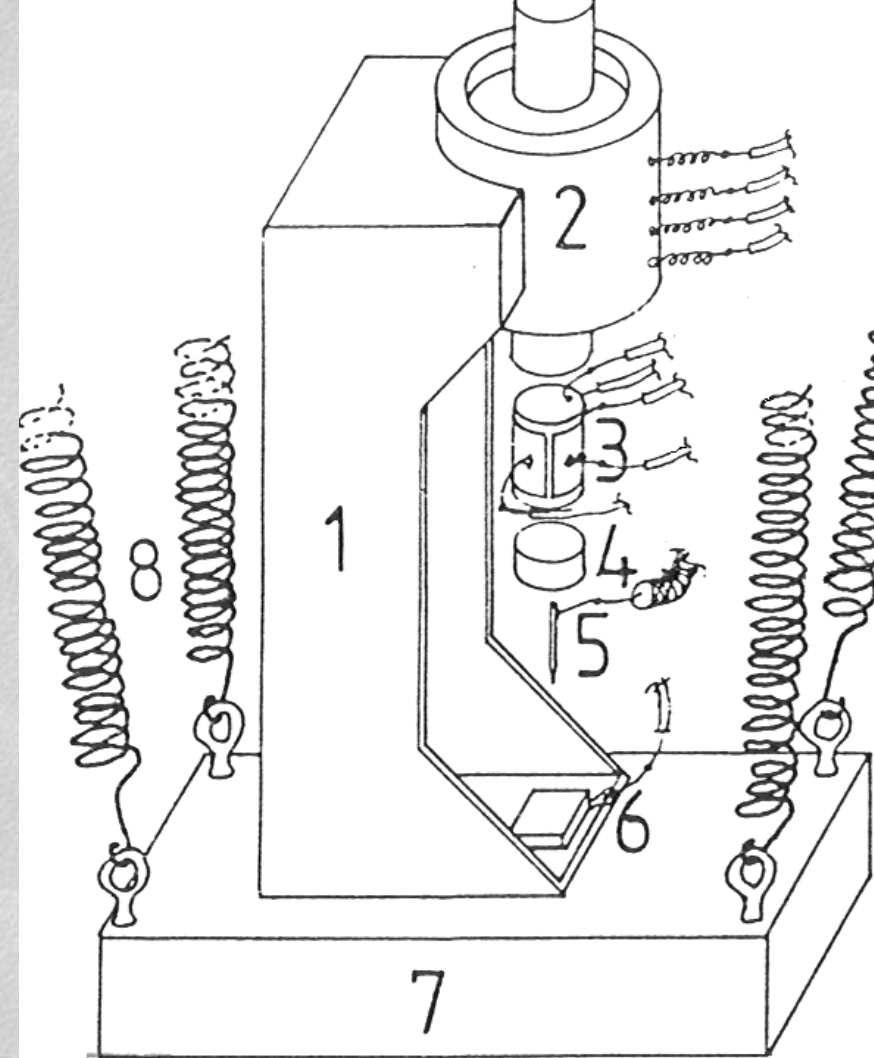
⌘ KOH at 4 Volts and 19 mA for 45 min.



Tip Crashing (shortage of STM)

- ⌘ 在操作过程中，不可避免第发生探针与样品表面碰撞，即使很小心地操作及精心设计电学控制系统。
- ⌘ 优势这种碰撞可提高探针的工作条件，但一般而言会导致探针针尖变钝。

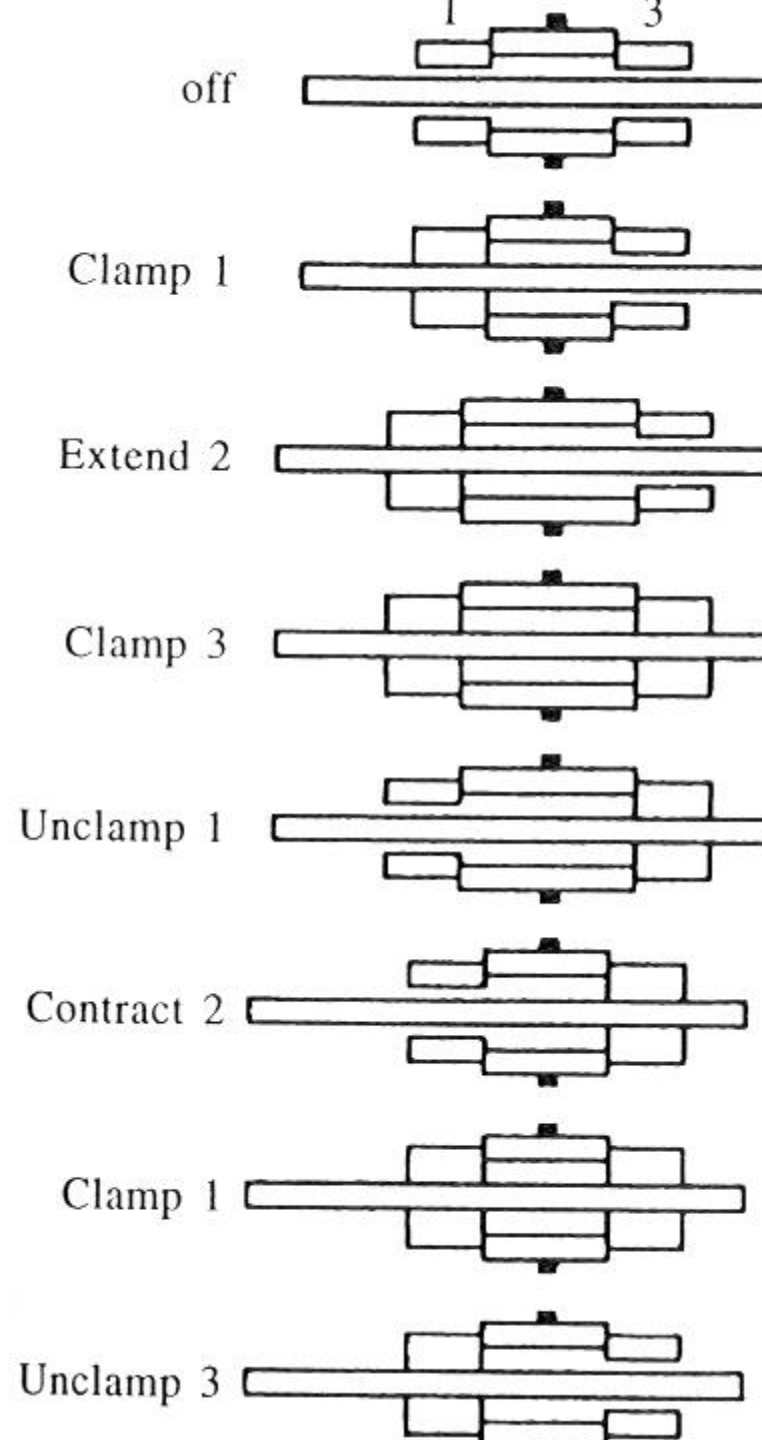
STM Construction



- 1 Light rigid connection between tip and specimen
- 2 Inchworm for tip approach
- 3 Piezo cylinder for control of x and y (scanning) and z (tunneling gap)
- 4 Insulating shield/ tip holder
- 5 Tip with low noise/ bias connection
- 6 Specimen
- 7 High mass base
- 8 Soft springs to damp vibrations
- 9 Electrical connections

粗略地逼近样品表面

探针由设计成柱面夹钳状的压电晶体驱动，通过轴向伸缩及交替反向夹紧动作，可驱动探针以1纳米的步距移动至几个毫米的范围。



探针扫描头设计要求:

- ☒ 高分辨 – 横向(x,y)分辨率 <1 埃 , 垂直分辨率 <0.01 埃(z);
- ☒ 正交性 – 三个方向的运动必须独立, 无相互影响;
- ☒ 线性度高 - 移动量与施加的电压成正比;
- ☒ 机械刚度 – 振动隔离和高反馈性能希望扫描头具有较高的共振频率;
- ☒ 范围大 – 移动范围最好能覆盖整个样片的表面积。

Scanner

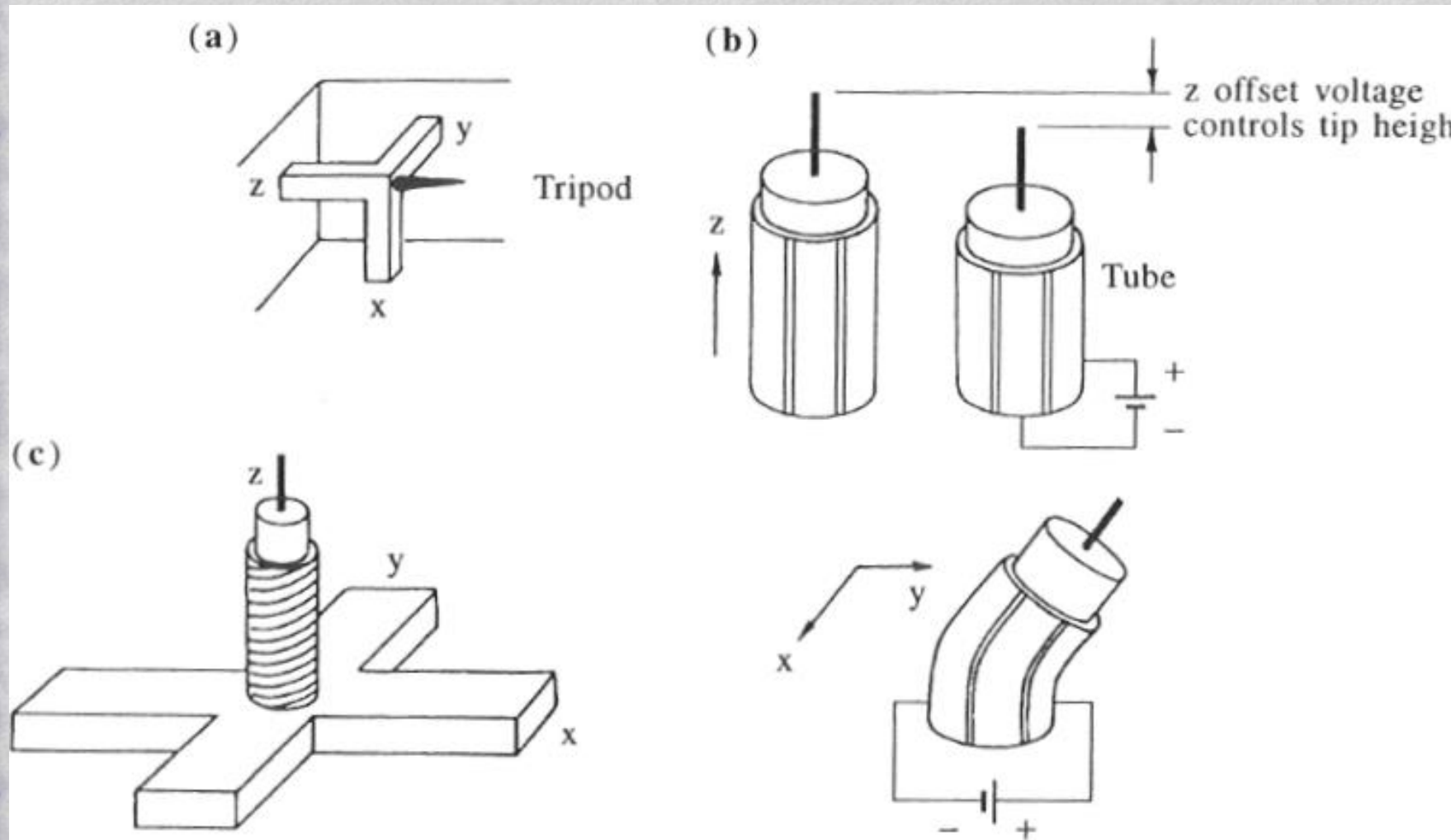
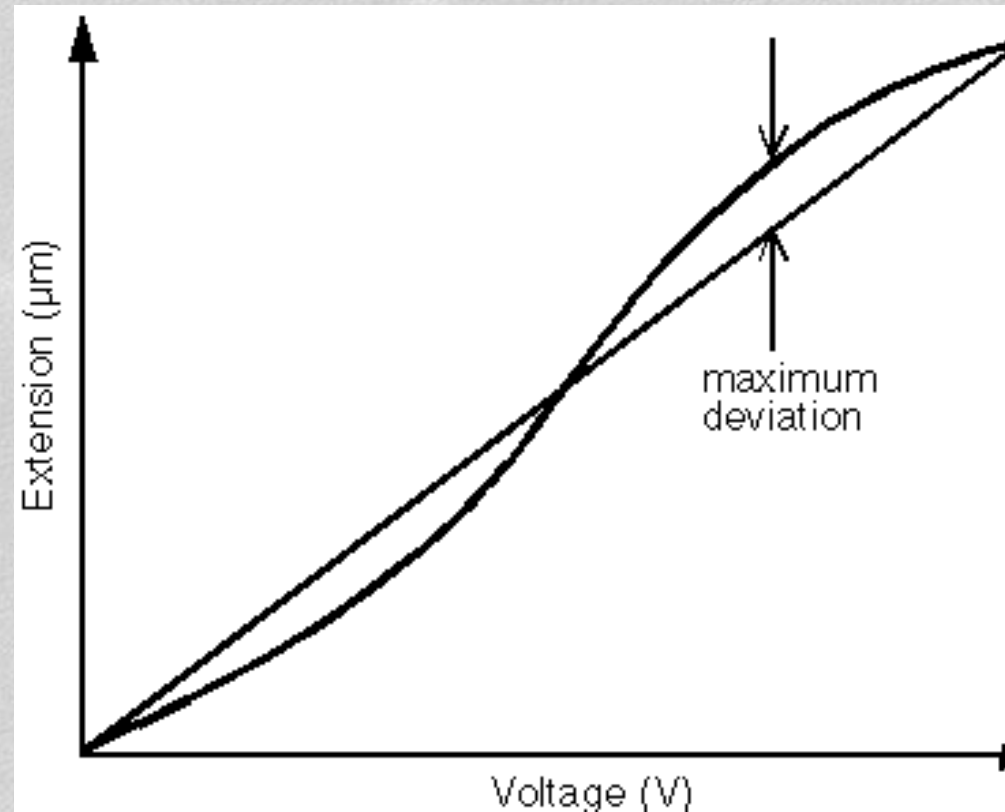


Fig. 4.4. Common three-dimensional scanners: (a) tripod, (b) single tube, and (c) a cross combined with a single tube

Scanner - Nonlinearity

- ⌘ 非线性 – 对应同一电压下，实际移动量与理想移动量的最大比值。
- ⌘ 用百分比表示。
- ⌘ 典型的范围是 2%~ 25%

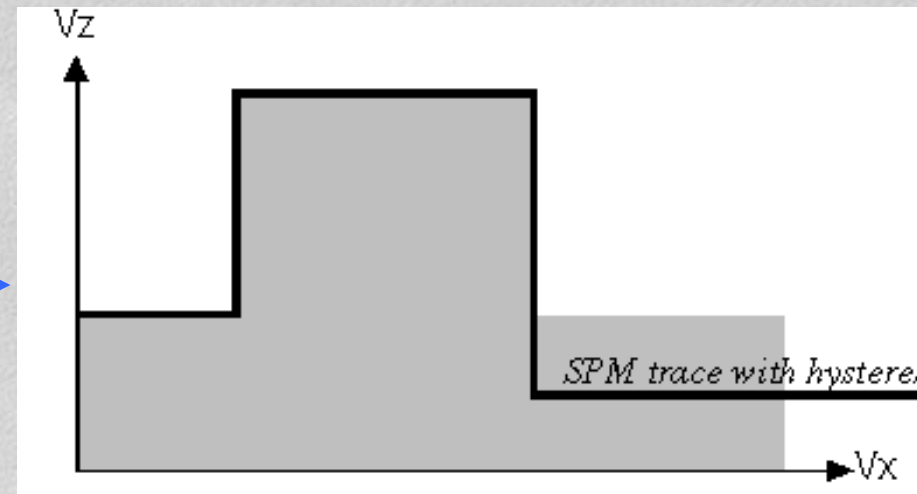
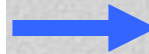
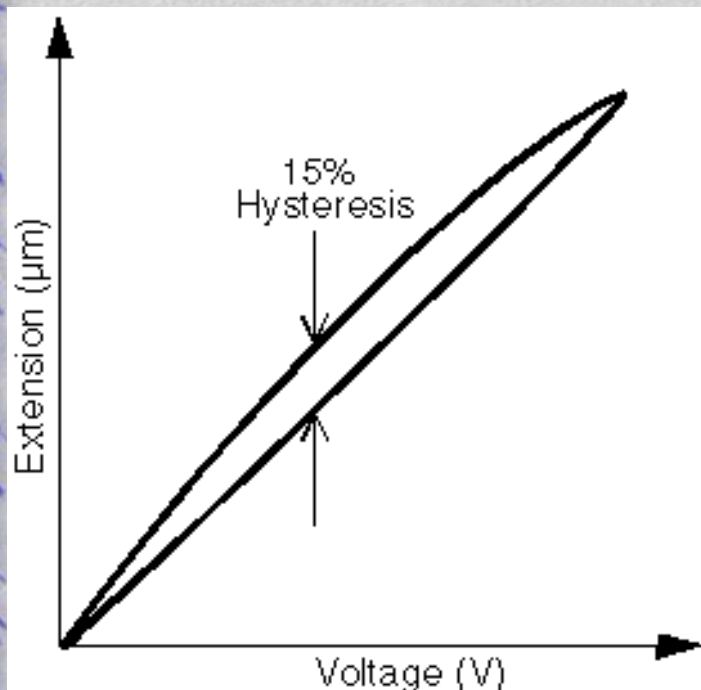


Scanner – Hysteresis (滞后作用)

⌘ 由滞后作用导致的两条发散曲线的最大偏差之比

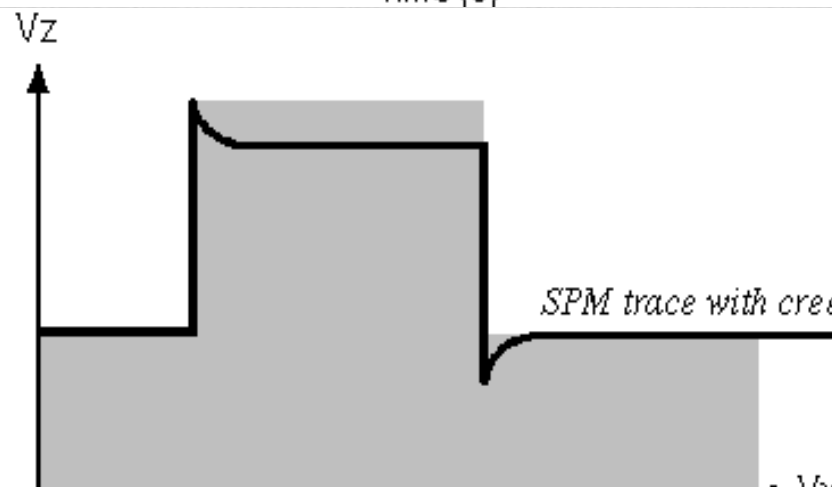
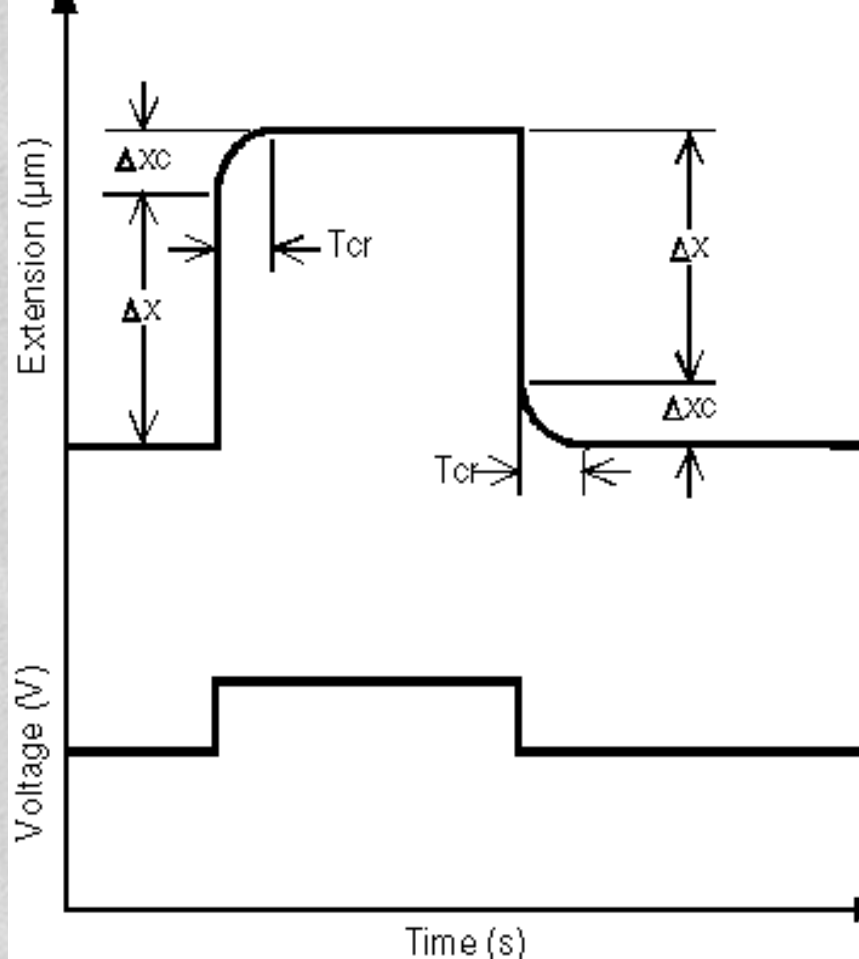
$$Y/Y_{\max}$$

⌘ 最高可达 20%



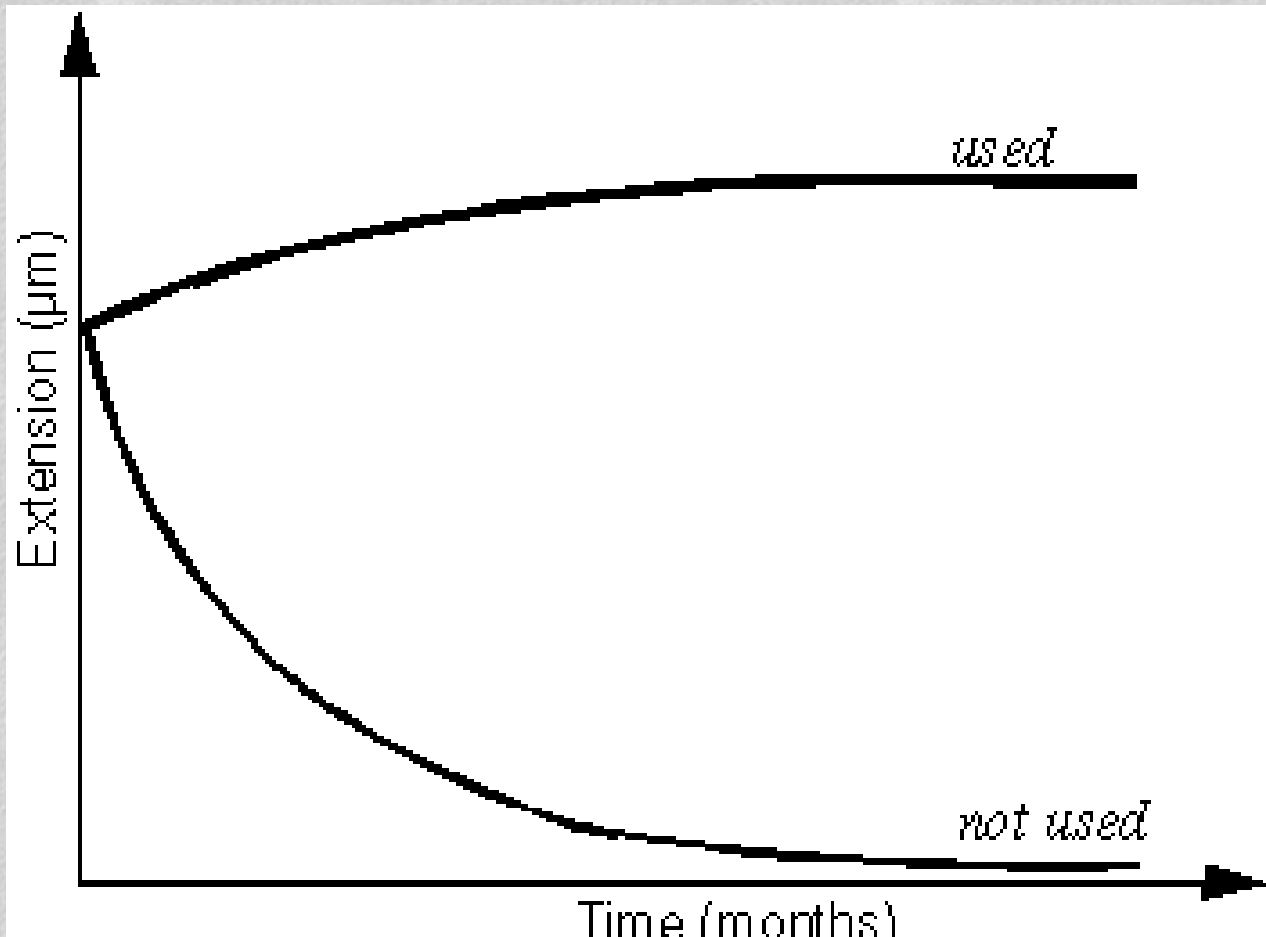
Scanner – 爬行

- ⌘ 爬行 – 驱动电压突然改变时压电材料没有及时作出尺度变化的响应。
- ⌘ 表示为下一个尺度变化与前者的比值。
- ⌘ 典型值为1% ~ 20% 对应的时间变化为10 ~ 100秒。



Scanner – 压电材料老化

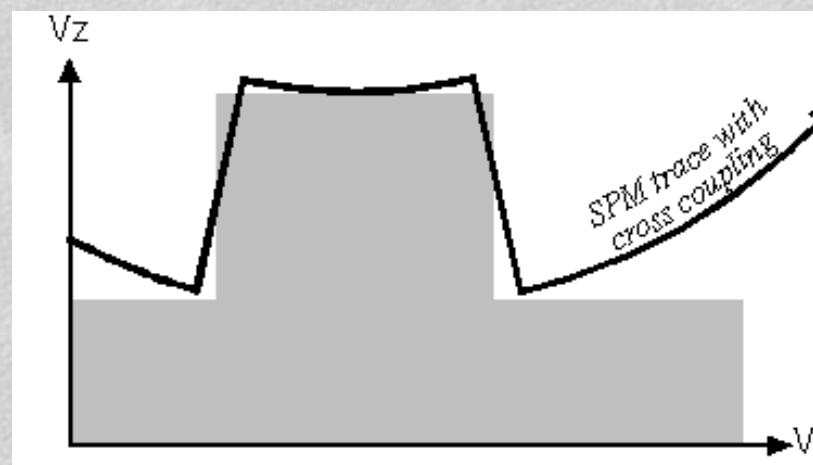
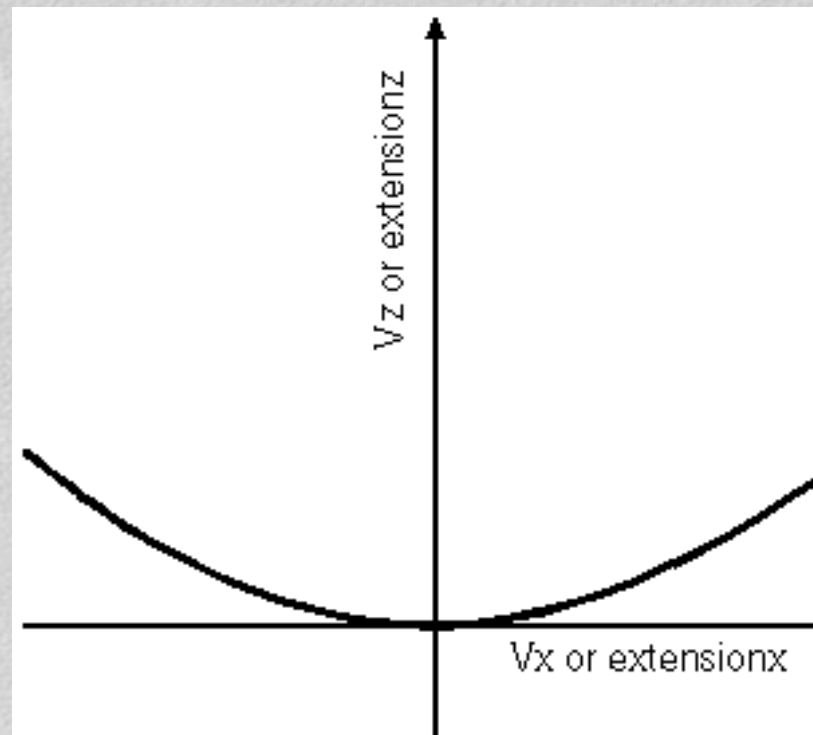
- ⌘ 老化 – 压电材料的应变系数 d 随时用时间发生指数变化。
- ⌘ 老化率为每十年应变系数的改变。



Scanner – 交互耦合

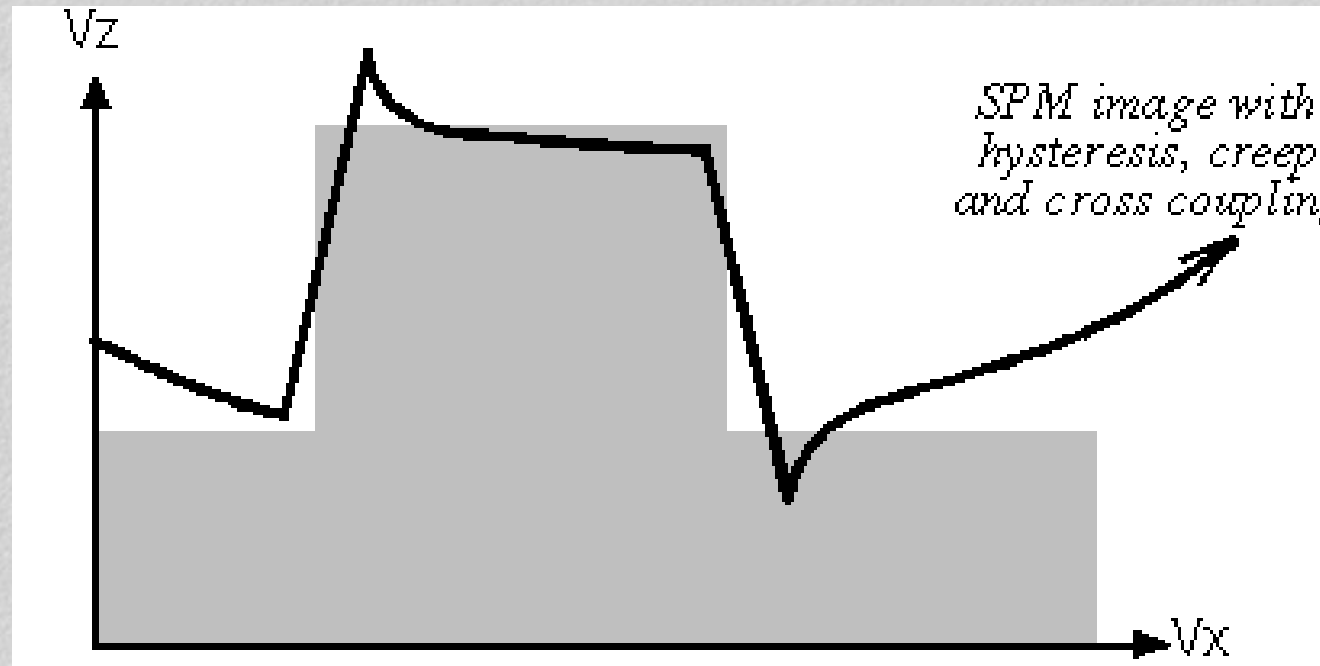
⌘ 交互耦合- 由于X、Y轴的移动导致的Z方向的伪移动。

⌘ 原因是电场的非均匀以及扫描头制作及装配时的几何误差。



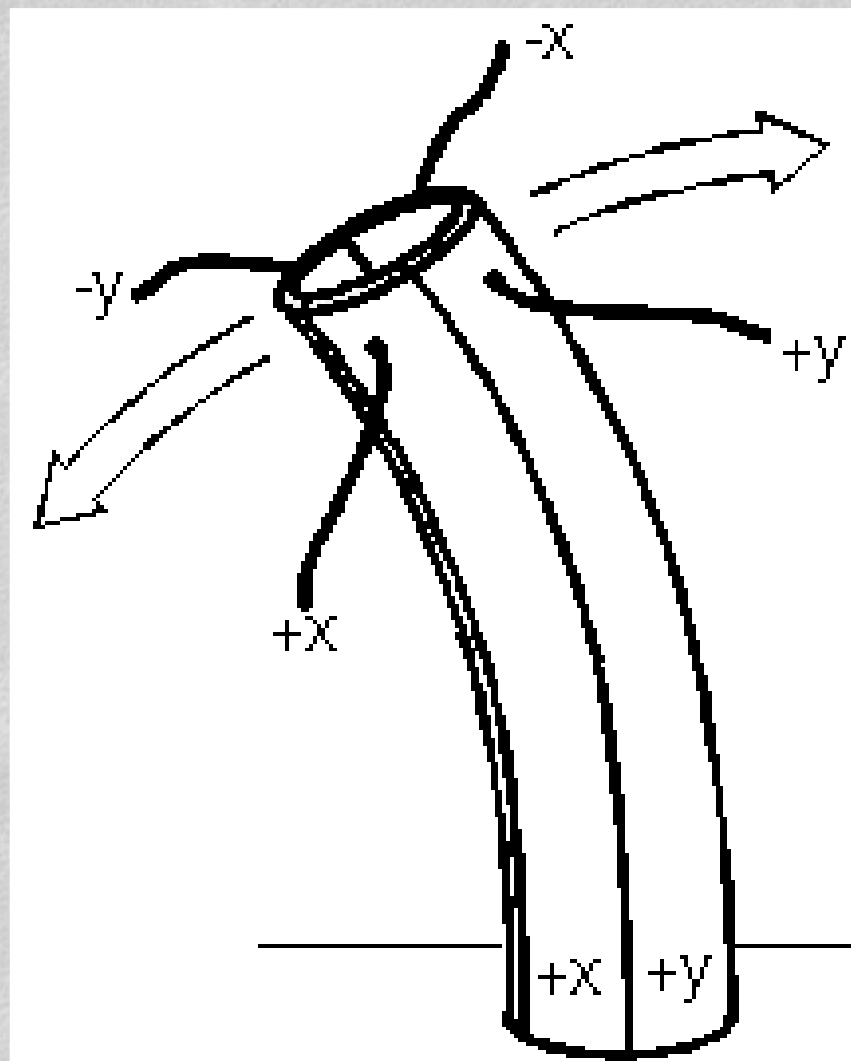
Scanner – 混合影响

- ⌘ 扫描头移动滞后导致沿样品侧壁上下移动时产生的不同程度的斜坡，原因是探针向上所需的驱动电压小于向下的步距所需的电压。
- ⌘ 爬行导致的指数衰减造成顶部左侧移动步距高于右侧。
- ⌘ 交互耦合：导致整个测量轮廓弯曲。



Scanner – 工作原理

- ⌘ 简单的套管设计；
- ⌘ 扫描头是中空的；
- ⌘ 电极附着在套管的外侧，加电驱动使之产生 $+x$, $+y$, $-x$, $-y$ 方向的移动。



Scanner – 工作原理

最大扫描范围由压电扫描头决定，具体取决于下列因素：

- ☒ 套管长度；
- ☒ 套管直径；
- ☒ 套管壁厚；
- ☒ 压电陶瓷的应变系数。

误差 & 振动

⌘ 振动、热漂移及电学系统噪声限值了探针-样品间隙的精确控制。

⌘ 振动源有三个：

☒ 房间的声波振动；

☒ 系统内部共振；

☒ 外部地板的振动

振动隔离措施

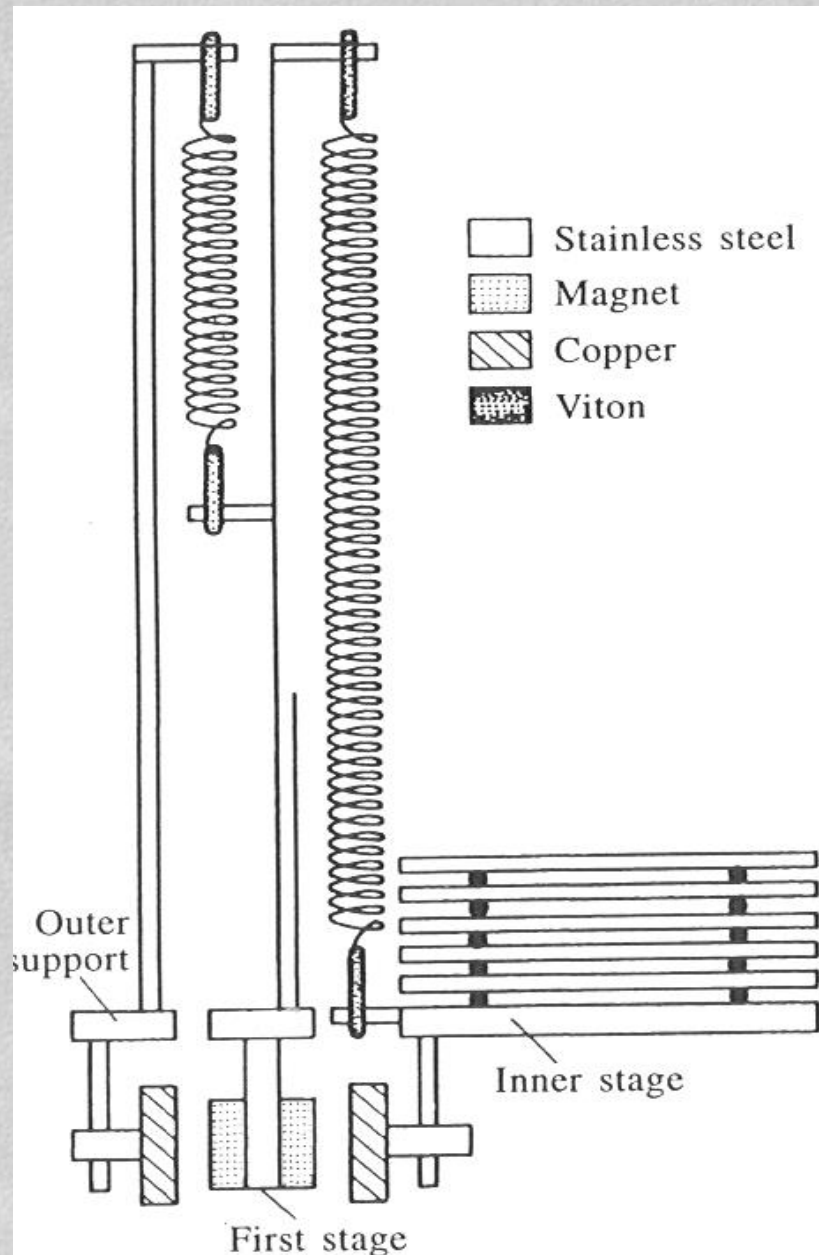
⌘ 系统安置于安静的房间隔离声波的影响

⌘ 第二个影响因素可通过提高共振频率亦即系统扫描频率来减小：扫描头设计成即轻刚性又好，将逐渐设计成更紧凑化。

振动隔离

⌘针对第三个问题，将STM放在大质量的平台如花岗岩台面上，用较软的弹簧将二者相连。

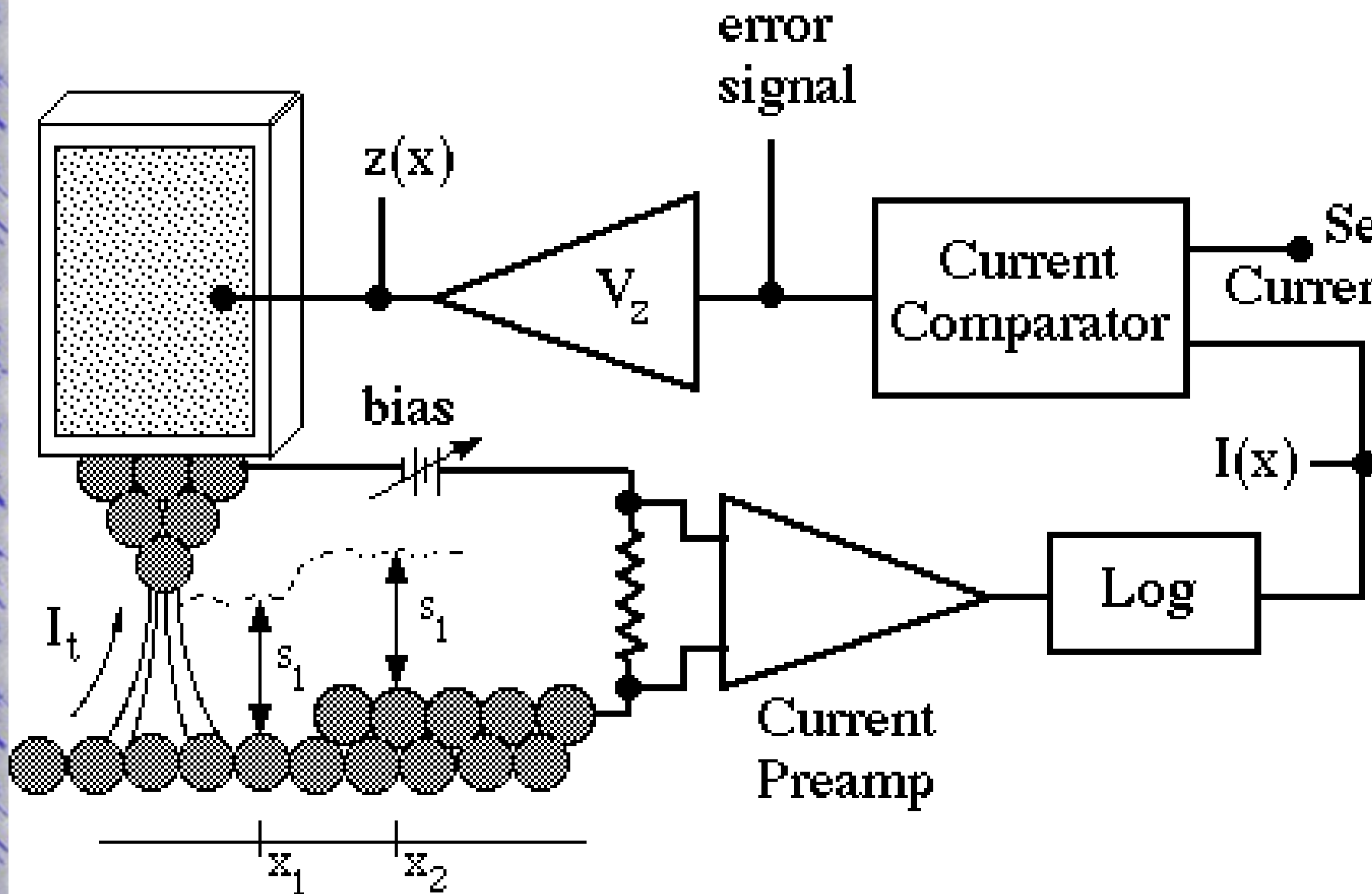
⌘或者：安置于很深的地下室里。



电学噪声问题

- ⌘ 控制高灵敏器件需要从设计上仔细考虑的因素是电学噪声和温度漂移。
- ⌘ 目前的最新技术可提供的原件具有长时间内的超低噪声和最小的温度漂移。
- ⌘ 然而，电路布局及屏蔽是决定其性能的关键因素。
- ⌘ 对地低电压(传感隧道电流)，高电压(压电控制)，及数字信号(计算机控制及图像处理)应彼此分离，信号线应尽可能远。

Electronics



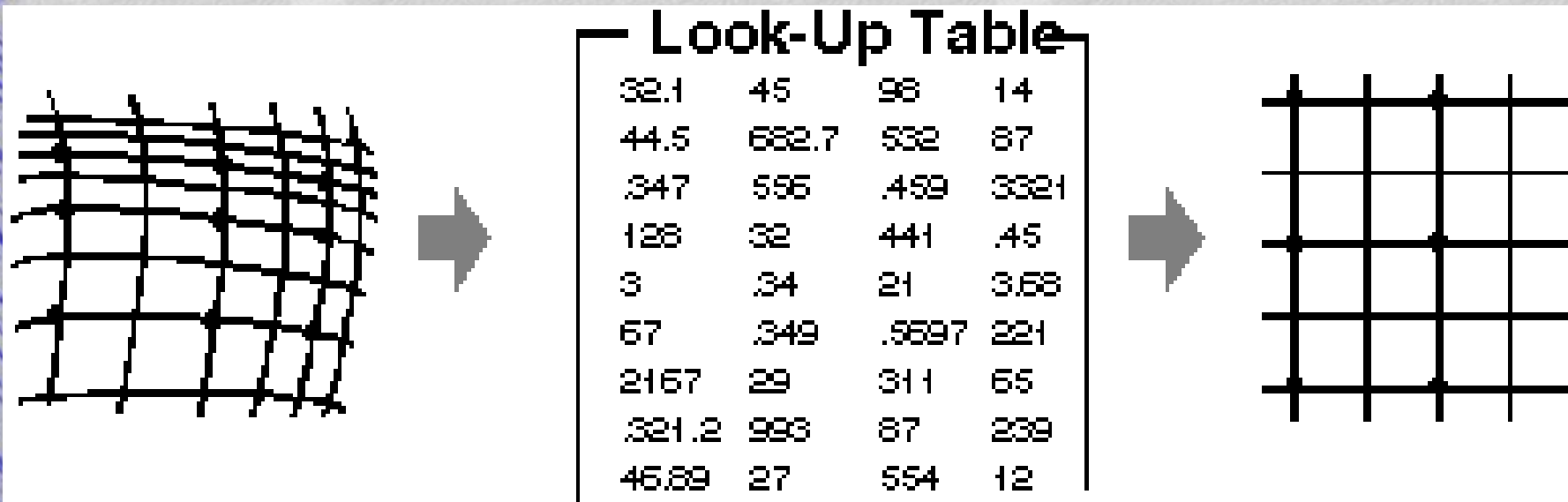
Calibration

校准方法如下：

- 精准的机械量块；
- 已知结构的成像结果；
- 软件校准

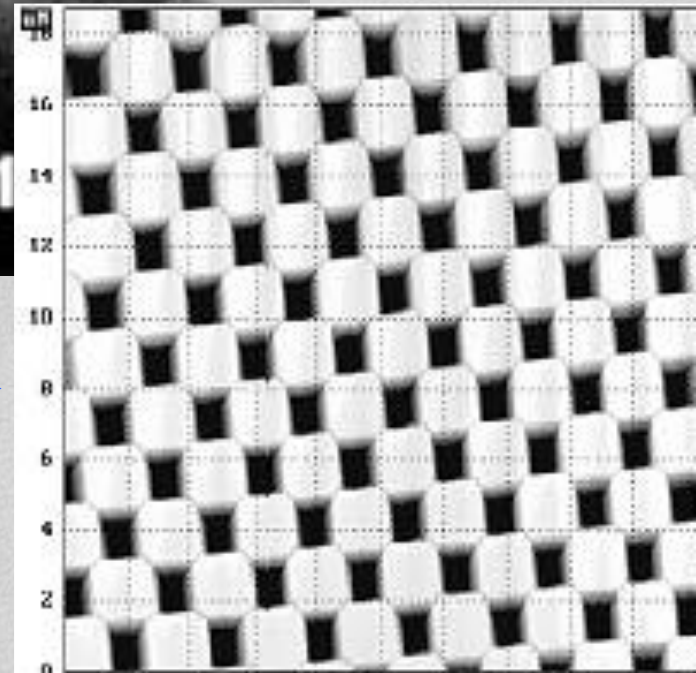
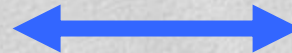
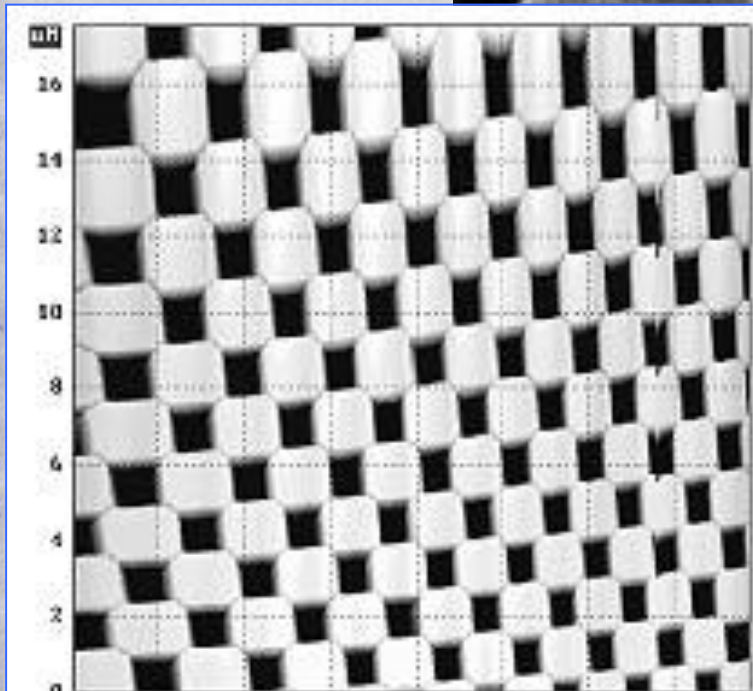
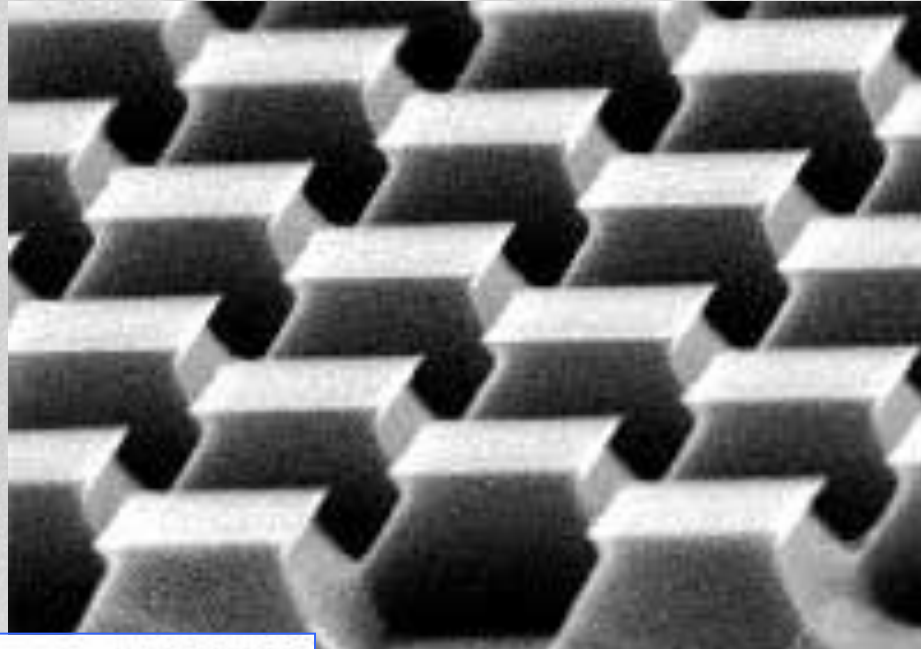
硬件校准

- ⌘ 常用校准非线性误差的技术是扫描校准光栅。
- ⌘ 光栅的形状和尺寸已知，系统调整测量的数据并与其期望的数值相匹配。
- ⌘ 数据以查找表格的形式保存。



- ⌘ 也可用软件算法建模校准扫描头套管的非线性误差。

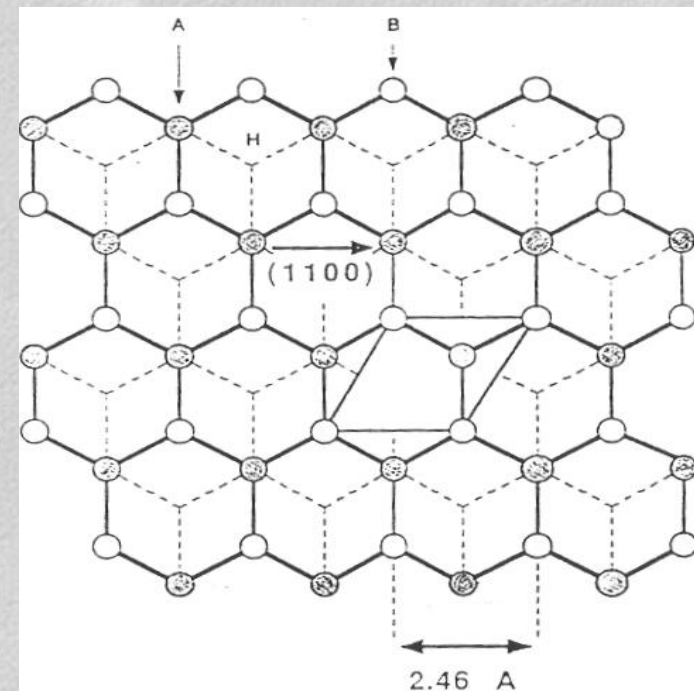
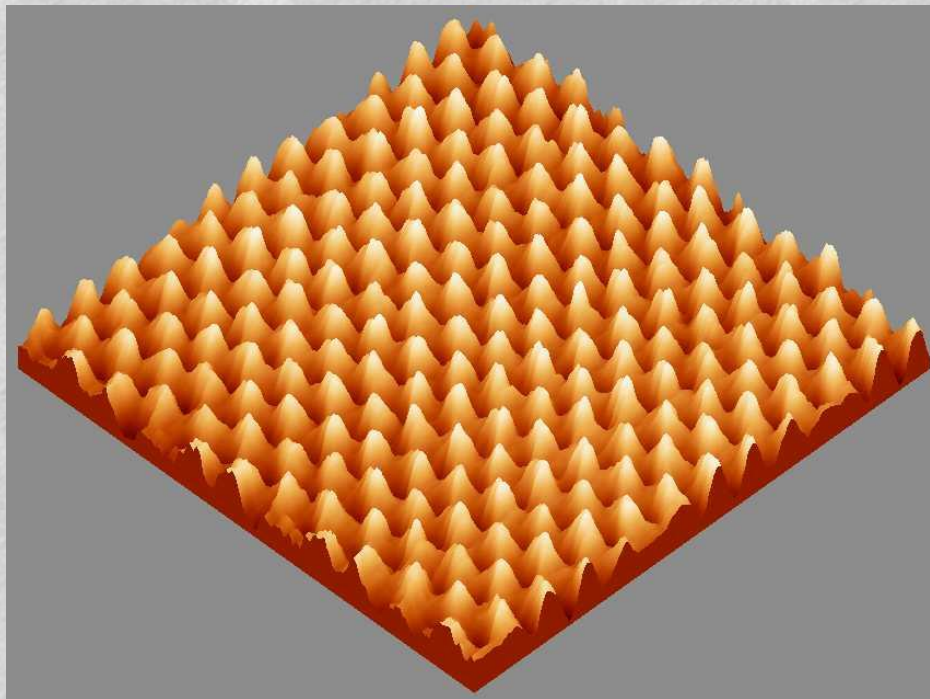
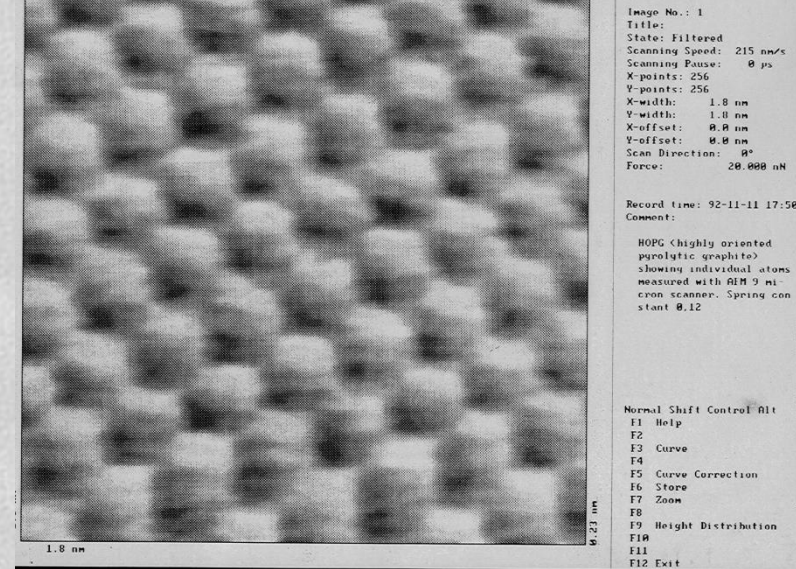
Hardware Calibration



软件校准

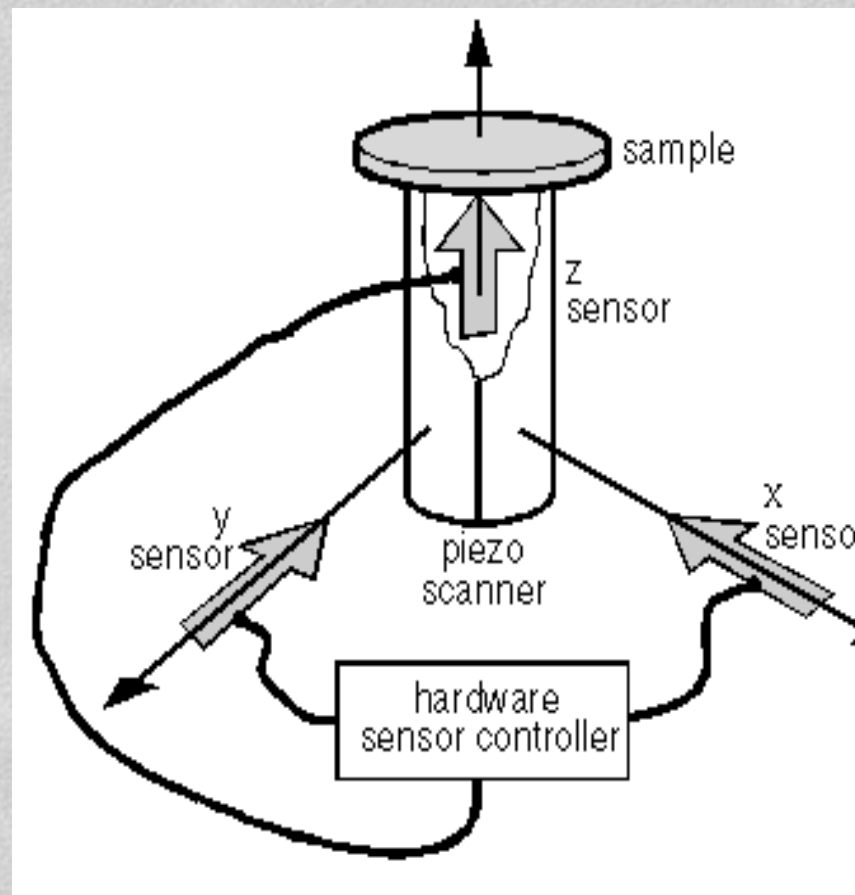
- ⌘ 软件校对方法相对简单且廉价。
- ⌘ 主要不足是只能部分补偿扫描头非线性误差。
- ⌘ 校准精度主要取决于：
 - ⊡ 扫描速度
 - ⊡ 扫描方向

Calibration : HOPG

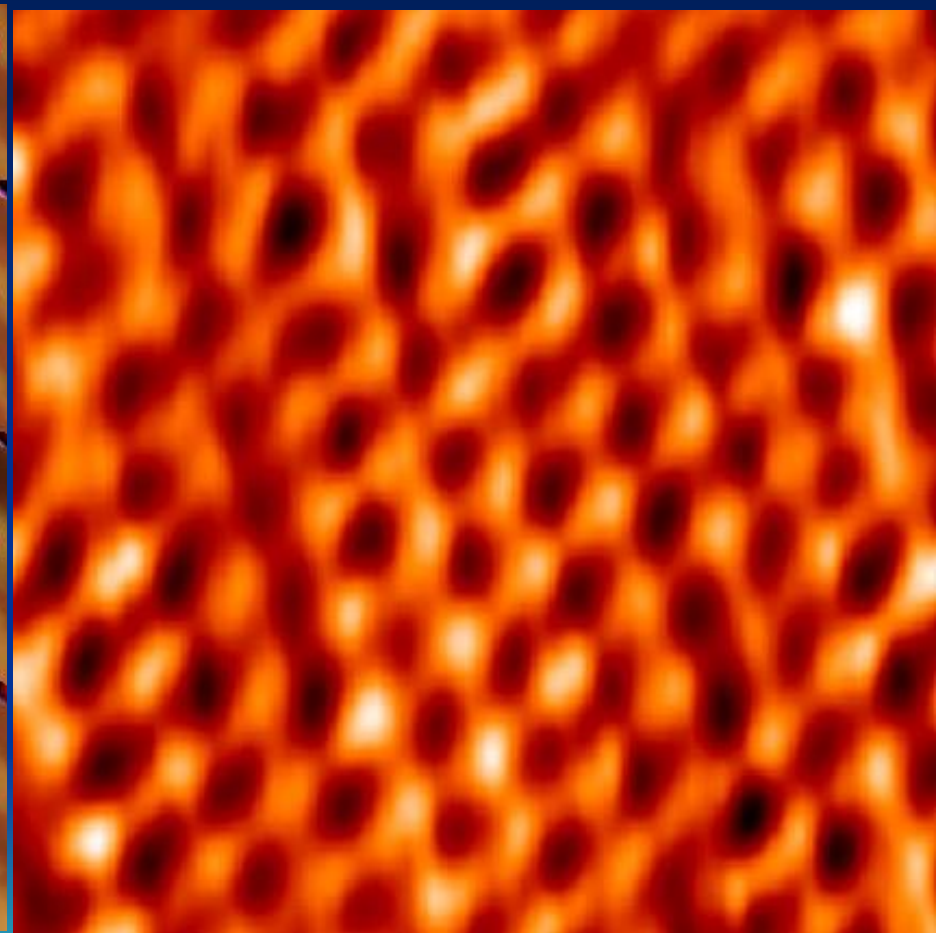
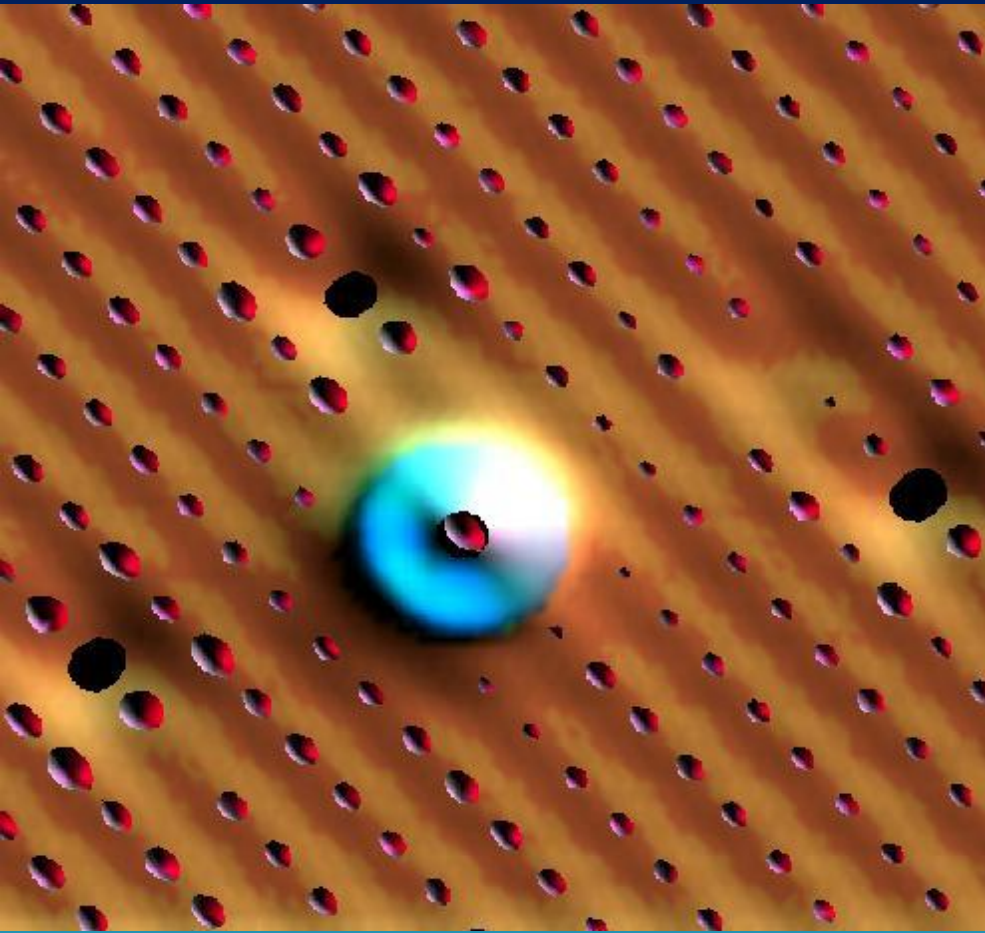


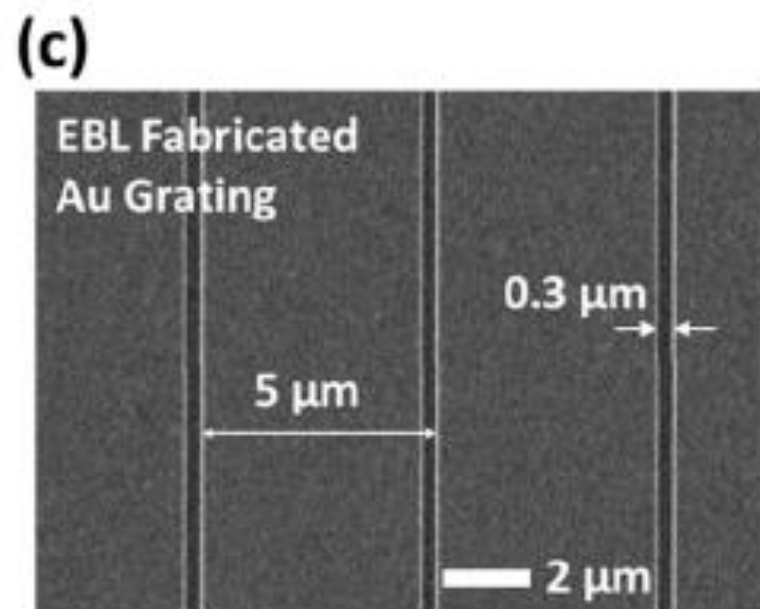
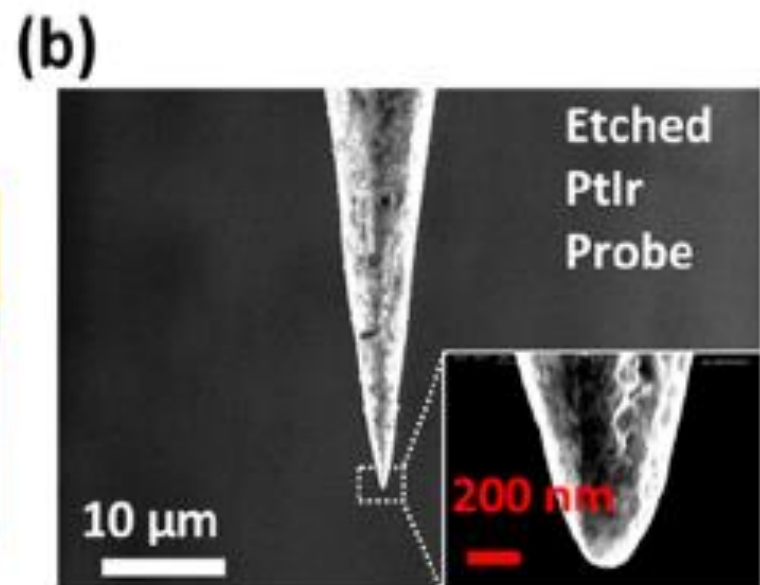
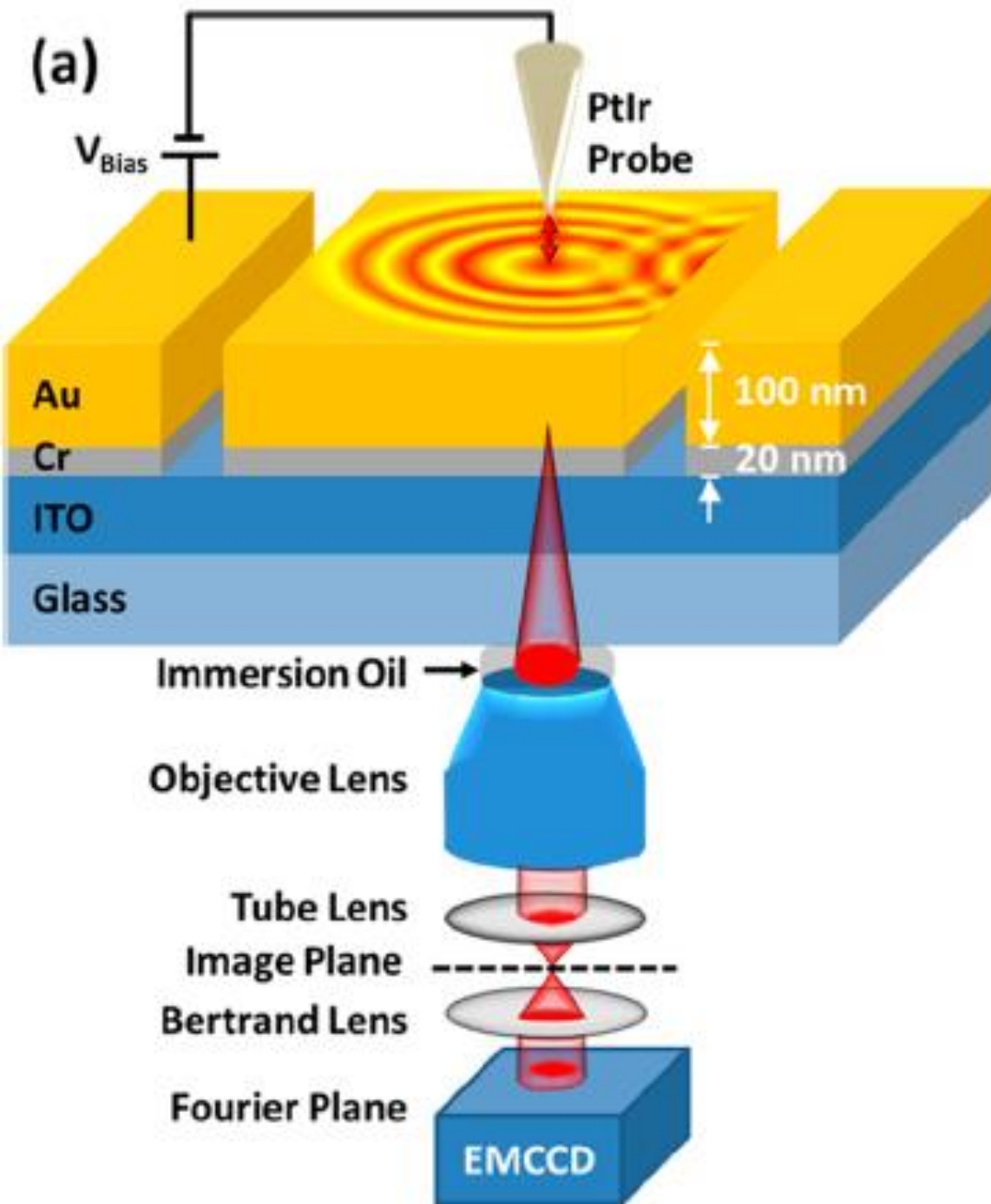
使用位移传感器校准

- ⌘ 附着的三个传感器分别负责校准三个移动坐标轴。
- ⌘ 反馈系统施加电压于扫描头上并驱动至期望的位置。借助于硬件传感器可将总的非线性误差减少至小于1%。



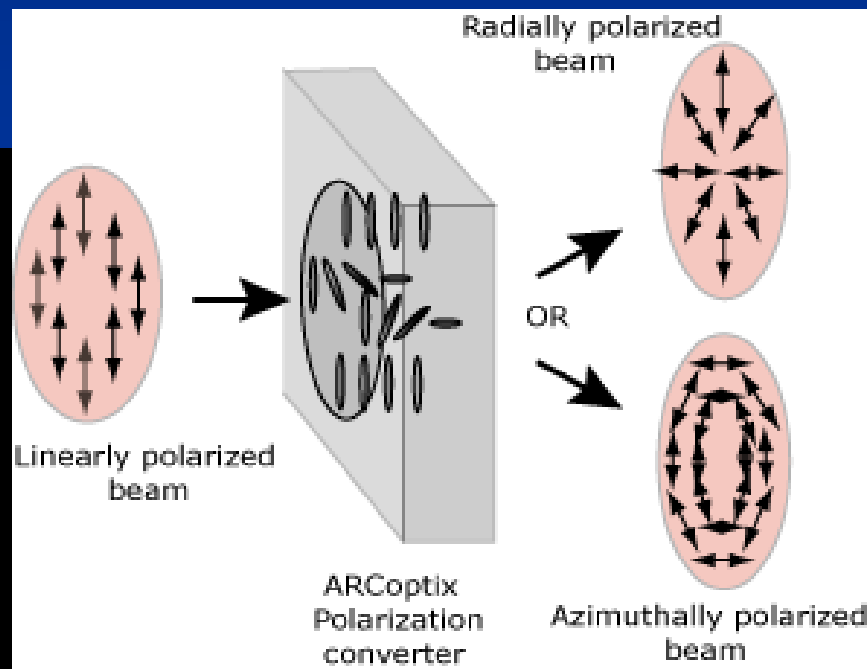
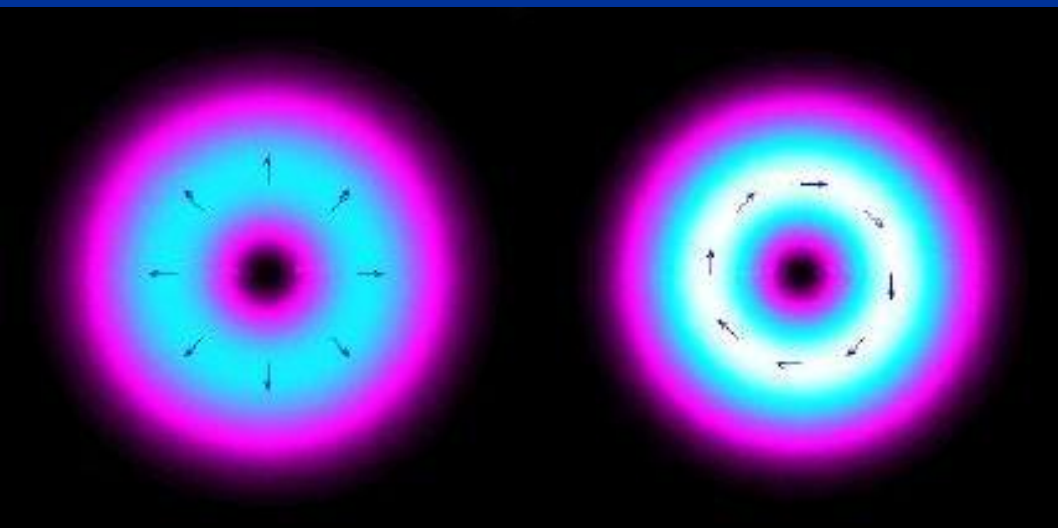
Applications



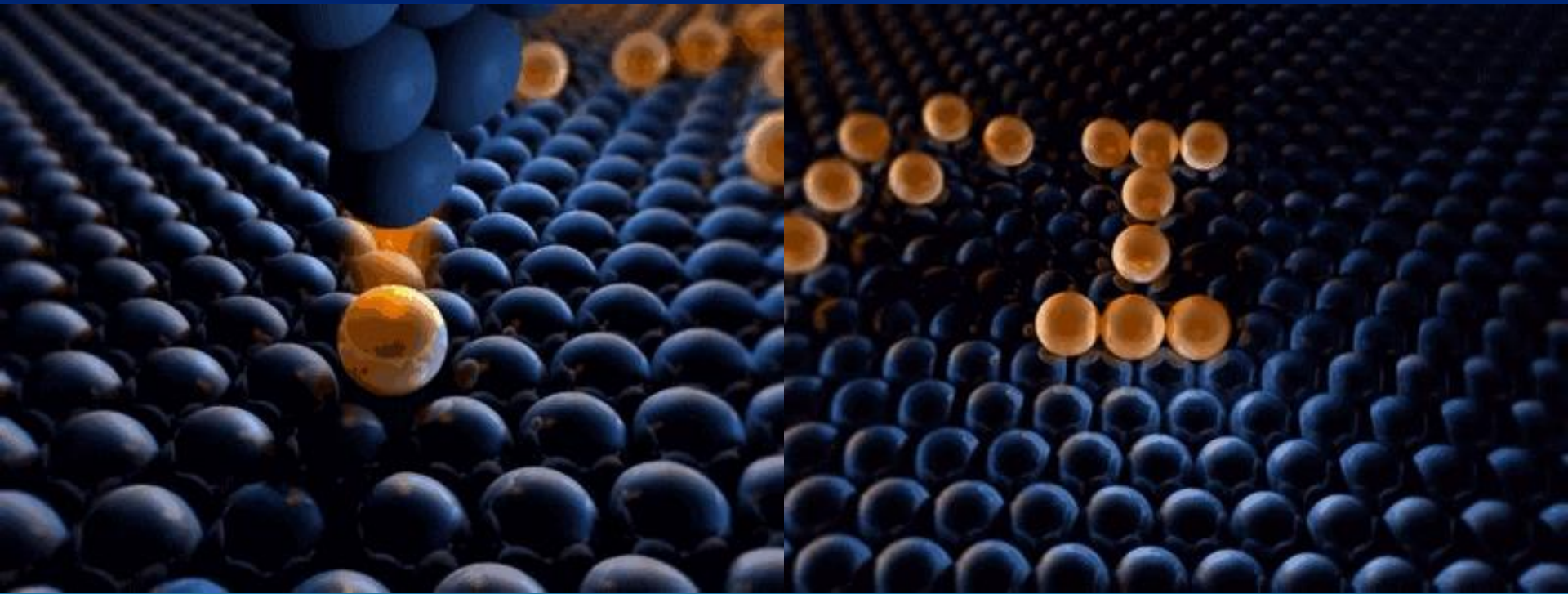


径向偏振光束

径向偏振光束(radial polarization)是一种新颖的、形式独特的偏振光模式,其偏振机制与传统的线偏振和圆偏振有所不同。径向偏振光属于轴对称偏振,属于各向异性偏振形式。

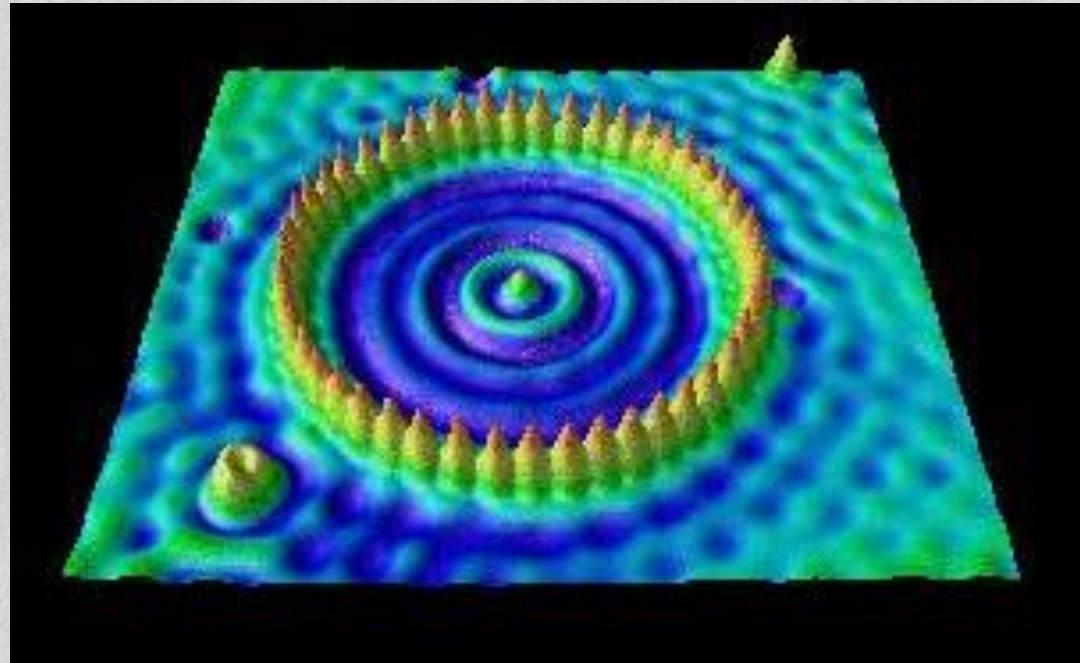


单原子操纵：用探针把单个原子从表面提起而脱离表面束缚，横向移动到预定位置，再把原子从探针重新释放到表面上，可以获得原子级别的图案。



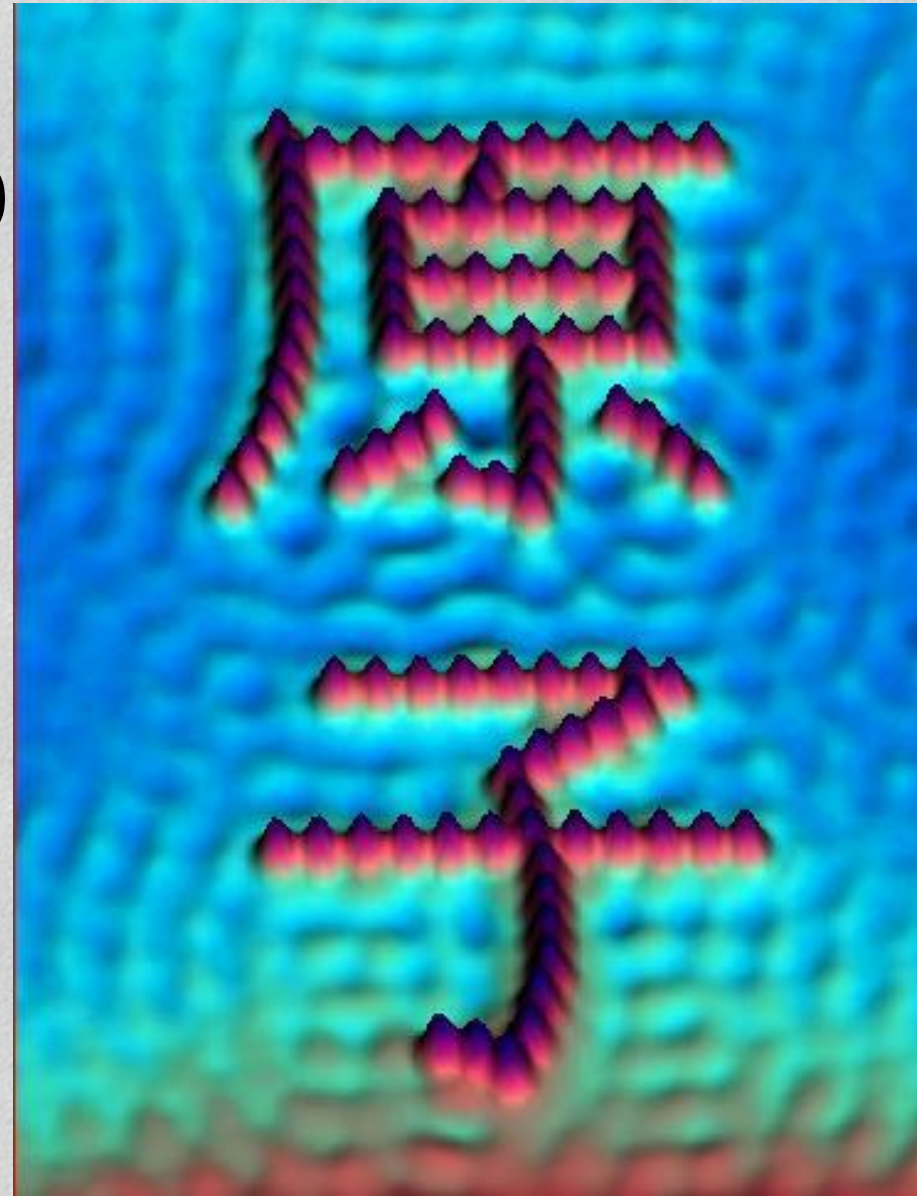
Applications

- ⌘ Here is a STM image showing iron atoms adsorb on a copper (111) surface forming a "quantum corral" in a very low temperature (4K).
- ⌘ Actually, the image shows the contour of the local density of electron states. The corral is about 14.3 nm in diameter.



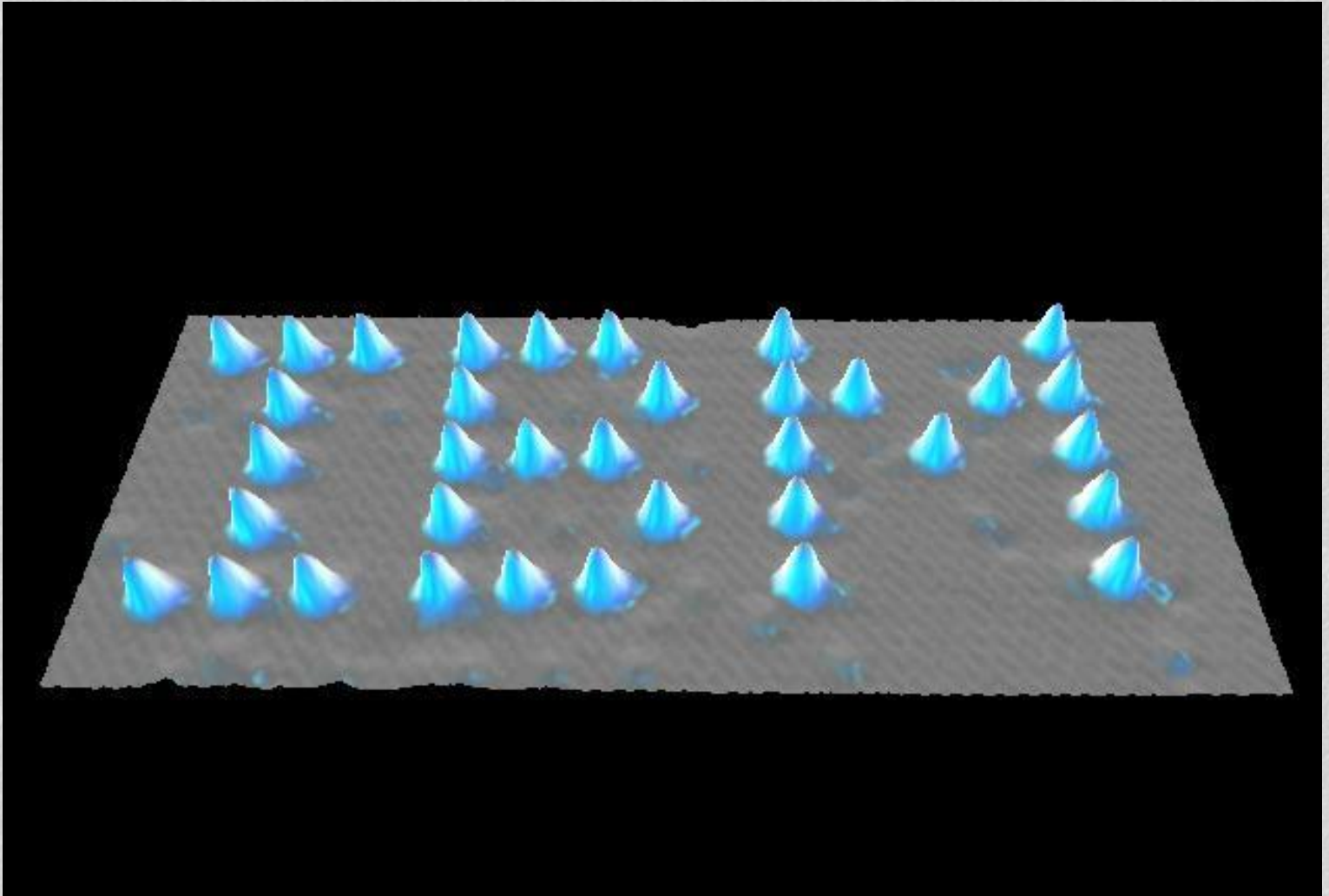
Applications : Nanotechnology

⌘ Iron on Copper (111)



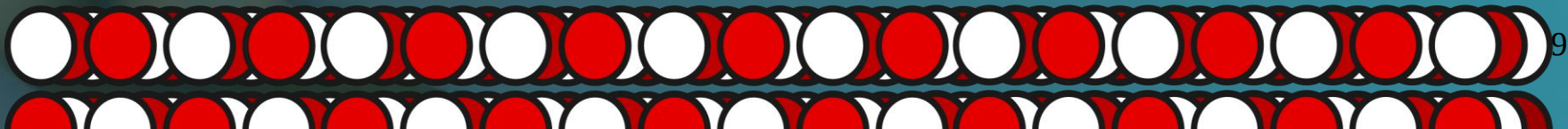
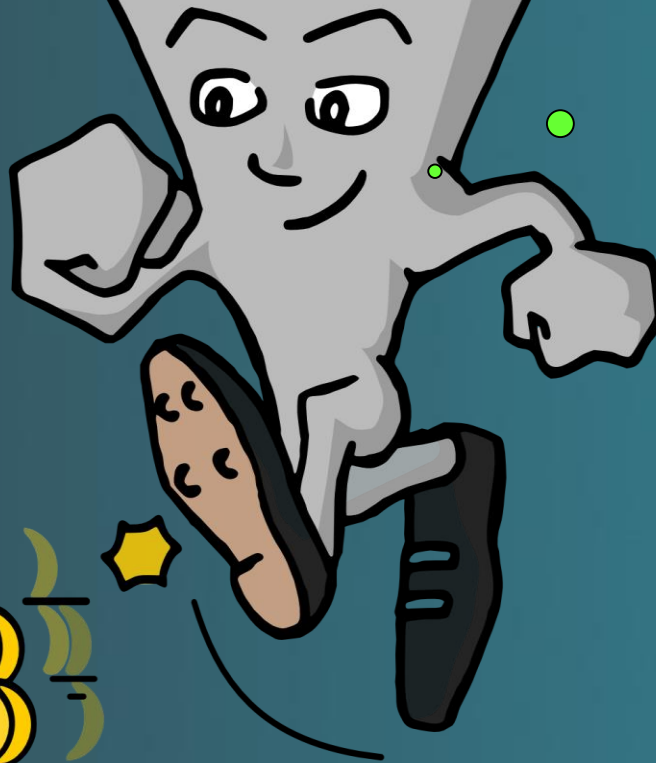
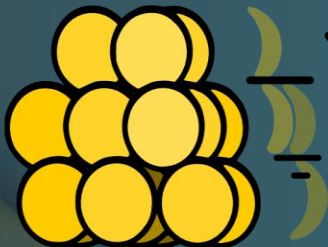
Applications : Nanotechnology

⌘ Xenon atoms on Nickel (110)



SPM

Bye-bye!!



Techniques

Table 1 : Characteristics of Common Techniques for Imaging and Measuring Surface Morphology

	Optical Microscope	SEM	SPM
Sample operating environment	ambient air, liquid, or vacuum	vacuum*	ambient air, liquid, or vacuum
Depth of field	small		
Depth of focus	medium		
Resolution: x,y	1.0 μm		
Resolution: z	N/A		
Effective Magnification	1X-2x10 ³ X		
Sample preparation requirement	little		
Characteristics required of sample	sample must be completely transparent to wavelength of light		

* Environmental SEMS can be operated at higher pressures

