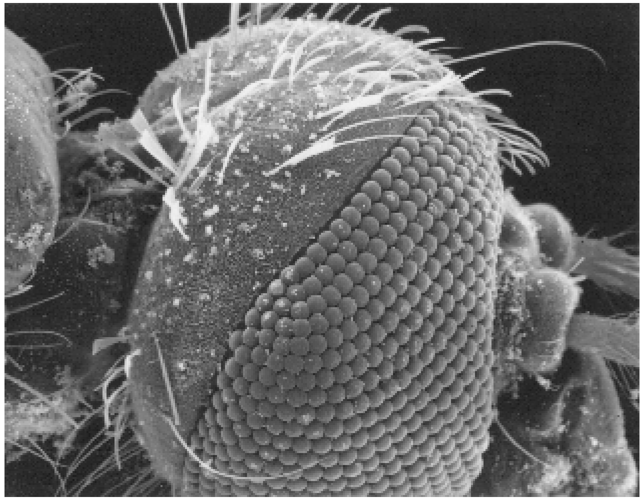
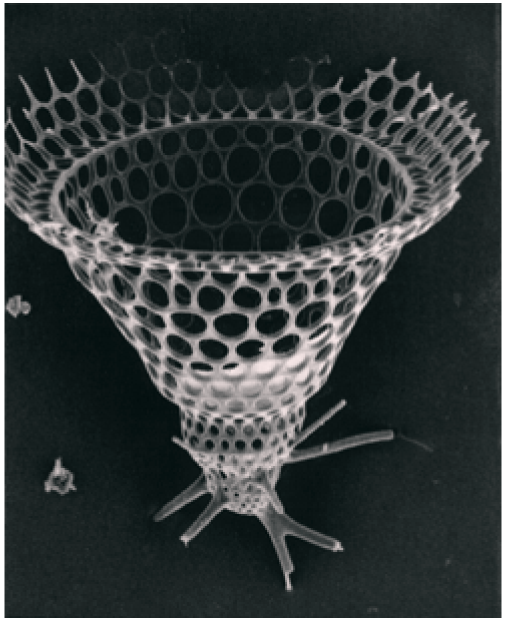
表面 分析中的电与磁

张增明

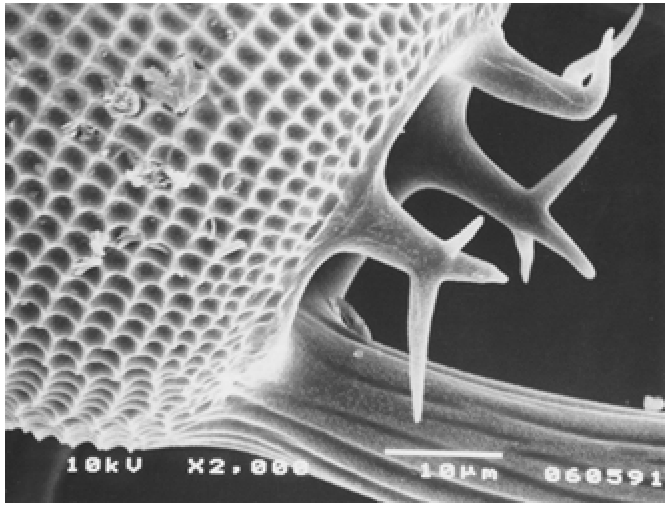
2006年12月23日



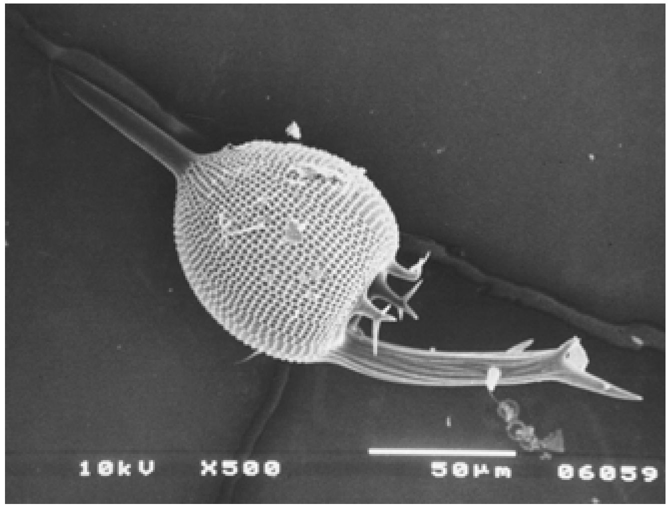
蚊子头部



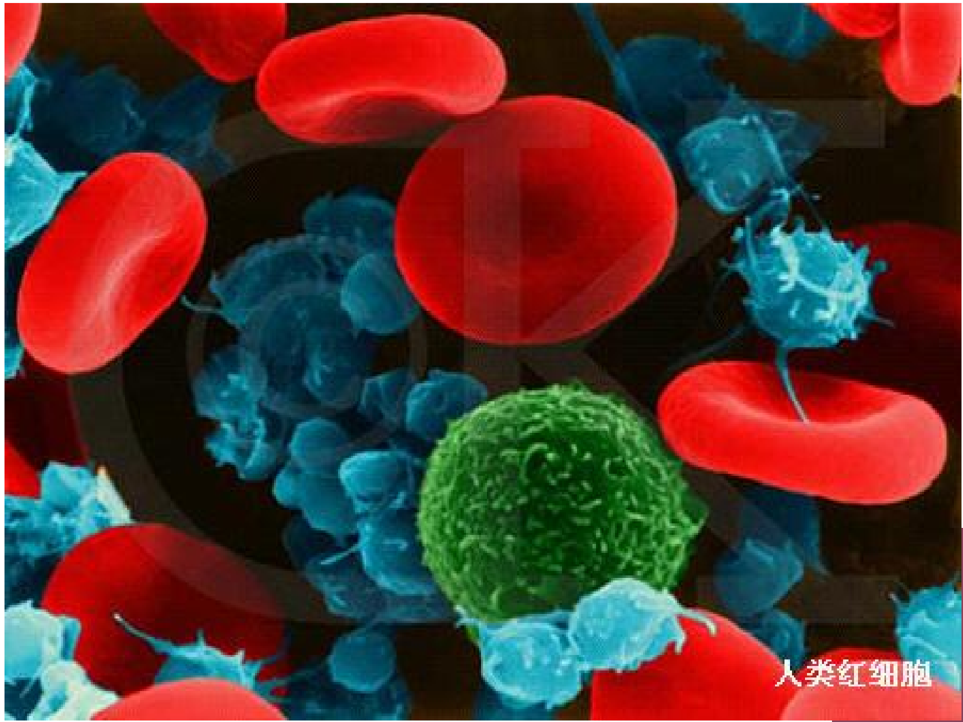
散线虫骨骼



单细胞散线虫



单细胞散线虫


人类红细胞


酵母

内容

- 什么是表面?
- 表面分析目标
- 表面分析手段
  - 成像分析
  - 谱分析

  表面分析中电与磁

表面的概念

物质同气体或真空的界面称为表面

固体表面
- 表面的第一原子层
- 上面几个原子
- 厚度达几微米的表面层

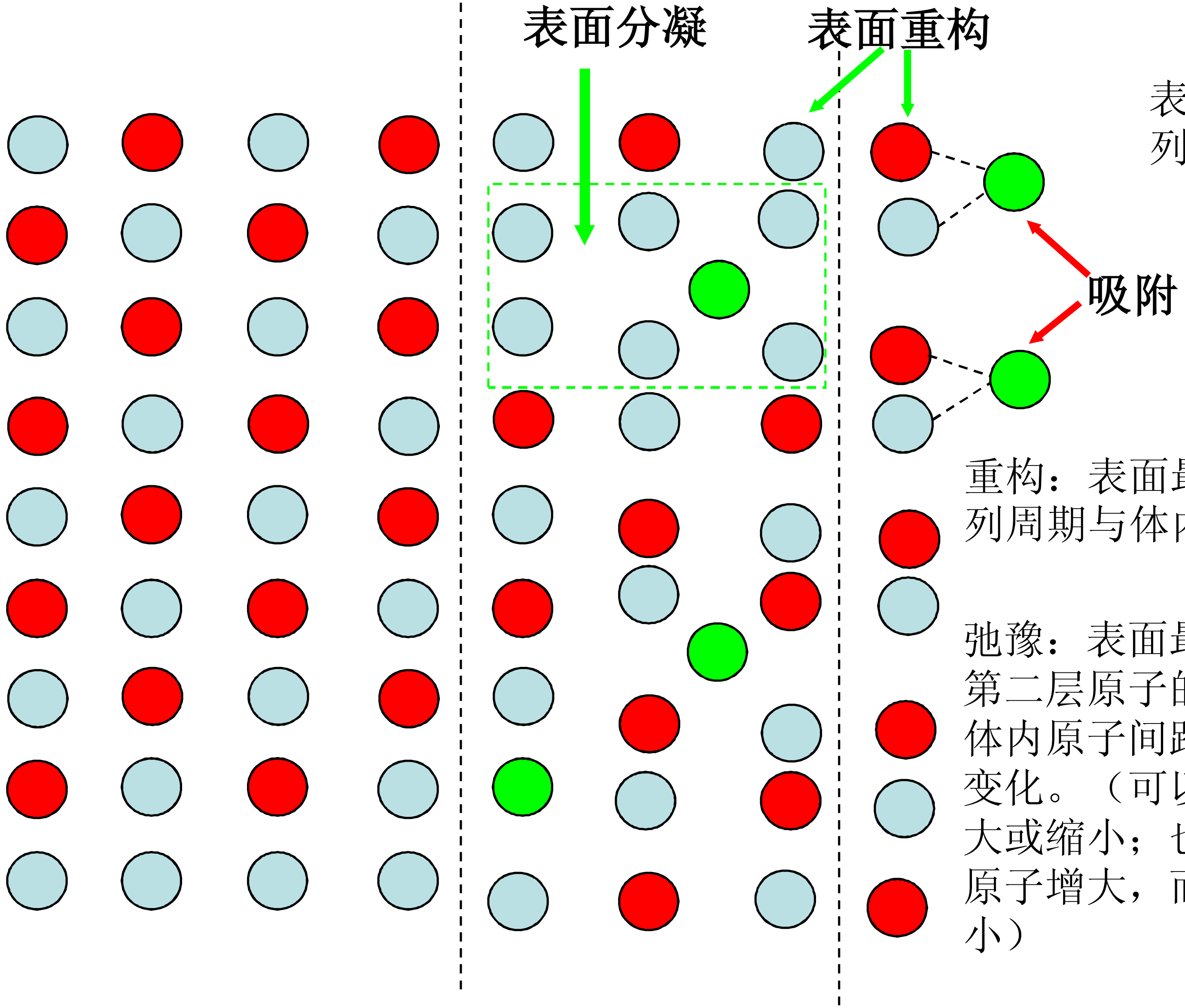
表面是固体的终端

物理化学性质和体内不同
- 化学组分
- 原子排列
- 原子振动状态

悬空键 → 活跃的化学性质

固体内部三维周期势场在表面中断
- 力学
- 光学
- 电磁
- 电子
- 化学性质

实际表面



表面的原子排列与体内不同

重构：表面最外层原子排列周期与体内不一样。

弛豫：表面最外层原子和第二层原子的间的距离与体内原子间距离相比有了变化。（可以是间距的增大或缩小；也可以是有些原子增大，而有些原子缩小）

表面分析手段

表面组分分析

- X射线光电子谱：XPS/ESCA
- 俄歇电子能谱：AES
- 二次离子质谱：SIMS
- 离子散射谱：ISS

表面结构分析

- 低能电子衍射：LEED
- 光电子衍射：XPD
- 扫描隧道显微镜：STM
- 原子力显微镜：AFM
- 广延X射线吸收精细结构：EXAFS
- 扩展能量损失精细结构：EELFS

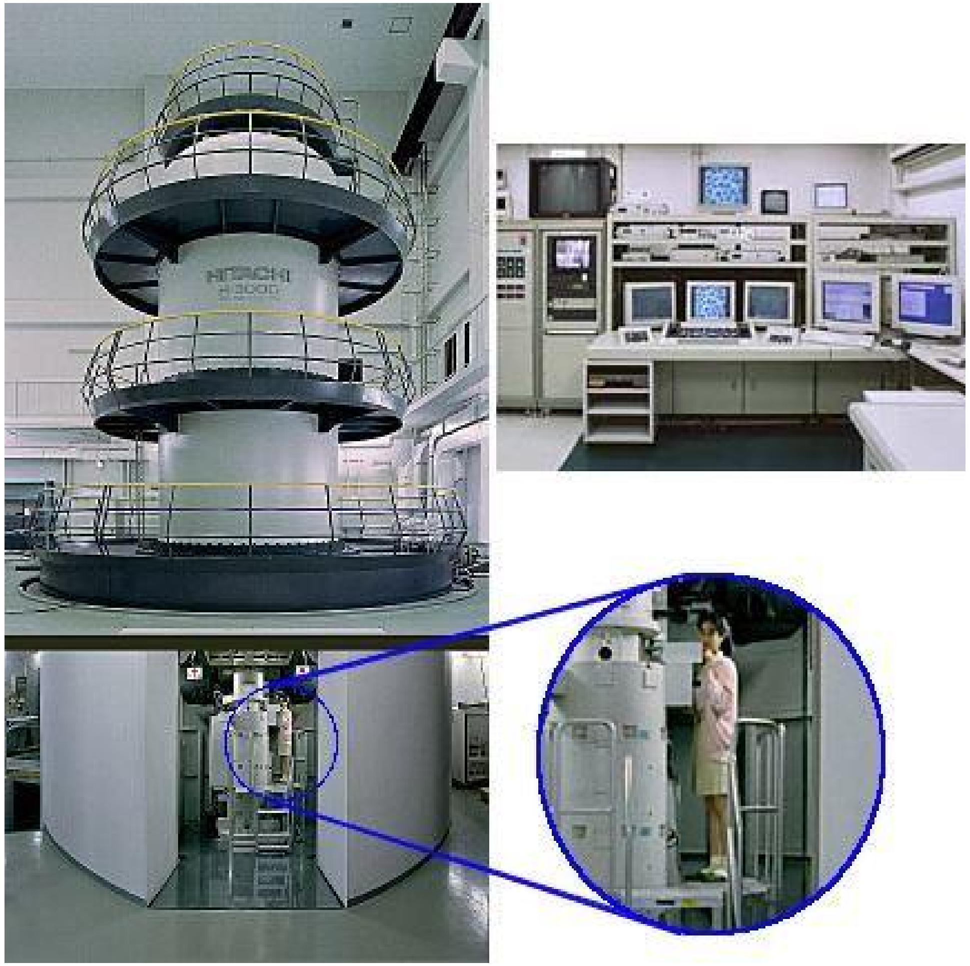
表面形貌分析

- 扫描电子显微镜：SEM
- 离子诱导扫描电子显微镜：IISEM
- 场离子显微镜：FIM
- 扫描隧道显微镜：STM
- 原子力显微镜：AFM

表面电子态分析

- 紫外光电子谱：UPS
- 电子能量损失谱：EELS
- 角分辨X射线光电子能谱：ARXPS
- 扫描隧道显微镜：STM
- 原子力显微镜：AFM

超高压电子显微镜（300万伏特）

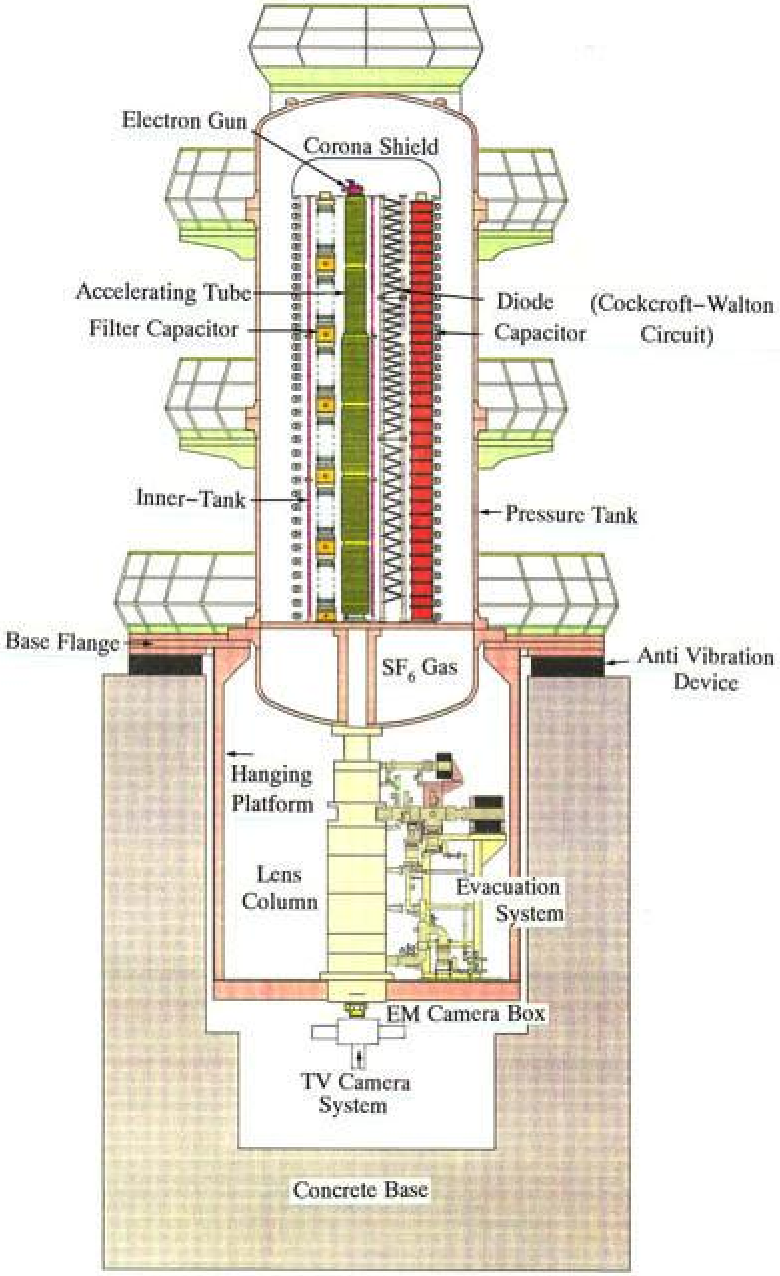


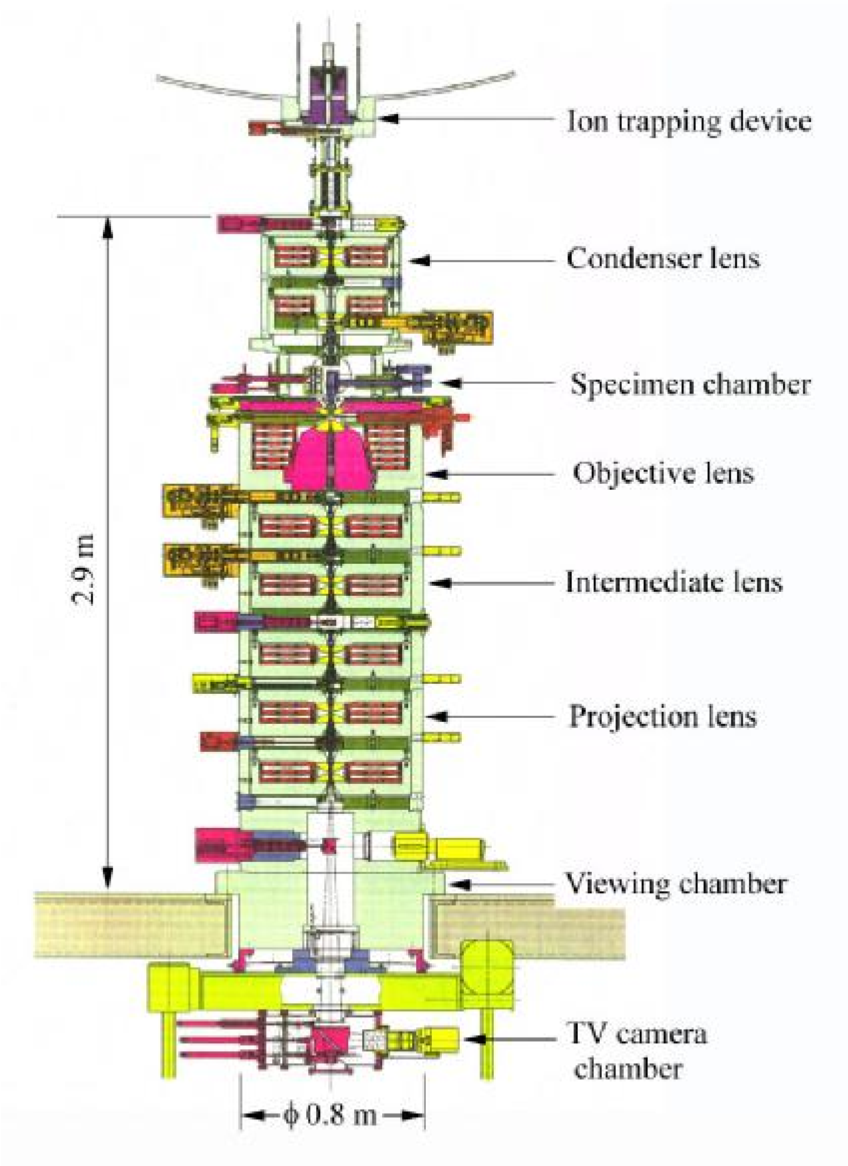
1. 晶格缺陷原位实验
2. 湿生物样品原位实验（活体细胞）
3. 新应用开发

材料科学

1. 纳米原子簇的扩散
2. LSI器件结构缺陷分析


HITACHI
H-3000


Electron Gun
Corona Shield
Accelerating Tube
Filter Capacitor
Diode
Capacitor
(Cockcroft–Walton
Circuit)
Inner–Tank
Pressure Tank
Base Flange
SF_6 Gas
Anti Vibration
Device
Hanging
Platform
Lens
Column
Evacuation
System
EM Camera Box
TV Camera
System
Concrete Base

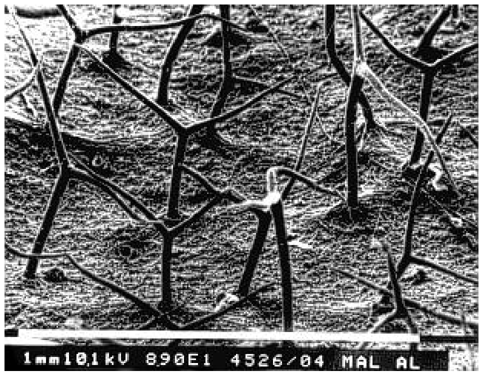


日本大阪大学

10000公里

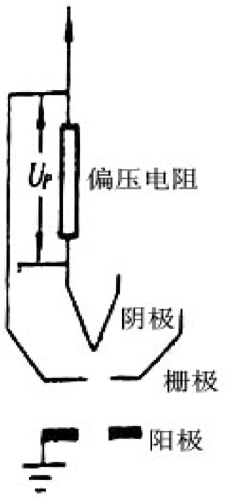
远程实时控制

美国加州大学

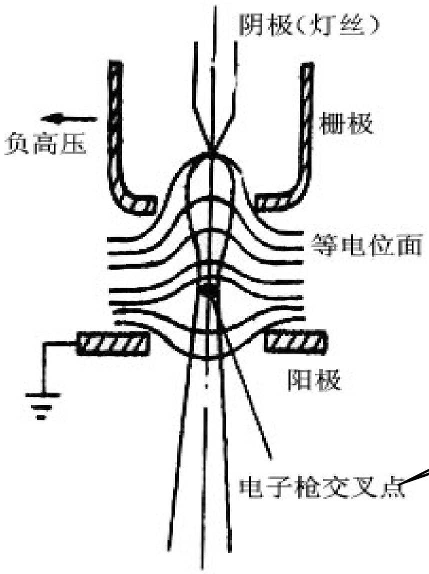


名　　称	可 见 光	紫外光	X 射 线	α 射 线	电　子　束	
					0.1KV	10KV
波长（nm）	390~760	13~390	0.05~13	0.005~1	0.123	0.0122

$$l = \frac{h}{m v}$$



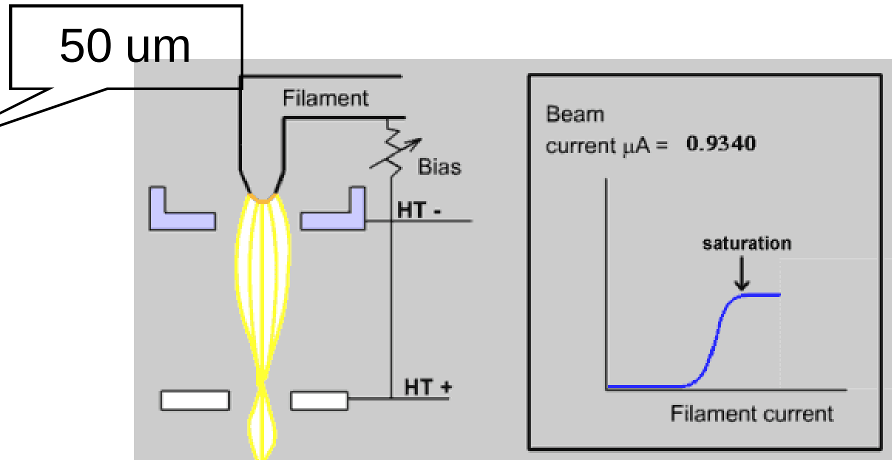
(a)



(b)

$$I_0 = AT^2 \exp(-b/T)$$

W： 2700 °C

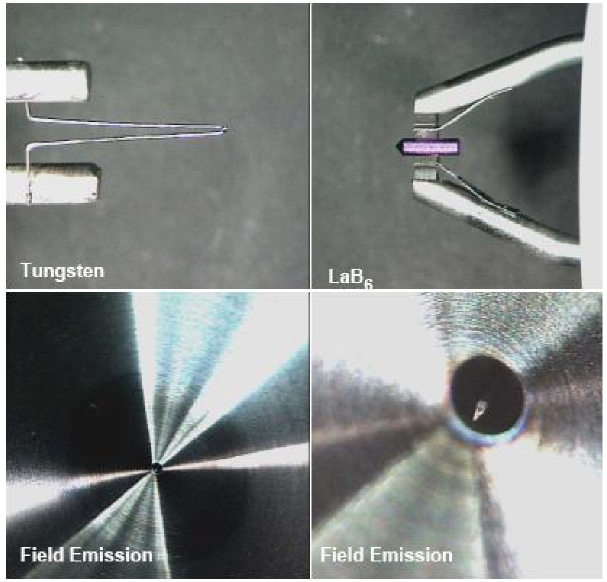


电子枪

The Electron Gun

Courtesy of James S. Young

Filaments



Lanthanum Hexaboride Filament

- Single crystal of LaB_6
- Tip is ~100μm
- Chemically reactive when it gets hot
- Crystal is held by glassy carbon or graphite supports
- Carbon not reactive with LaB_6

Comparison of Lanthanum Hexaboride and Tungsten Hairpin Filaments

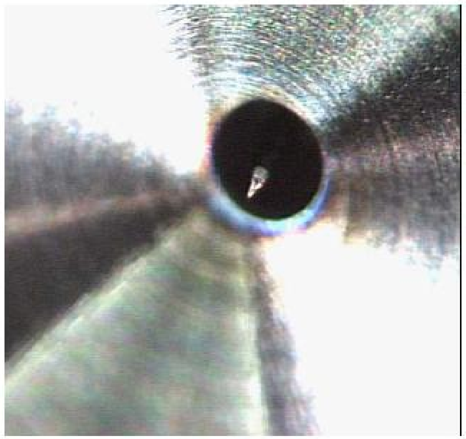
- **Tungsten Hairpin:**
  - stable beam current
  - short life
  - large tip
  - large area (probe diameter)
  - high work function
  - low brightness
  - lower vacuum
  - low resolution
  - 2700 K
- **LaB_6**
  - stable beam current
  - longer life
  - smaller tip
  - smaller area (probe diameter)
  - lower work function
  - higher brightness
  - higher vacuum
  - higher resolution
  - 1800 K

Field Emission Filaments

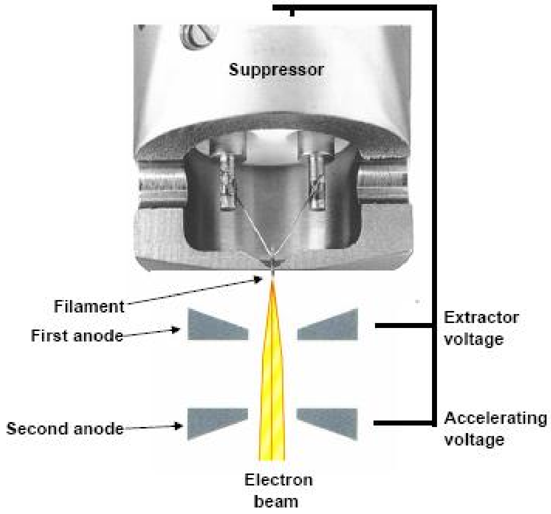
- Cold Field Emitter (CFE)
  - single crystal of tungsten
  - operate at room temperature
  - very bright
  - long lasting
  - require very high vacuum (< 10^{-10} Torr)
  - contaminates easily
  - require frequent flashing (sudden heating)
  - poor current stability
- Thermal Field Emitter
  - like a cold field emitter, but heated to 1800 K
  - does not contaminate easily, no flashing
  - larger energy spread than CFE
- The Schottky Field Emitter
  - single crystal of tungsten coated with zirconium oxide (ZrO)
  - heated to 1800 K
  - ZrO lowers the work function
  - larger emitting area than CFE
  - larger virtual source size
  - small energy spread
  - high current density
  - good current stability
  - does not easily contaminate; no flashing
  - long life

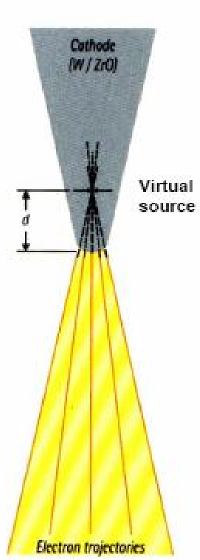
Field Emission Filaments

- A very fine wire of single-crystal tungsten fashioned to a sharp point
- Tip is 100nm or less
- Local electric field forms at tip, which decreases the energy (work function) needed by an electron to escape the cathode.
- Three types of FE cathodes

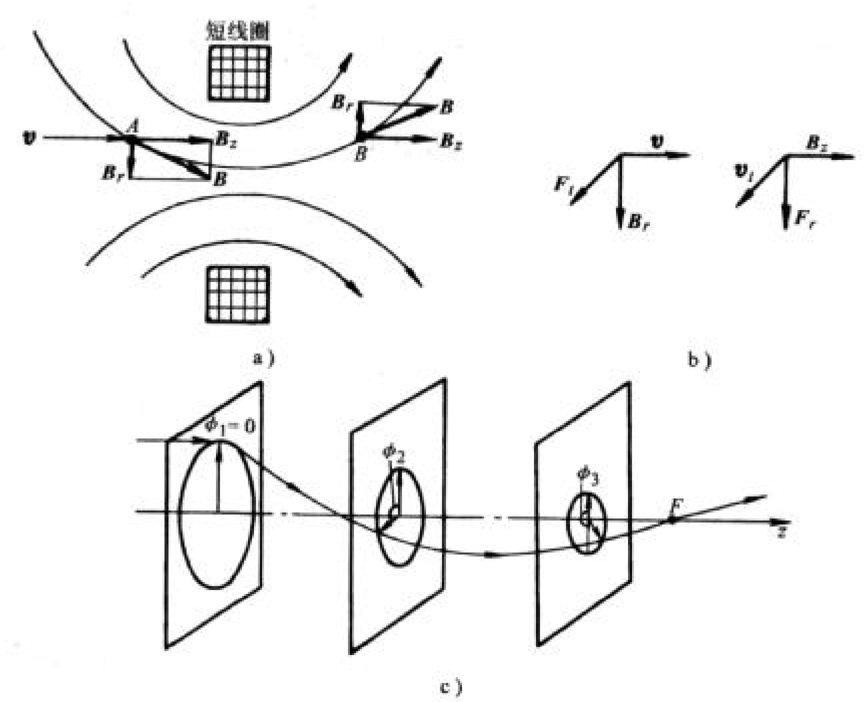


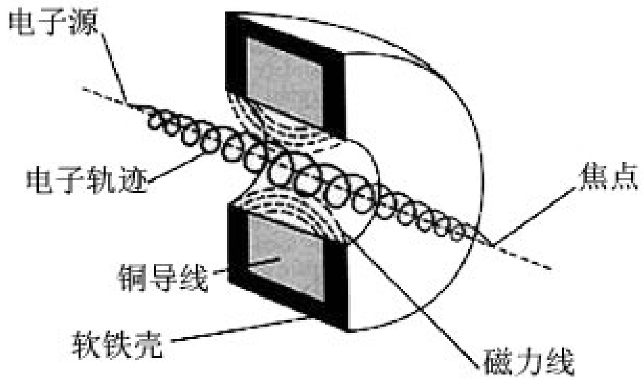
Field Emission Filaments

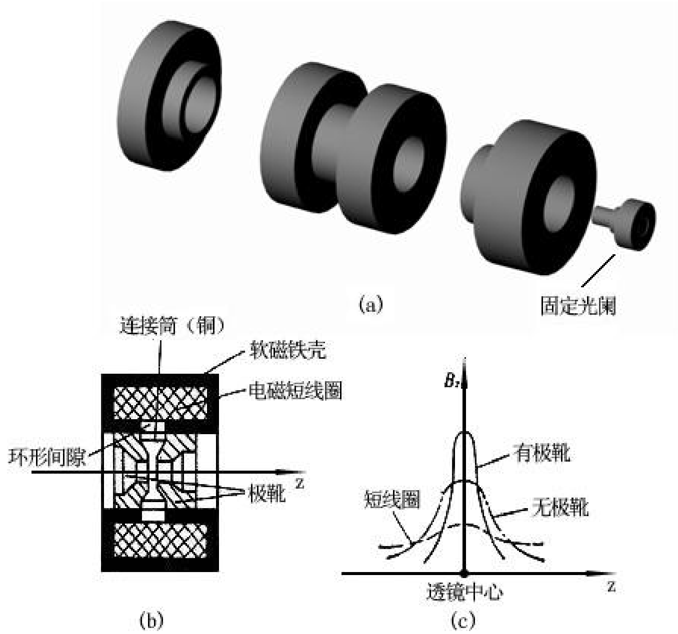




电磁透镜







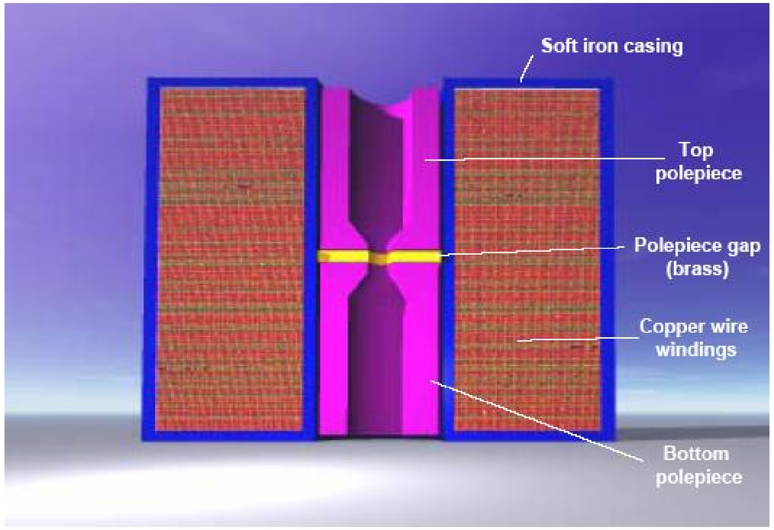
电子运动的轨迹是一个圆锥螺旋曲线

$$\frac{1}{f}=\frac{1}{L_1}+\frac{1}{L_2}$$

$$f \approx K\frac{U_r}{(IN)^2}$$

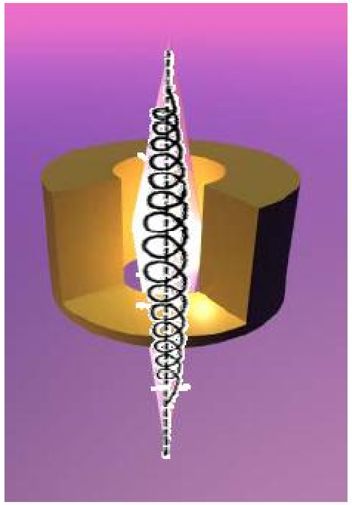
f>0，凸透镜

The Electromagnetic Lens



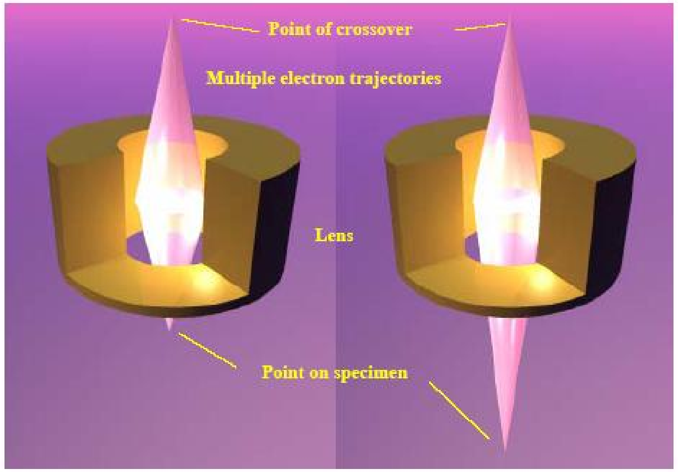
The Electromagnetic Lens

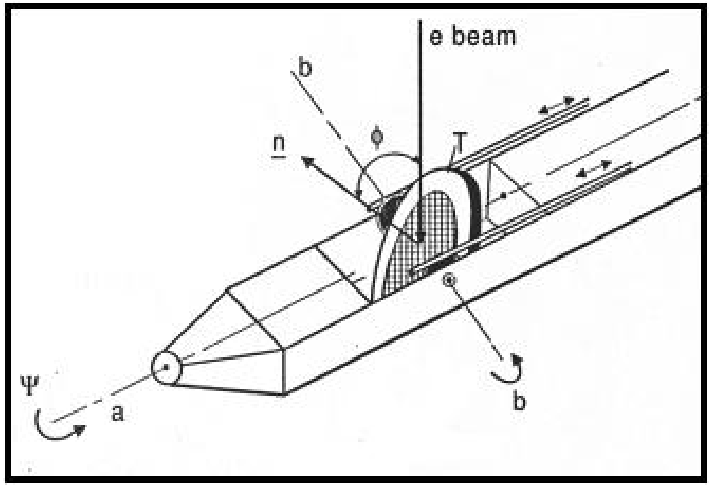
- The electrons move through the lens in a helical path, a spiral, not a straight line.
- One effect is that the image in an SEM will appear to rotate if you vary the accelerating voltage or the working distance.

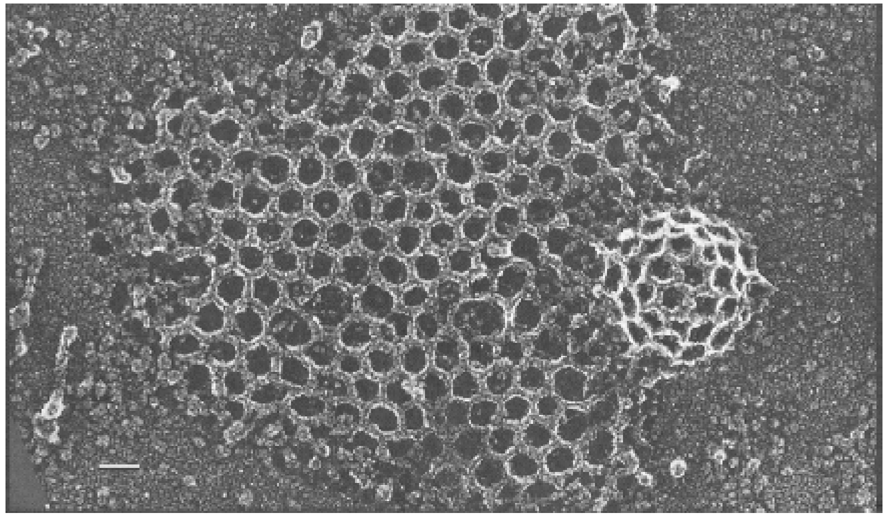


The Electromagnetic Lens

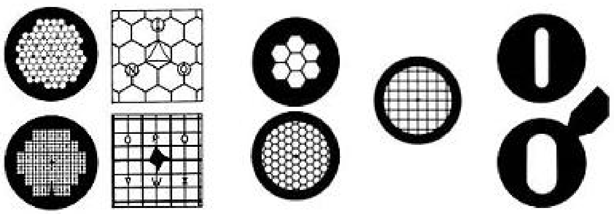
- The focal length of the lens can be adjusted changing the amount of DC current running through the coils.







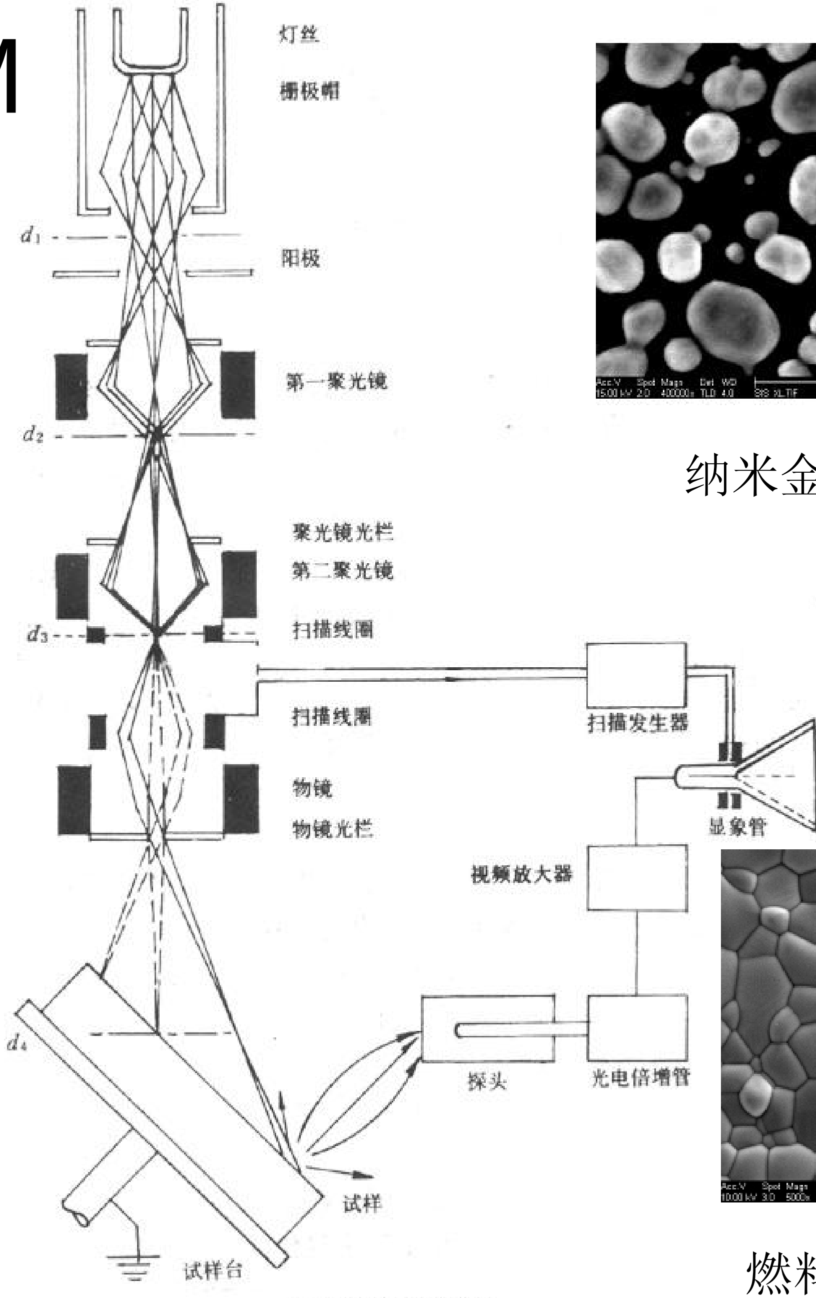
培养细胞内面的深度蚀刻电镜照片



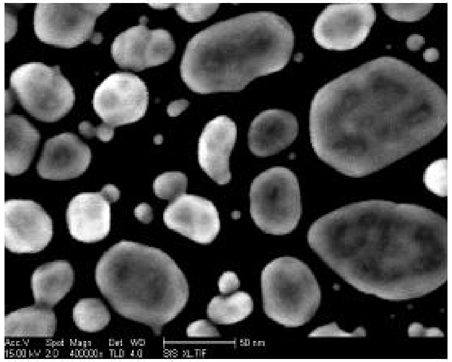
样品台与试样

内质网透射电镜图

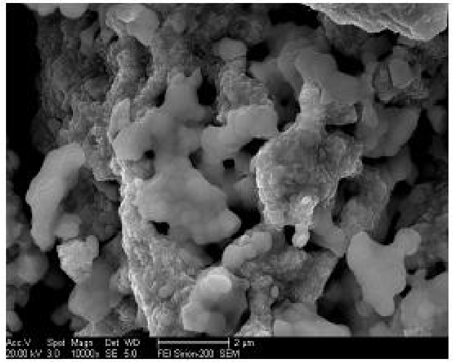
SEM



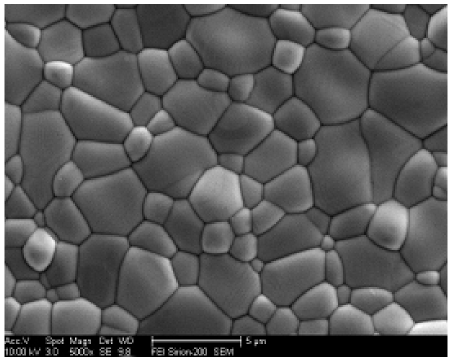
扫描电镜工作原理



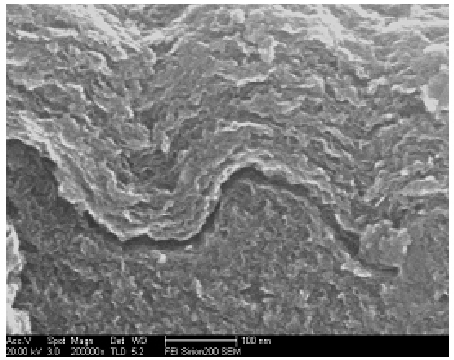
纳米金颗粒



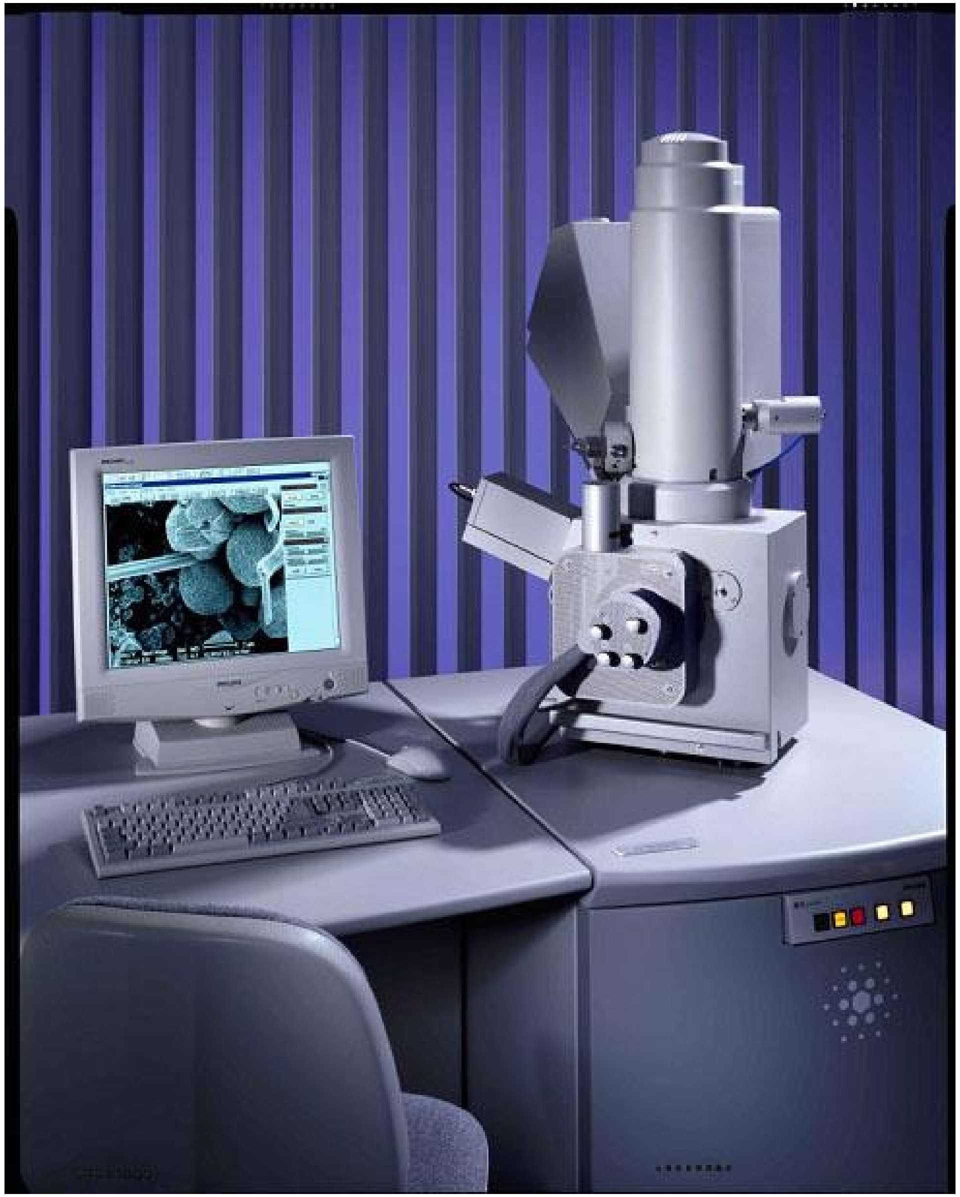
多孔金属陶瓷



燃料电池电极表面



碳纤维表面涂层



扫描电子显微镜（SEM）

Experimental resolution (Edge-to-edge resolution)

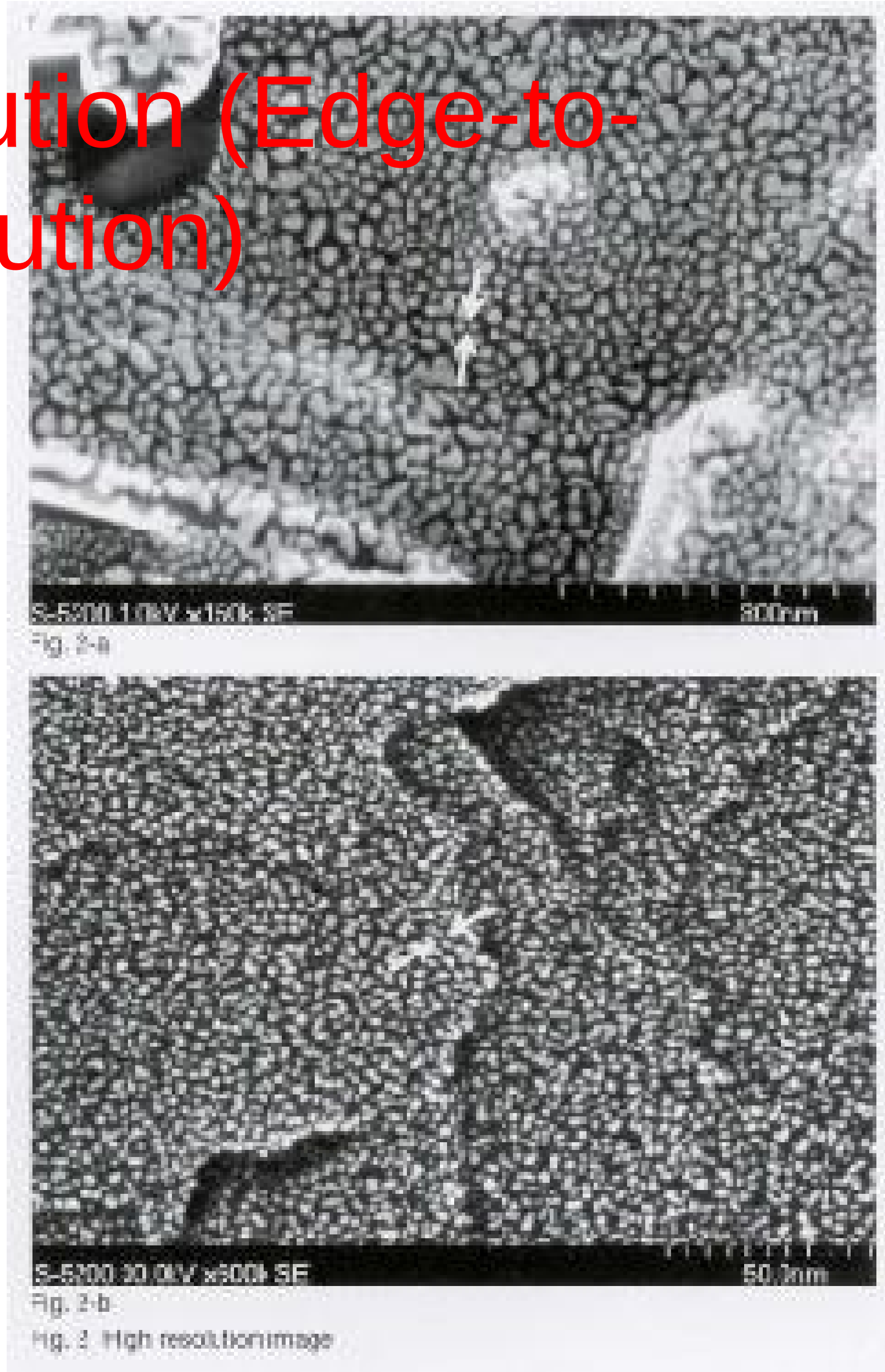
- In this case the resolution is assessed by the minimum distance observable between two edges.

Taken from

www.hitachi-hitec.com

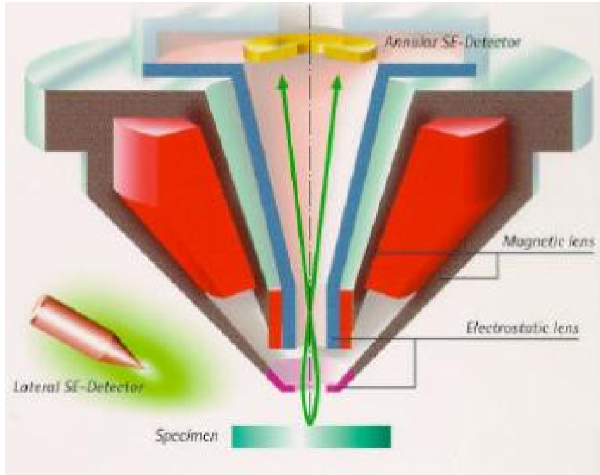
TOP: 1.8nm @1kV

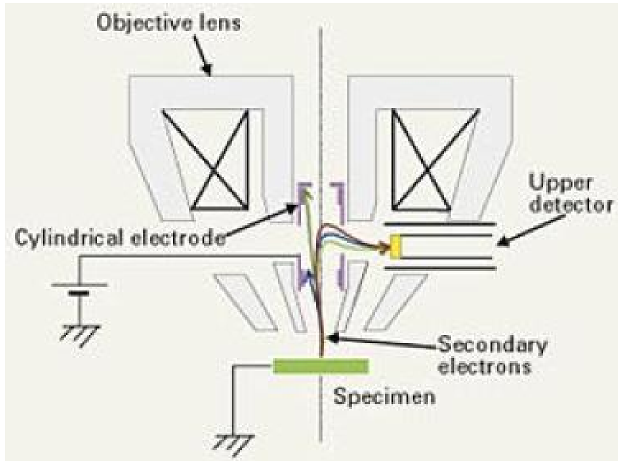
BOTTOM:0.5nm @30kV



Methods of improving resolution

- **In lens SE detector**
- In lens or SE1 detector, SEs travel back to the lense and are collected by a small detector.
- Electrode forms a type of filter to push the electrons to the detector.
- Shorter path length allows for more localized collection of SEs

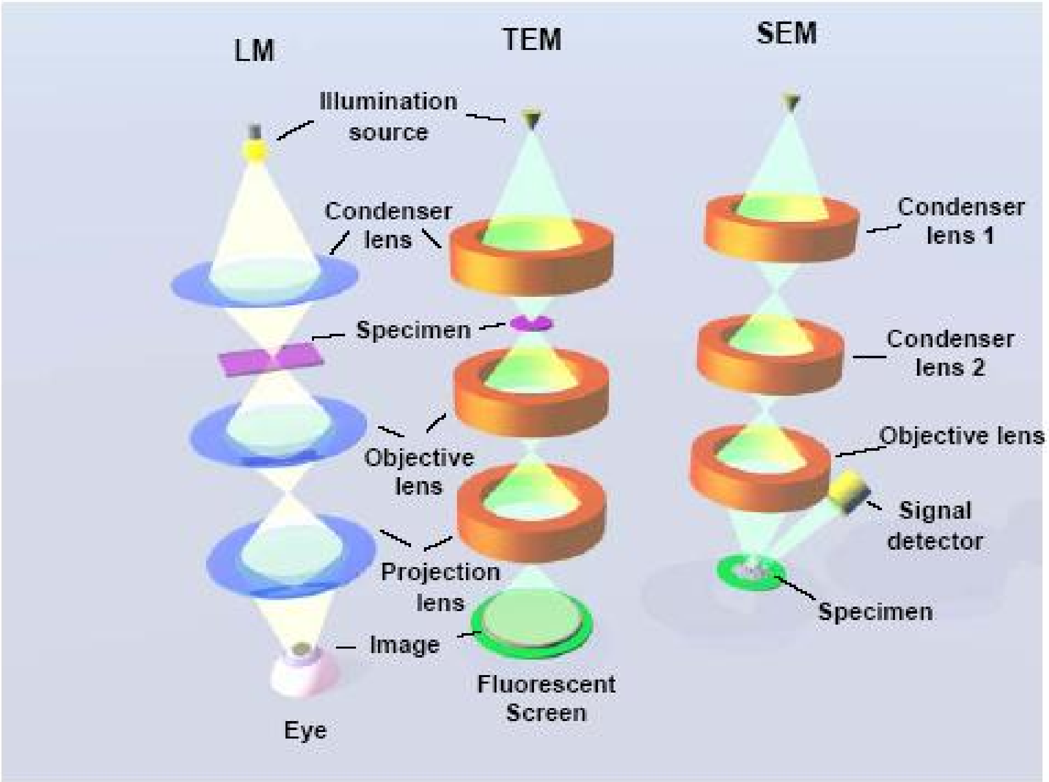




TOP: taken from **www.smt.zeiss.com**

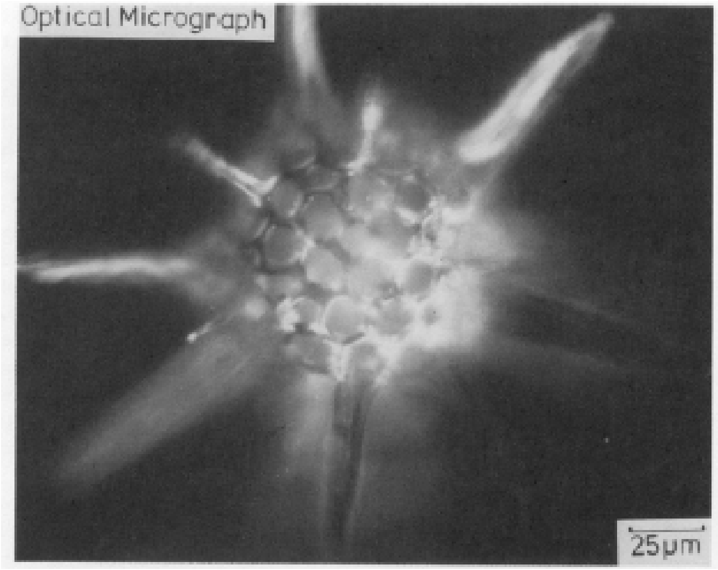
BOTTOM: Taken from **www.jeoleuro.com**

Comparison of the LM, TEM, and SEM

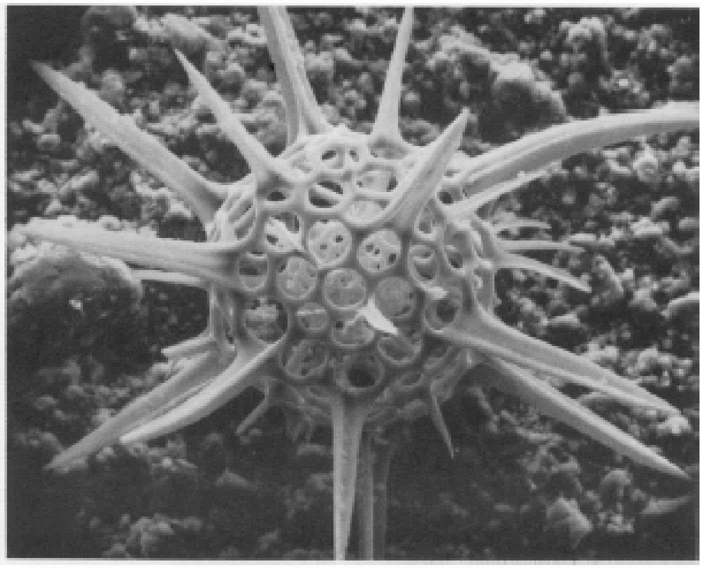


Courtesy of James S. Young

Comparison of Resolution and Depth of Focus



Optical Micrograph

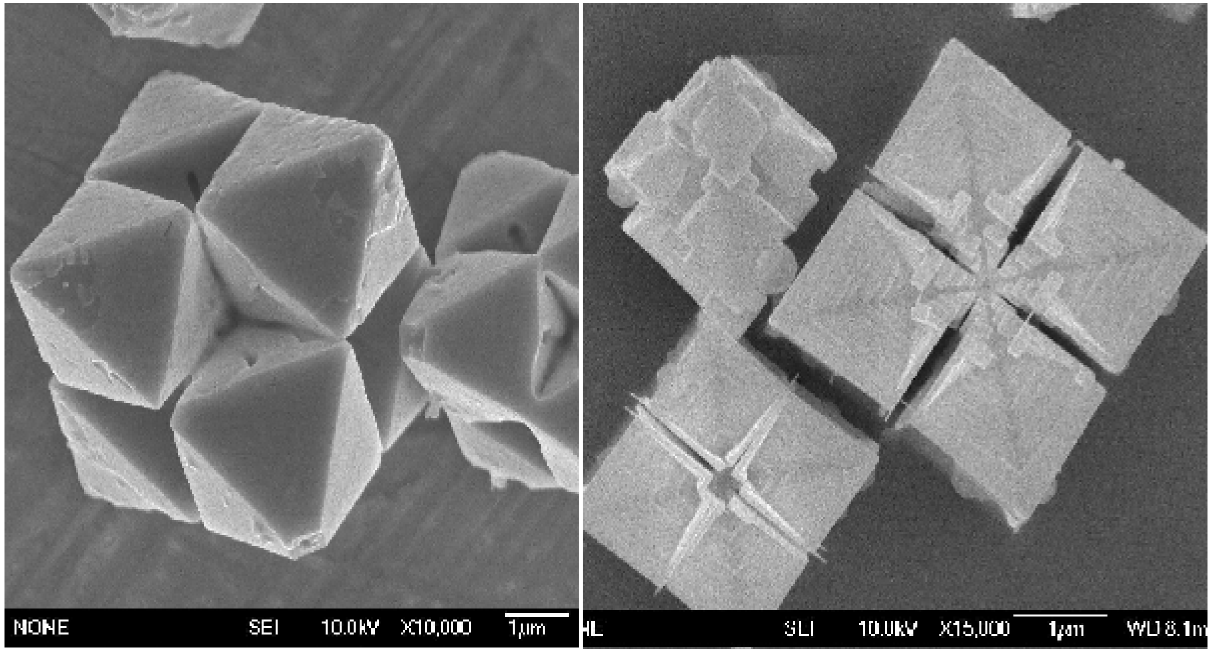


SEM Micrograph

SEM

Topographical contrast

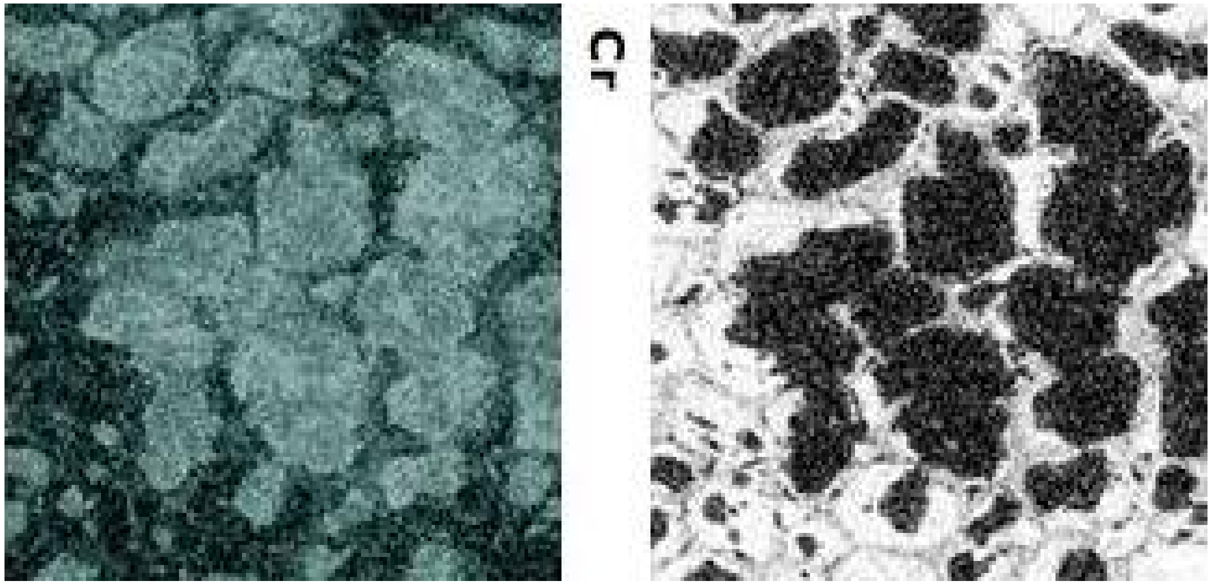
structure complex in morphology



SAM

Chemical contrast

structure complex in elemental distribution



电子与物质的相互作用

- 弹性散射
  - 同原子碰撞
  - 没有能量损失
  - 改变电子的散射方向
  - 背散射电子

- 非弹性散射
  - 同电子碰撞
  - 有能量损失
  - 单电子激发
    - 电离
    - 俄歇电子
    - 激发到空态
  - 集团振荡
    - 等离子体激元
  - 声子激发(晶格热振动)
  - 轫致辐射
  - X射线

Effects of Varying the Initial Electron-Beam Energy

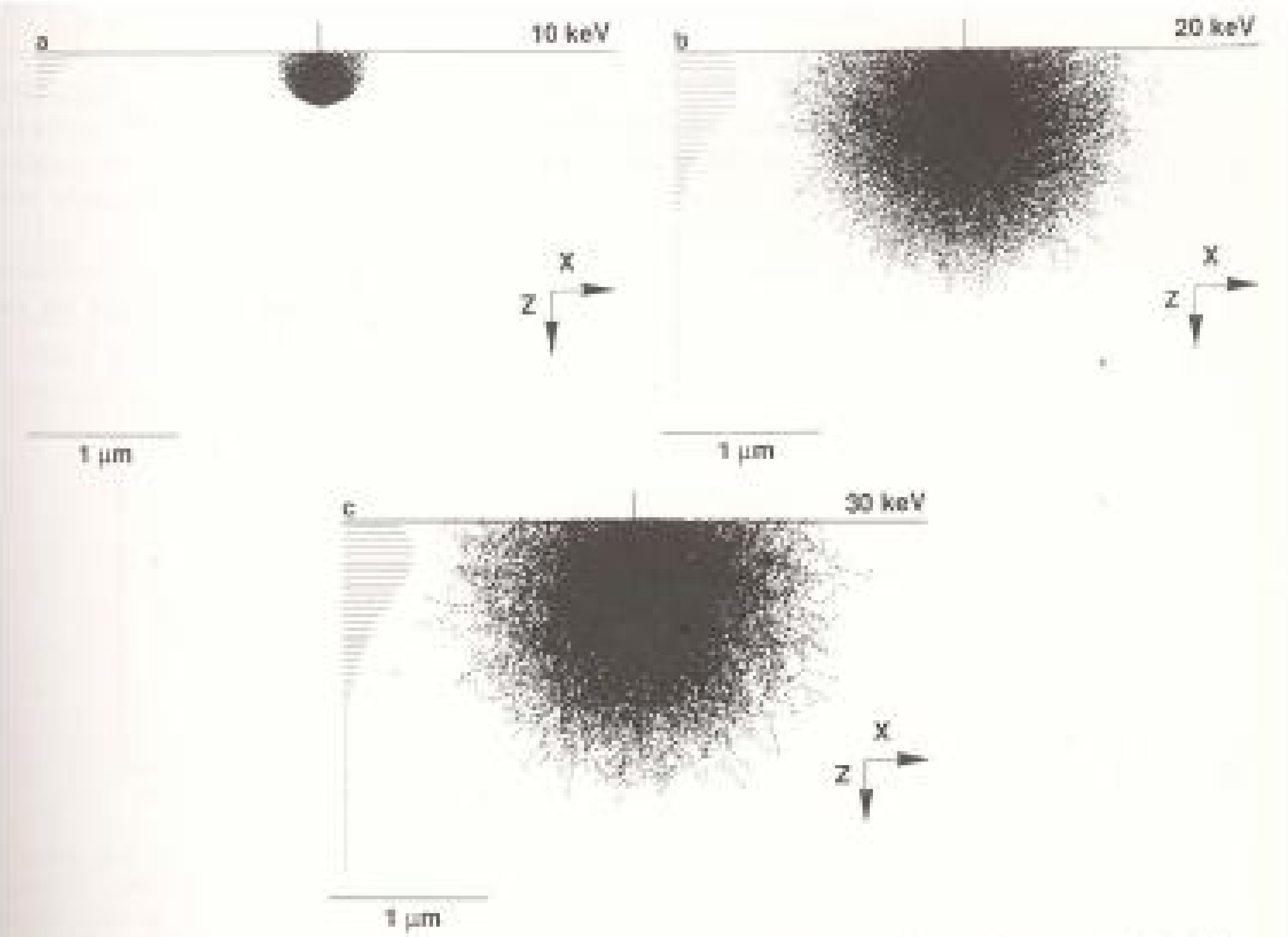
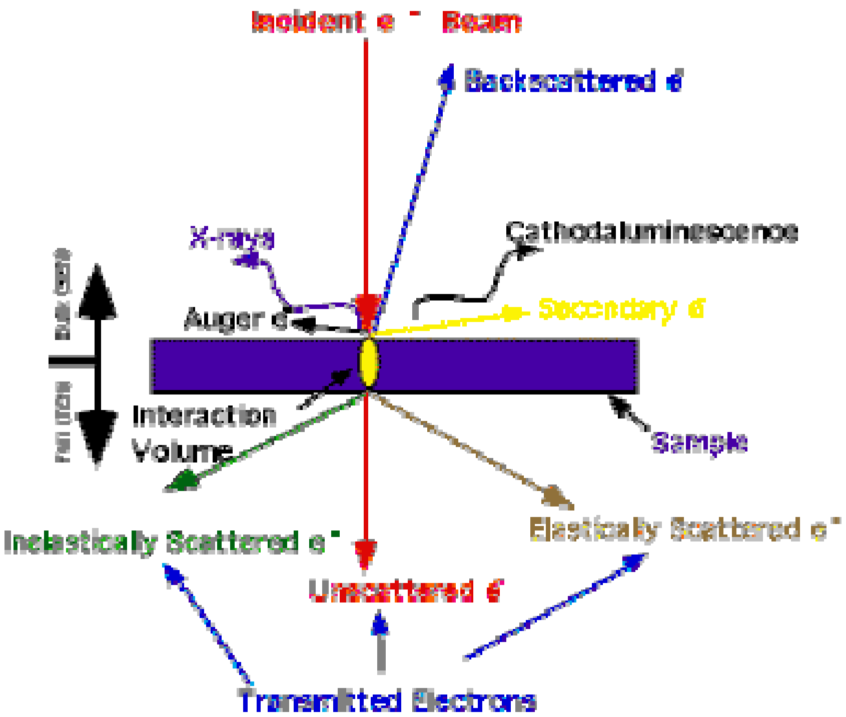
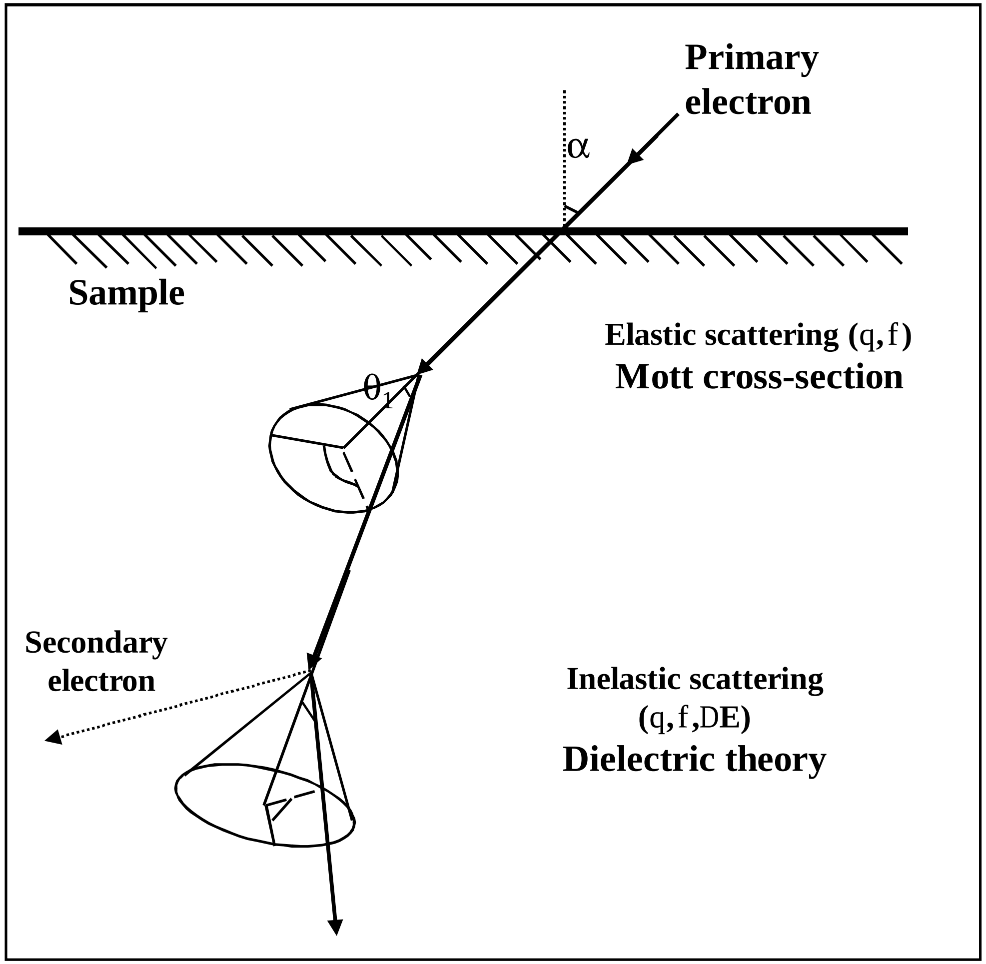
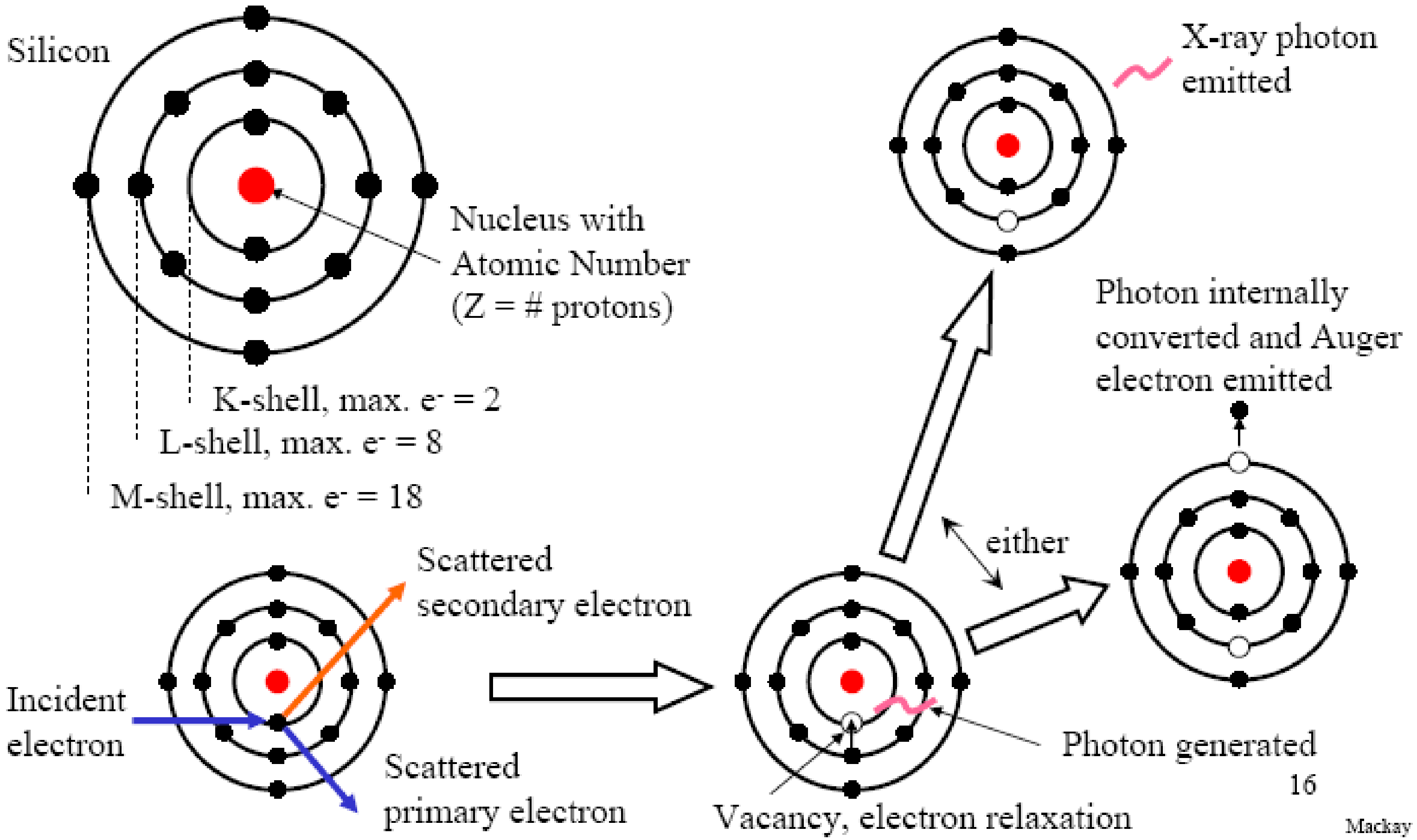


Figure 8.7. Monte Carlo calculations of x-ray generation volume for Cu at (a) 10, (b) 20, and (c) 30 keV.

- 电子与物质的相互作用过程

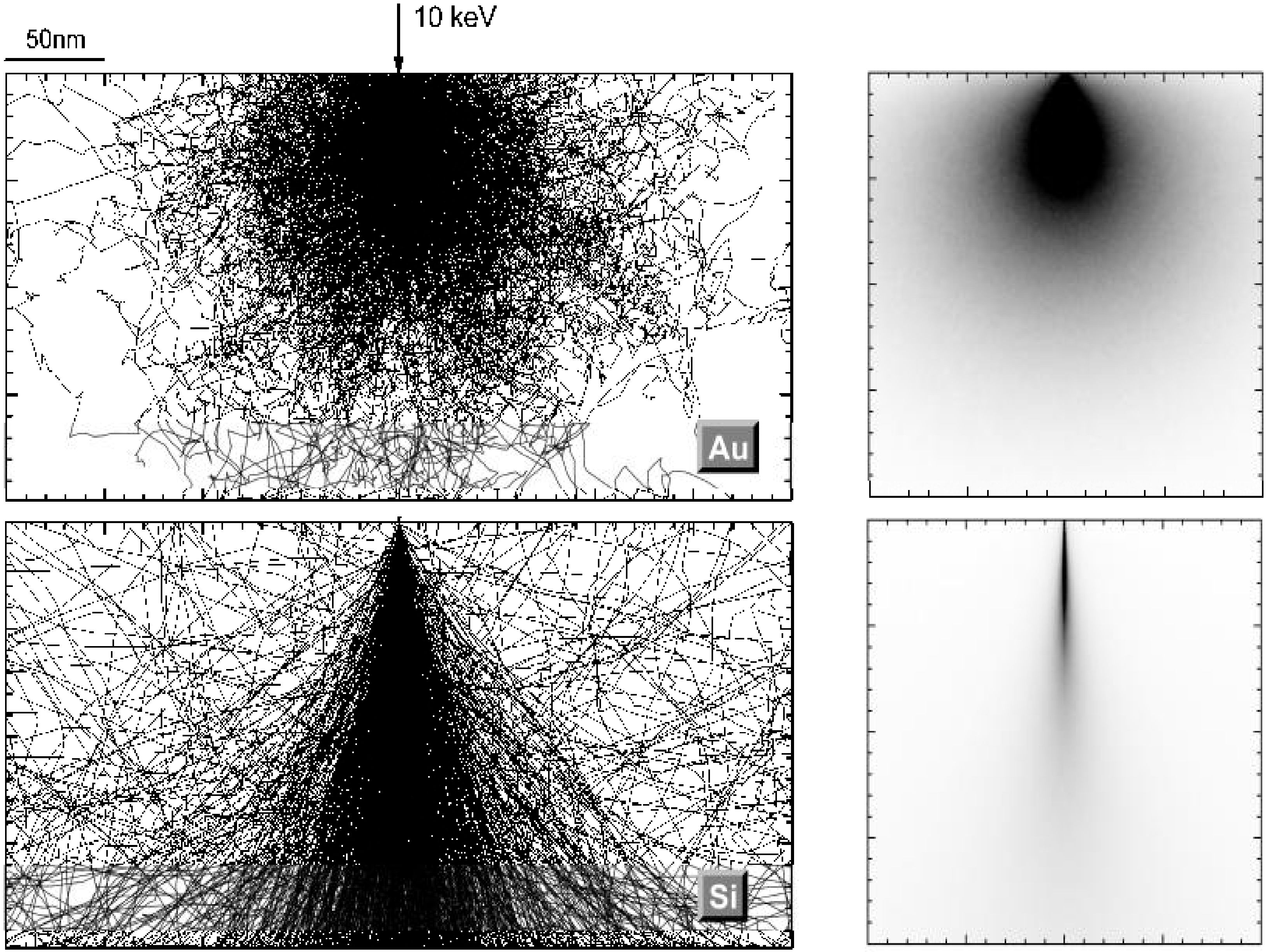




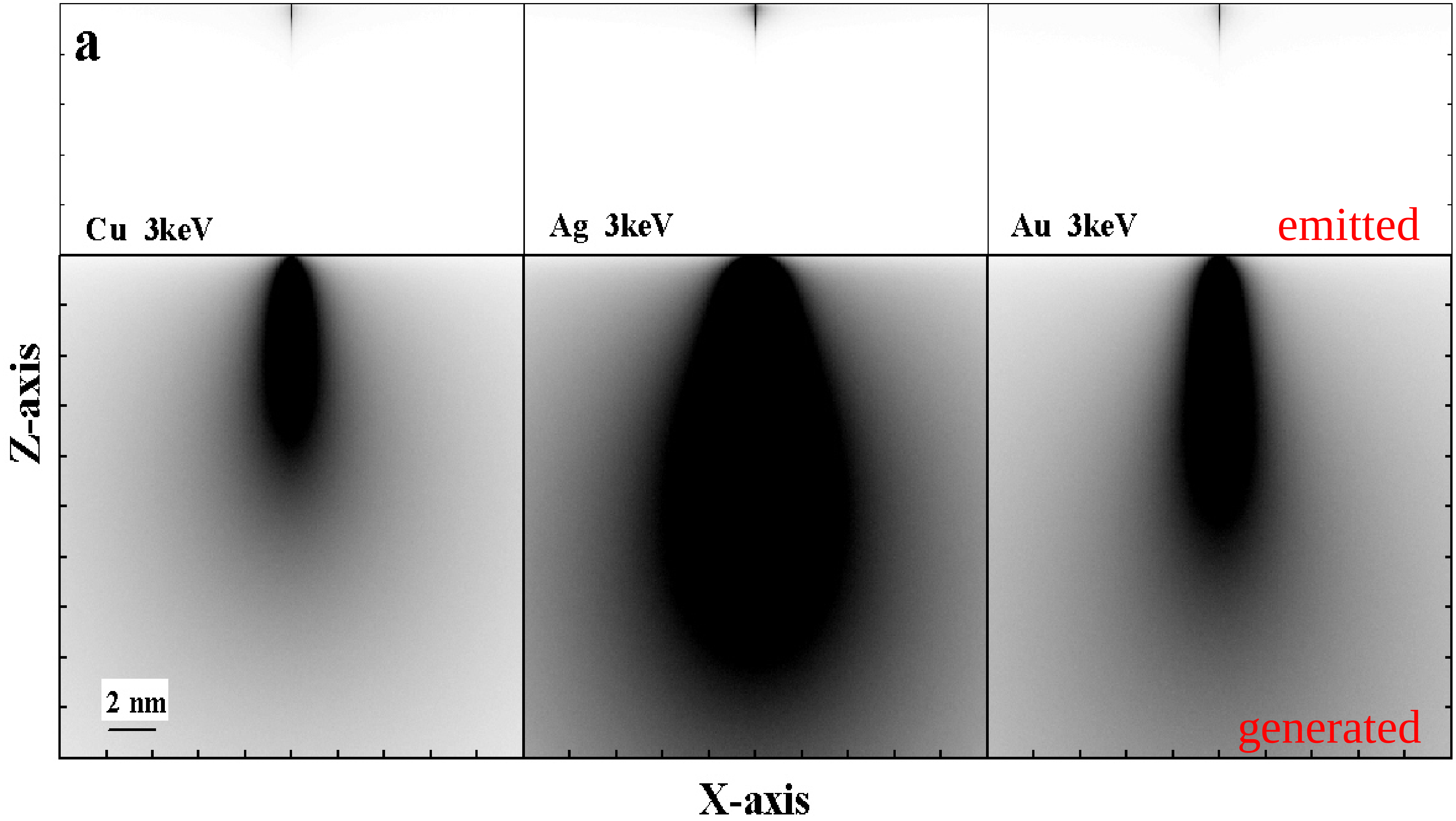

Silicon
Nucleus with
Atomic Number
(Z = # protons)
K-shell, max. e- = 2
L-shell, max. e- = 8
M-shell, max. e- = 18
X-ray photon
emitted
Photon internally
converted and Auger
electron emitted
either
Scattered
secondary electron
Incident
electron
Scattered
primary electron
Photon generated
Vacancy, electron relaxation

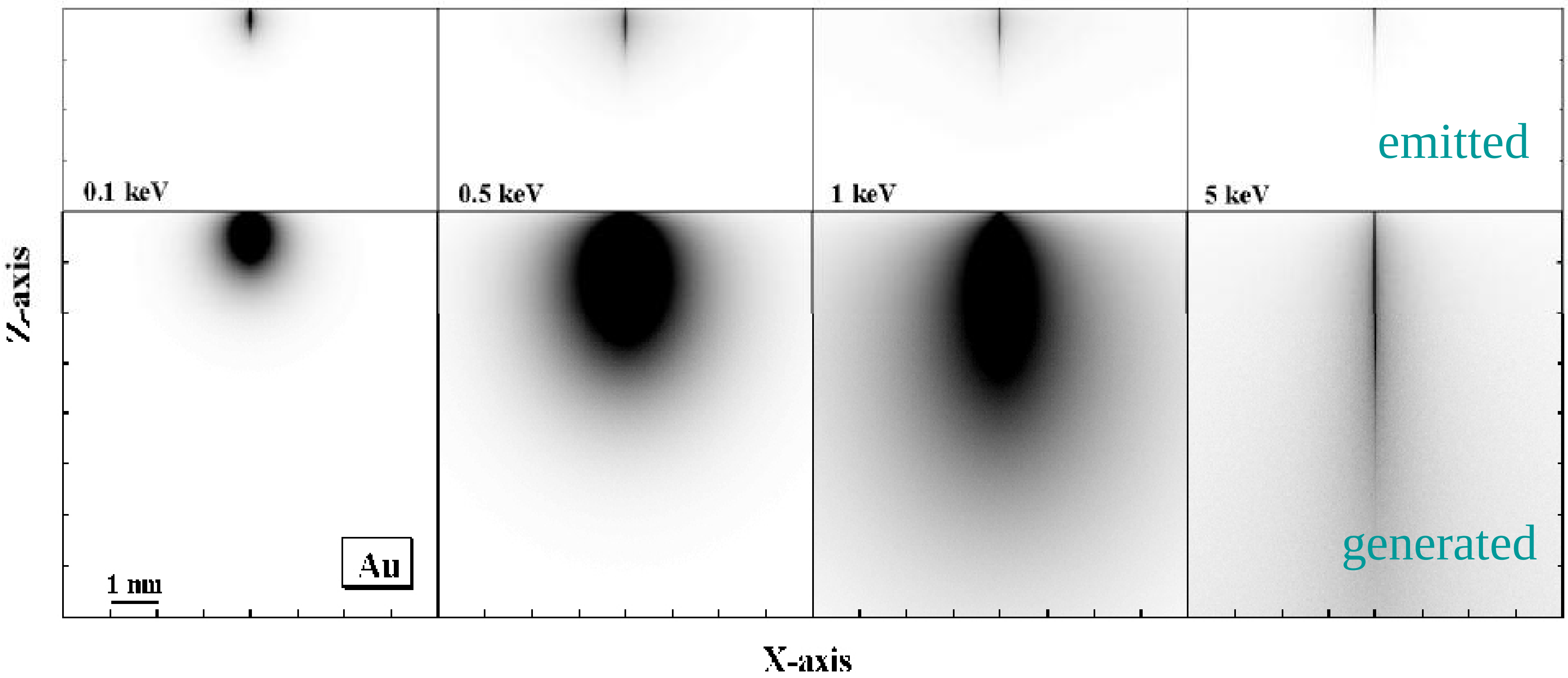
Mackay

电子散射轨迹



二次电子的产生和出射





emitted
0.1 keV
0.5 keV
1 keV
5 keV
Z-axis
generated
1 nm
Au
X-axis

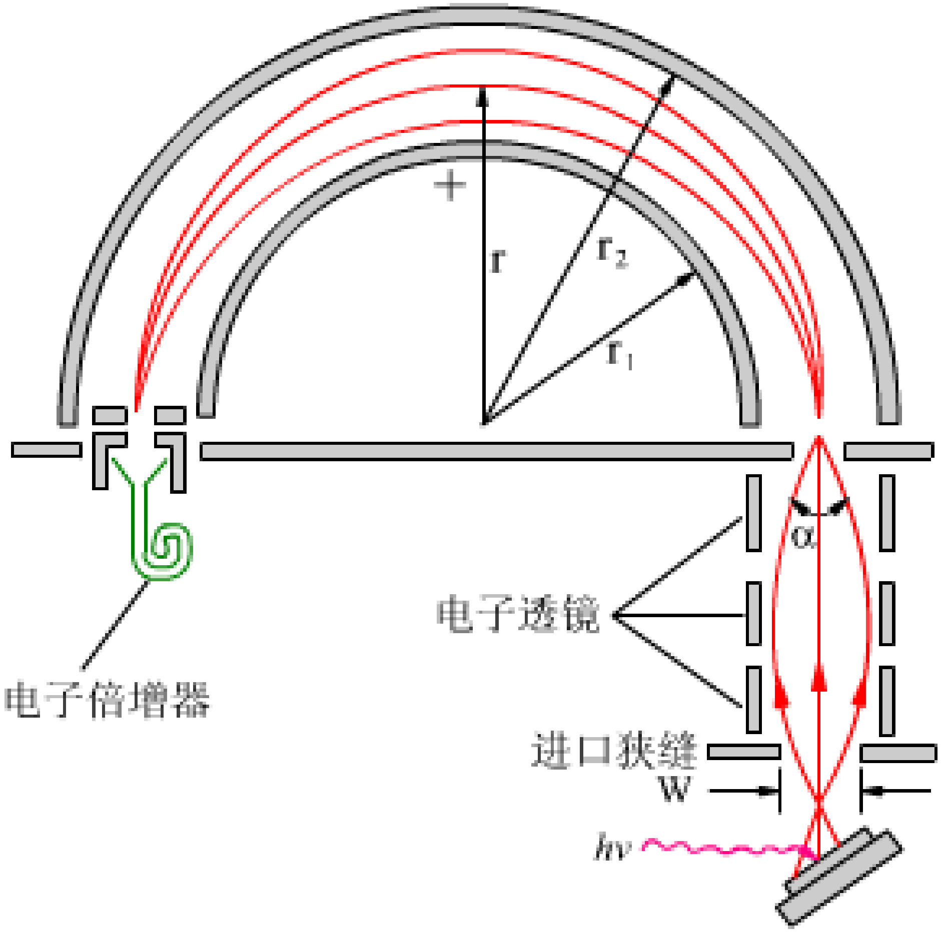
能量分析器

作用：是把不同能量的电子分开，使其按能量顺序排列成能谱。

常用的电子能量分析器为静电式能量分析器。

球形分析器、扇形分析器、筒形分析器

球形分析器是由两个同心半球组成，内外球之间加电压，在两球面之间形成径向电场，对于一定的电压，只有一定能量的电子可以通过分析器进入检测器，改变电压，可以使另外能量的电子被接收。



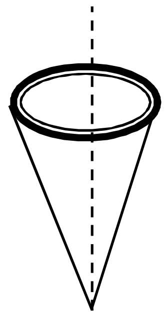
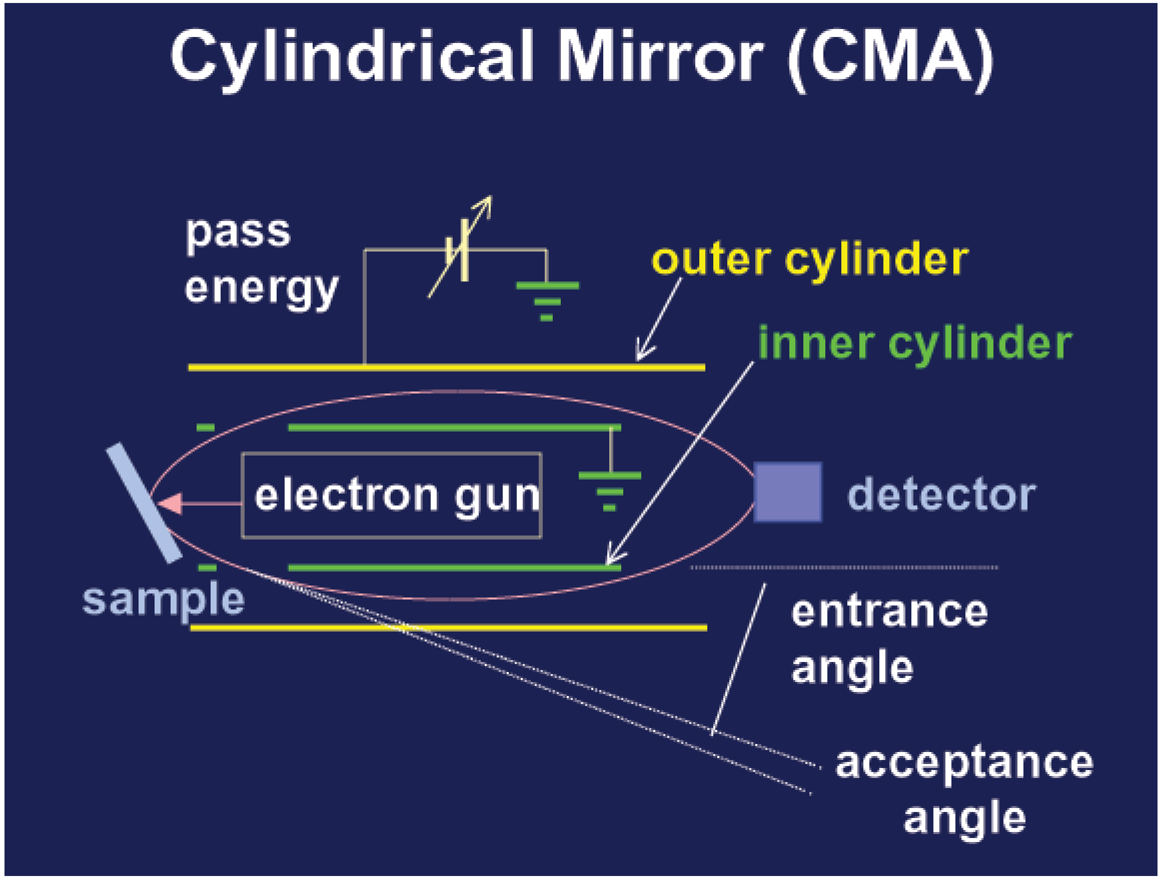
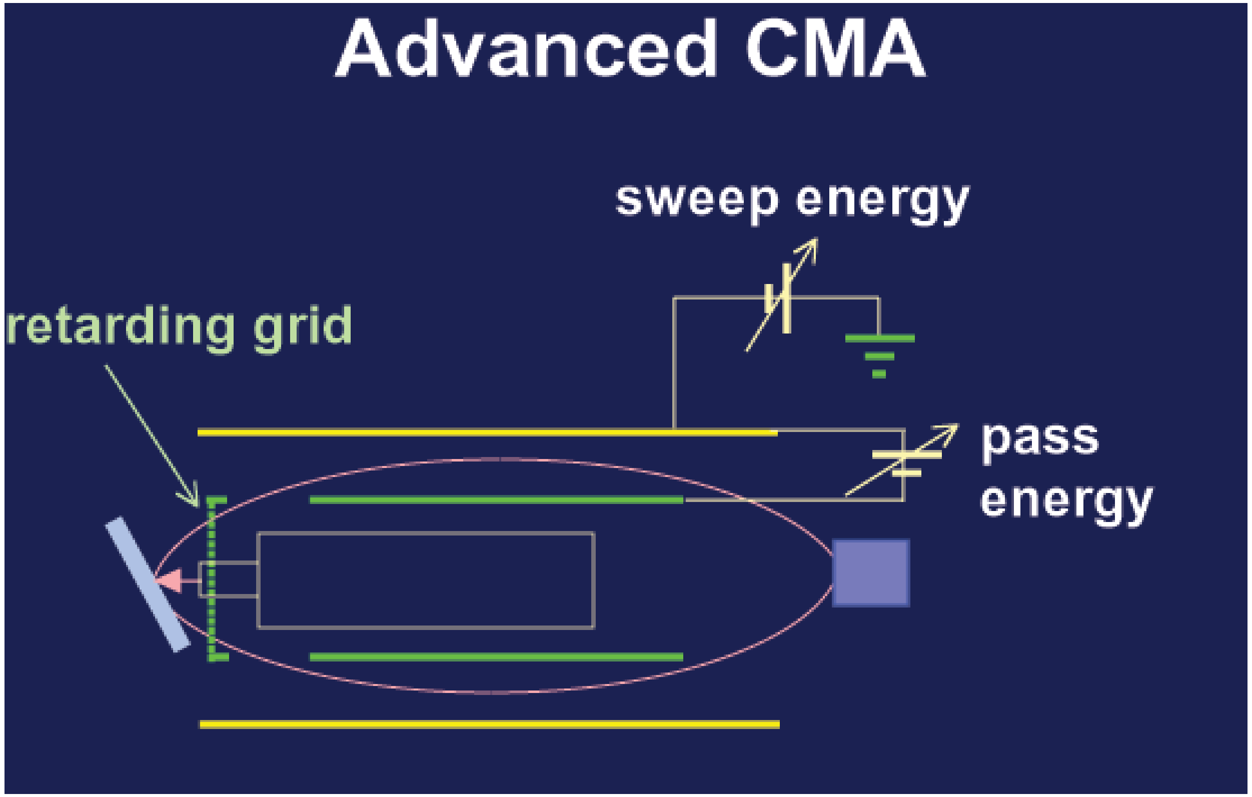


图10-11　半球形电子能量分析器示意图



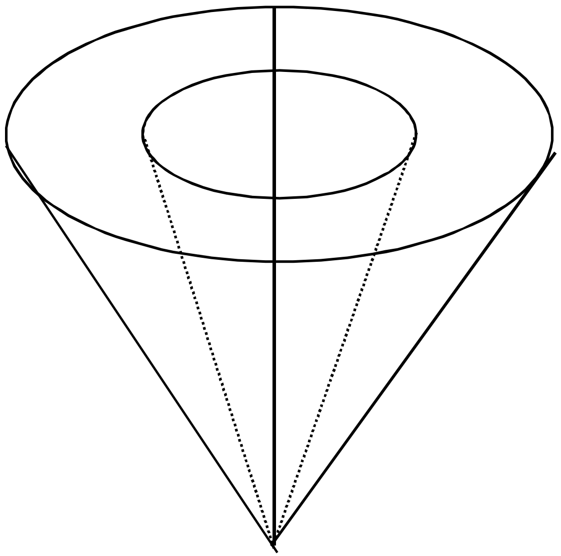
Operation Principles

Electrons enter the analyzer at the entrance angle,a, through an entrance slit. They are deflected by the (negative) potential on the outer cylinder. Only those electrons at the pass energy, Ep, reach the exit slits. This is called focusing. Electrons with energies of Ep ± DE will also be focused by the analyzer if they arrive at at the entrance slit at angles a ± Da (acceptance angle). The energy spread in the transmitted signal is dependent on slit width and acceptance angle.

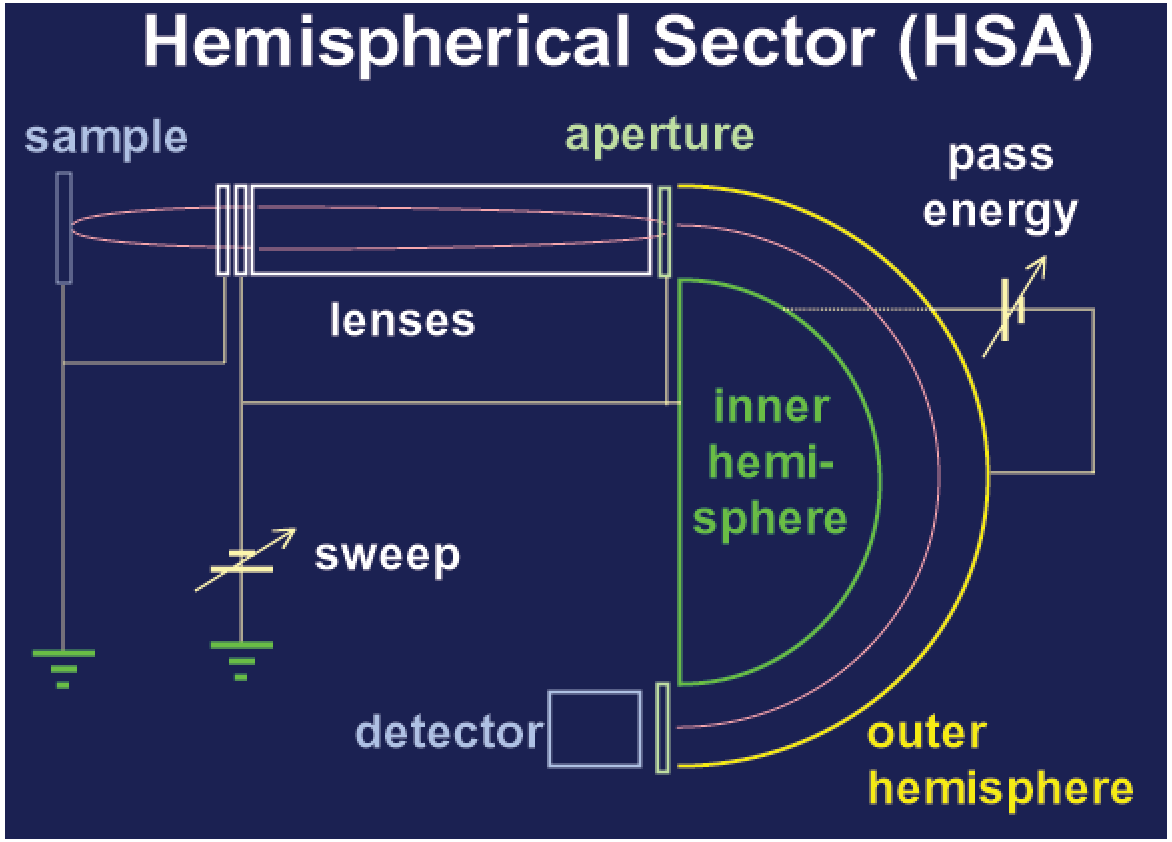


Advantages
The retarding grid slows down the incoming electrons to one given value of Ep regardless of their initial KE. The absolute resolution **D**E is therefore independent of initial KE.

大接收角

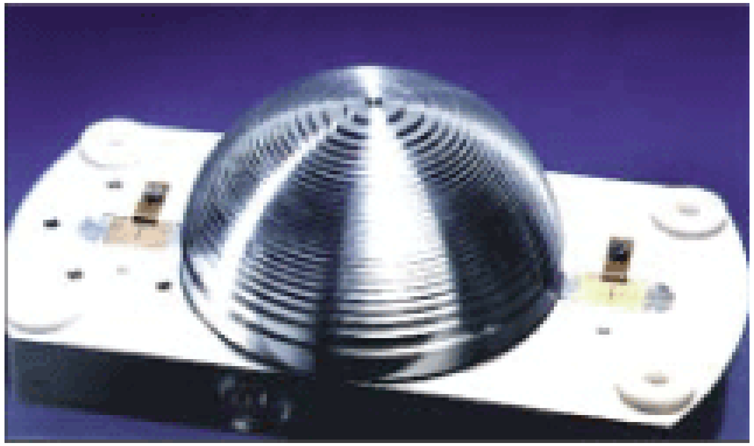


Concentric Hemispherical Analyzer (CHA)
also called Hemispherical Sector Analyzer(HSA)



Operation Principles

Electrons with an energy greater than the sweep energy enter the lenses at the entrance angle, a. They are focussed through the lenses onto the entrance slit of the analyzer. Only those electrons at the pass energy, Ep, reach the exit slits of the analyzer. Electrons with energies of Ep ± DE will also be focussed by the analyzer if they arrive at at the entrance slit at angles a ± Da (acceptance angle). The energy spread in the transmitted signal is dependent on slit width and acceptance angle.

Comparison of CMA with CHA

CMA is most effective in AES due to high transmission(signal electron /total electron generated).

CHA is always preferred for XPS because it can maintain adequate luminosity at high energy resolution with the addition of a lens

	CHA	CMA
resolution	0.8- 1.0 V	>1.4 V
transmission	high	higher
luminosity	high w/lens	irrelevant
energetic position	independent	dependent
angular dependence measurements	suitable	unsuitable
machining	high precision required	less precision required

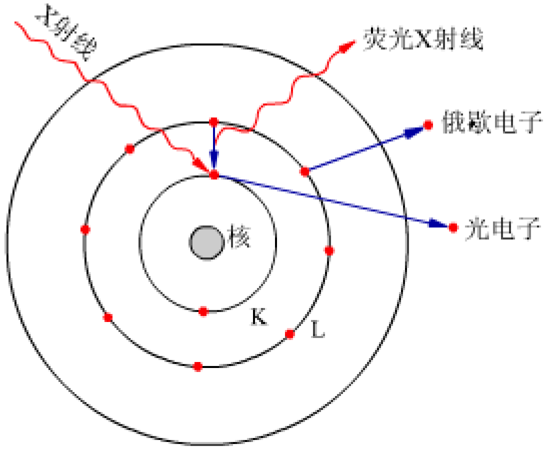


图10-1　荧光X射线及俄歇电子产生过程示意图

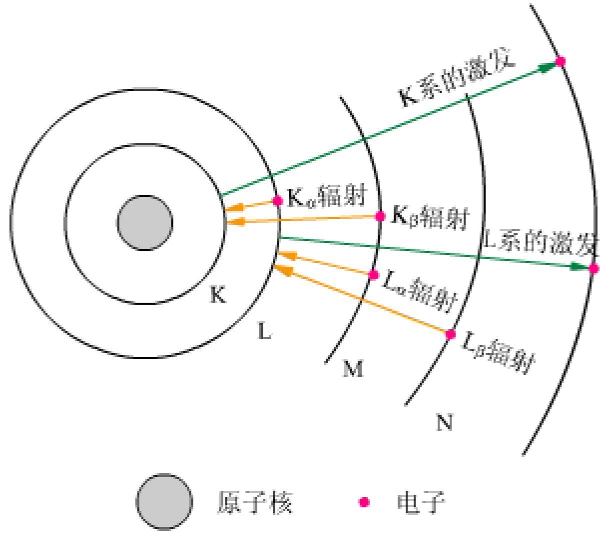
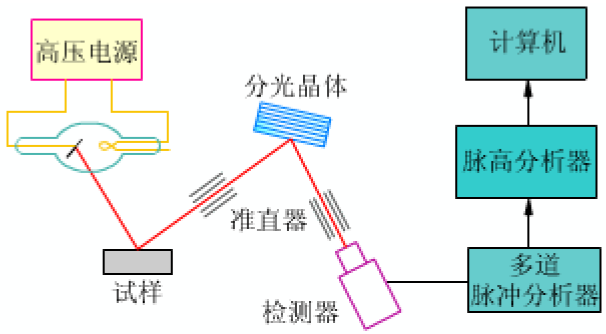
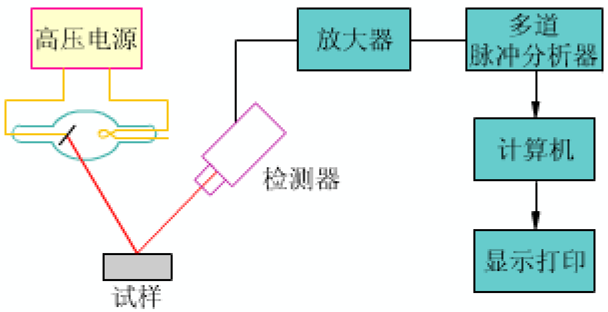


图10-2　产生K系和L系辐射示意图



（a）波长色散谱仪



（b）能量色散谱仪

图10-3　波长色散型和能量色散型谱仪原理图

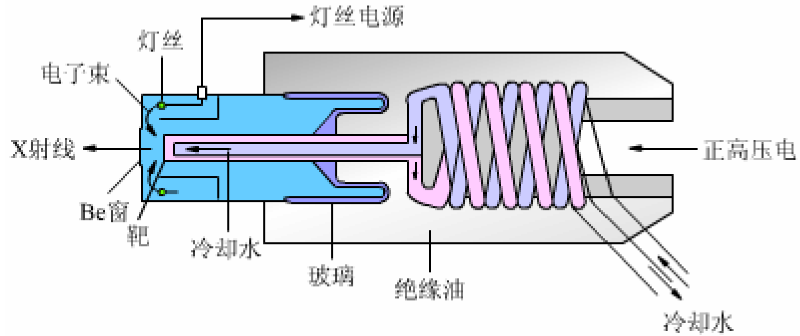


图10-4　端窗型X射线管结构示意图

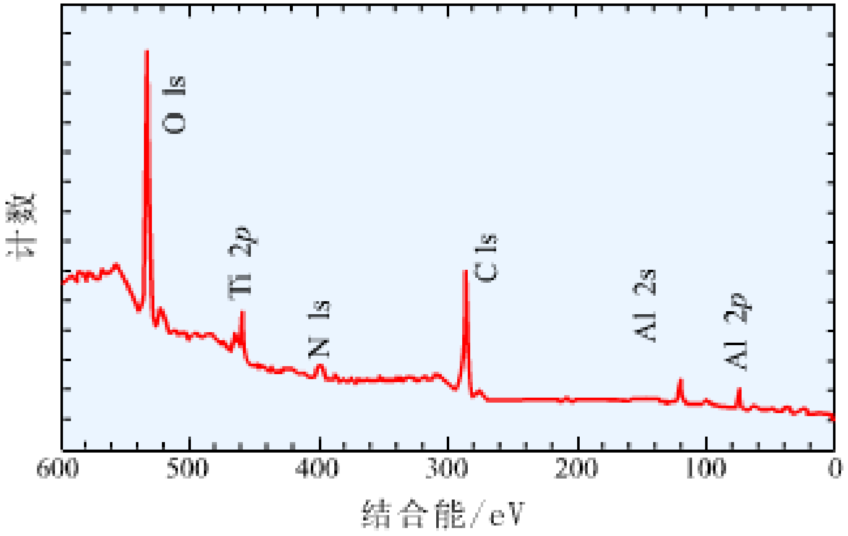


图10-12　高纯Al基片上沉积的Ti(CN)$_x$薄膜的XPS谱图(激发源为MgK$_\alpha$)

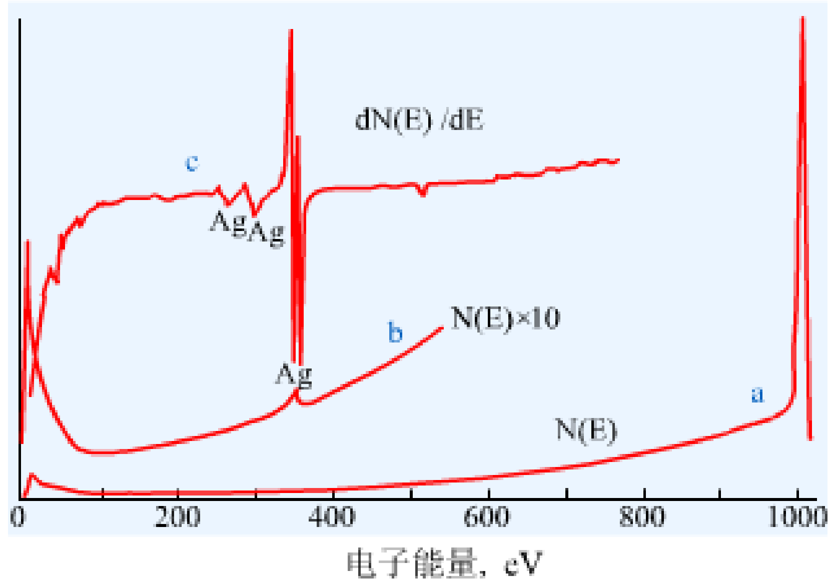


图10-14　Ag原子的俄歇电子谱

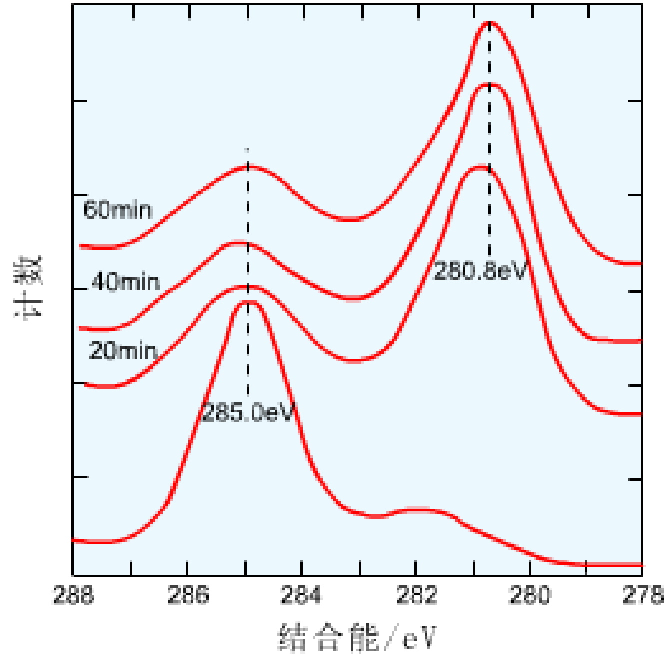


图10-13　PZT薄膜中碳的化学价态谱

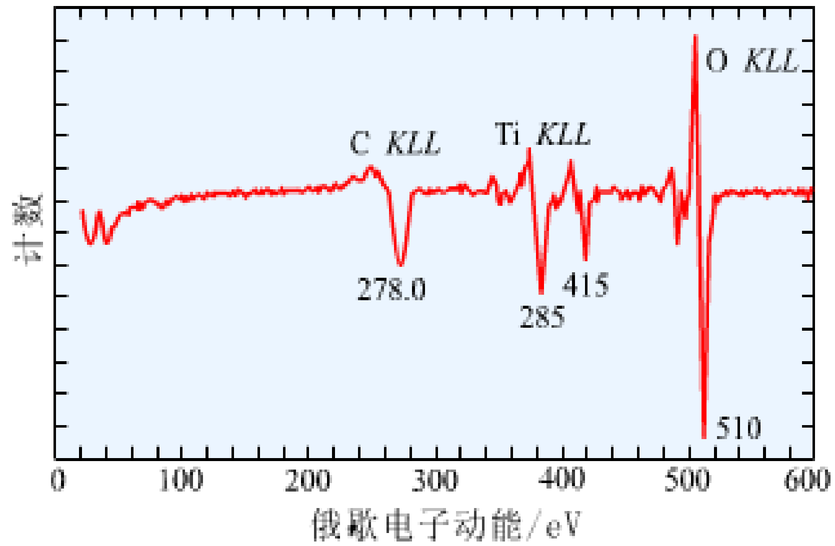


图10-15　金刚石表面的Ti薄膜的俄歇定性分析谱

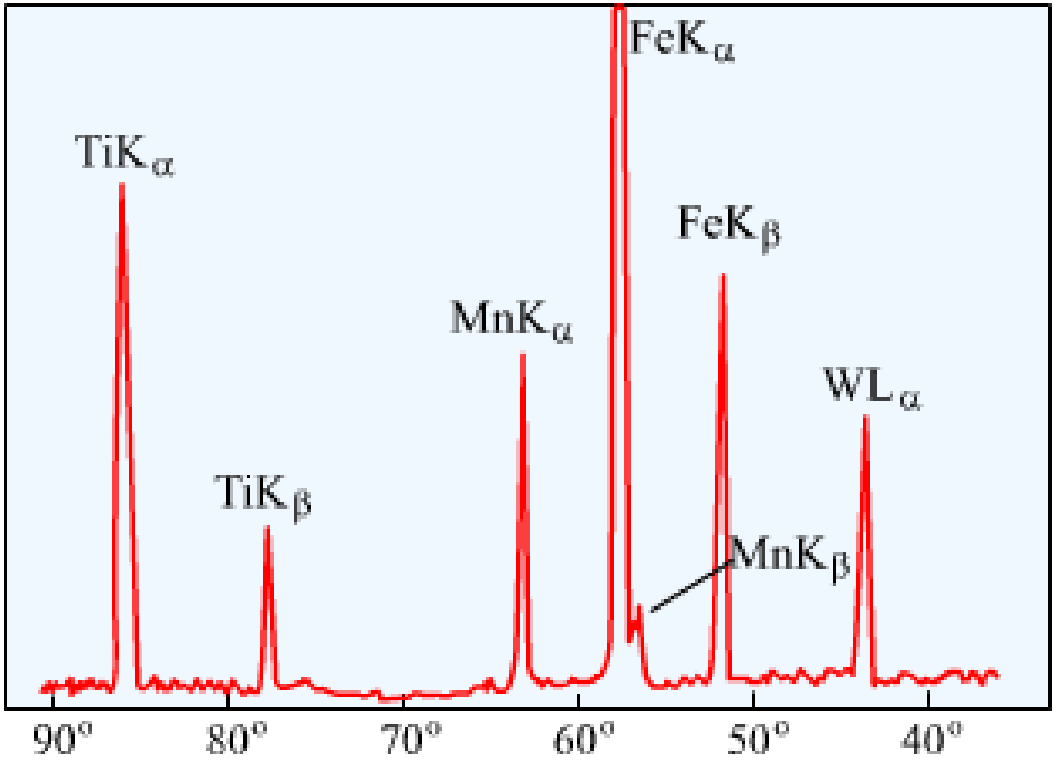


图10-9　一种合金钢的荧光X射线谱

谱技术的发展

XPS：X射线光电子能谱

1887年：赫兹发现光电效应光电离

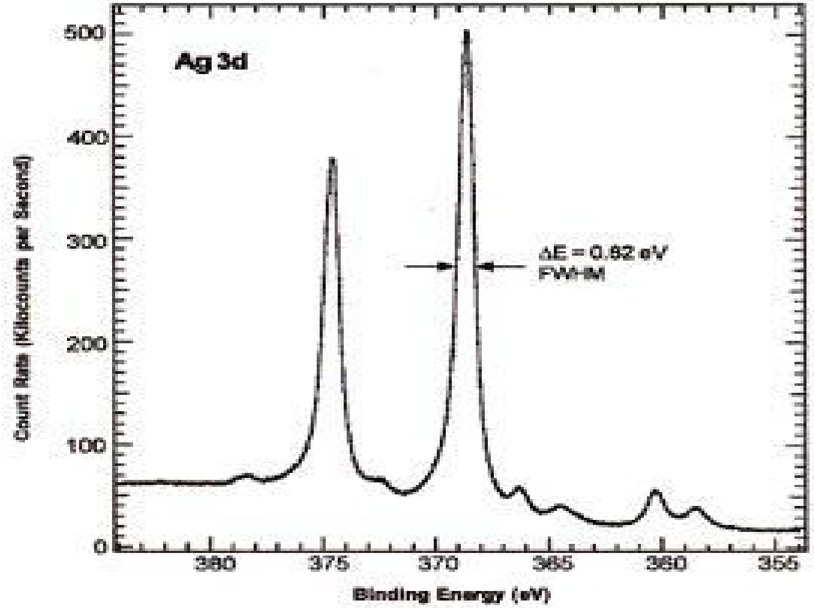
1905年：爱因斯坦解释光电效应

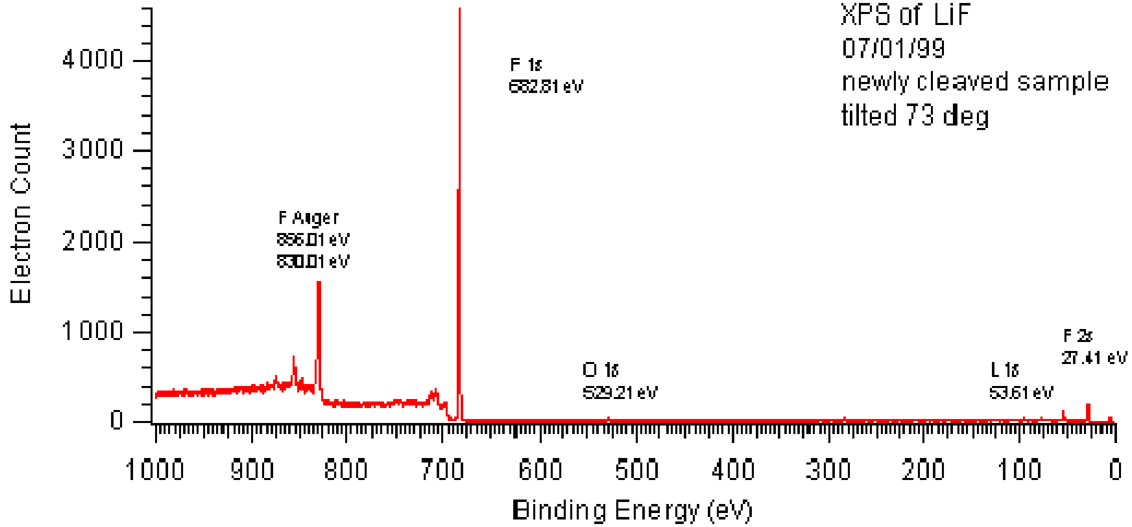
1954年：瑞典Uppsale和 Siegbahn制成ESCA（即XPS）

1962年：英国Turner制成UPS

化学位移

表面成份分析

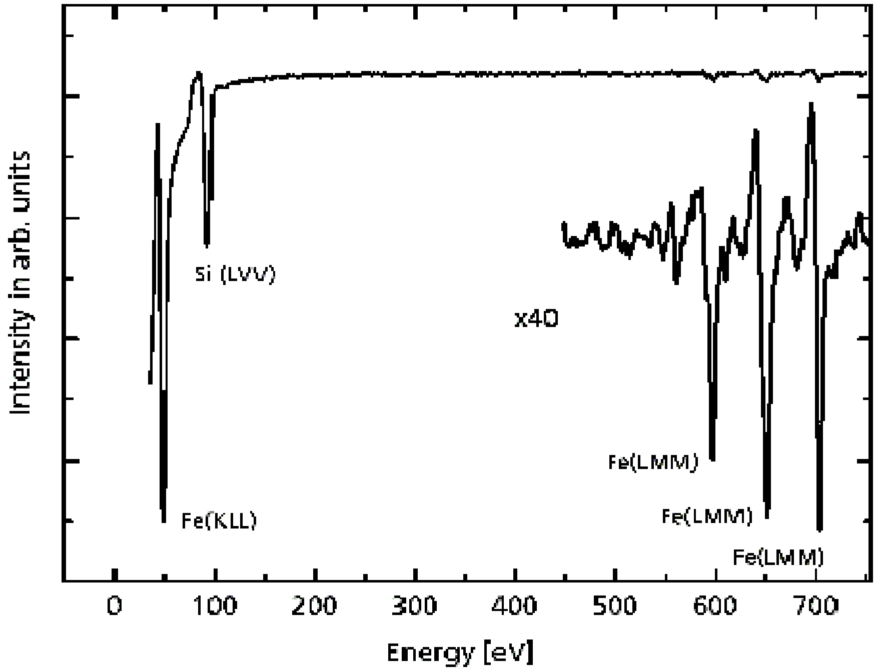




AES：俄歇电子谱

1925年：俄歇效应

1968年：Harris采用电势调制技术，获得AES

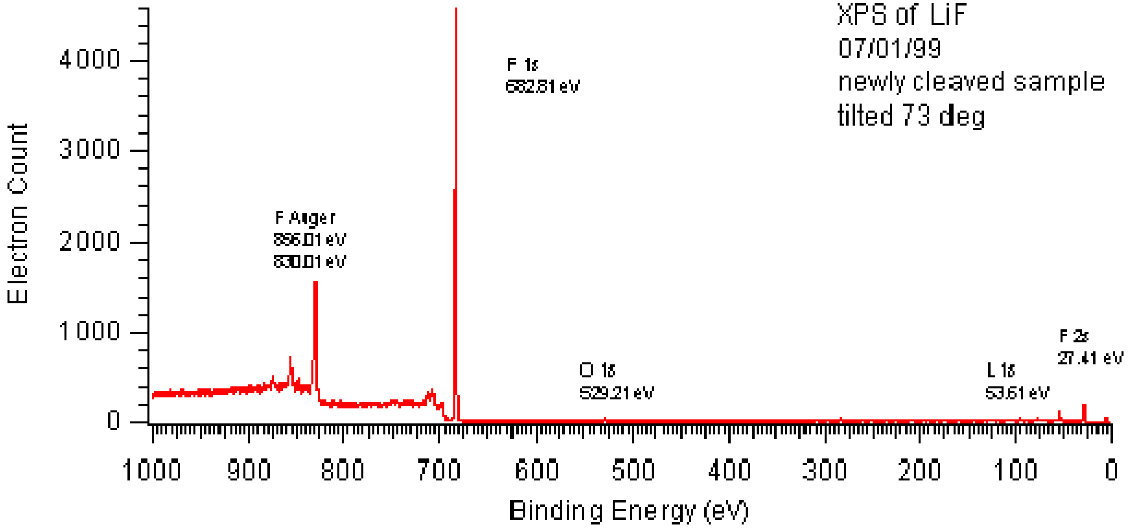


谱技术的发展

元素鉴定

表面深度分析

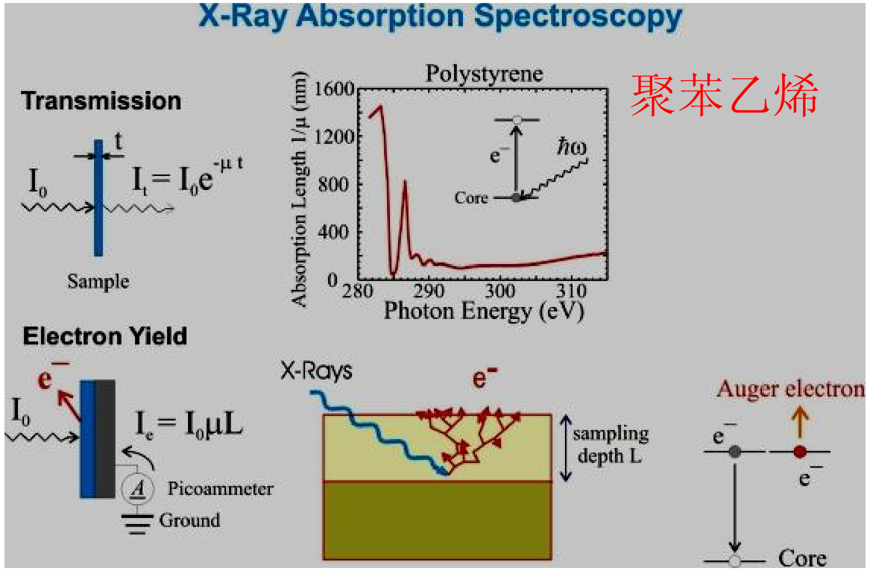
另外一些谱技术：

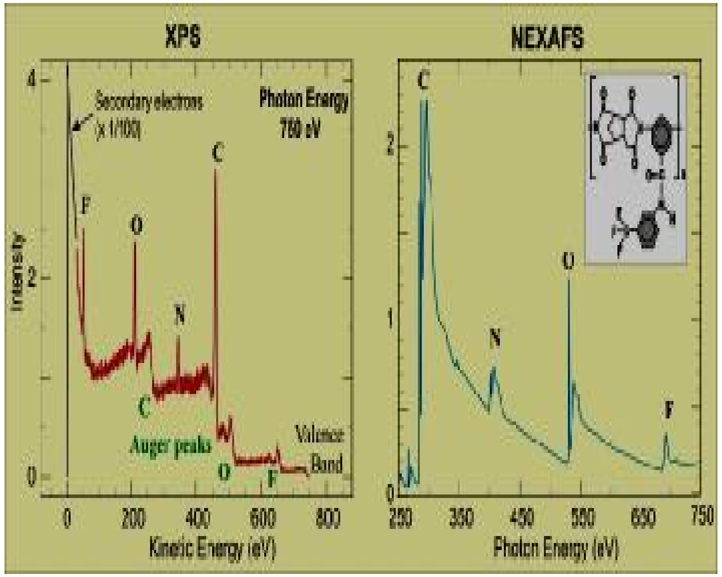


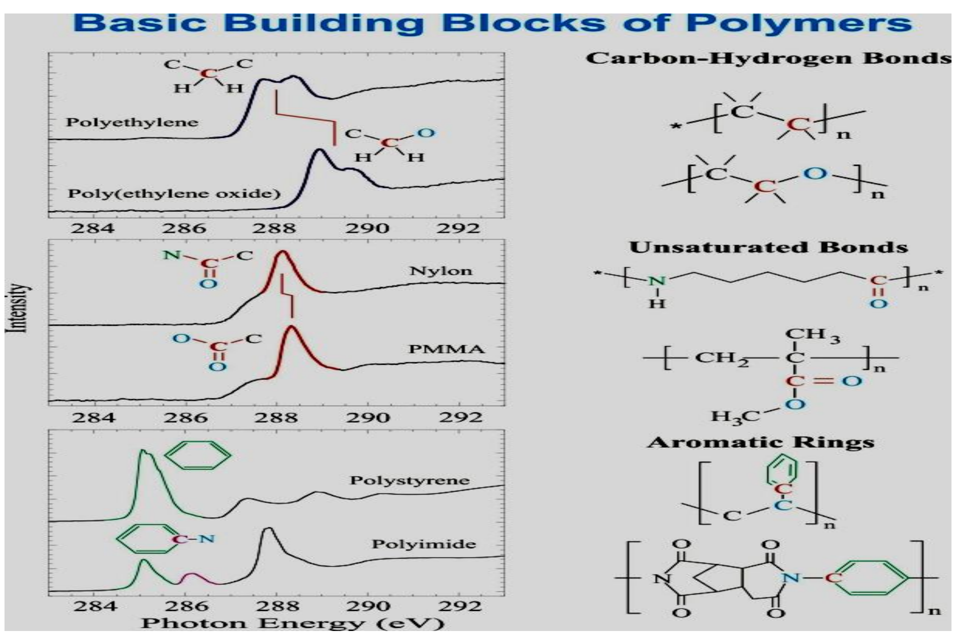
反射电子能量损失谱

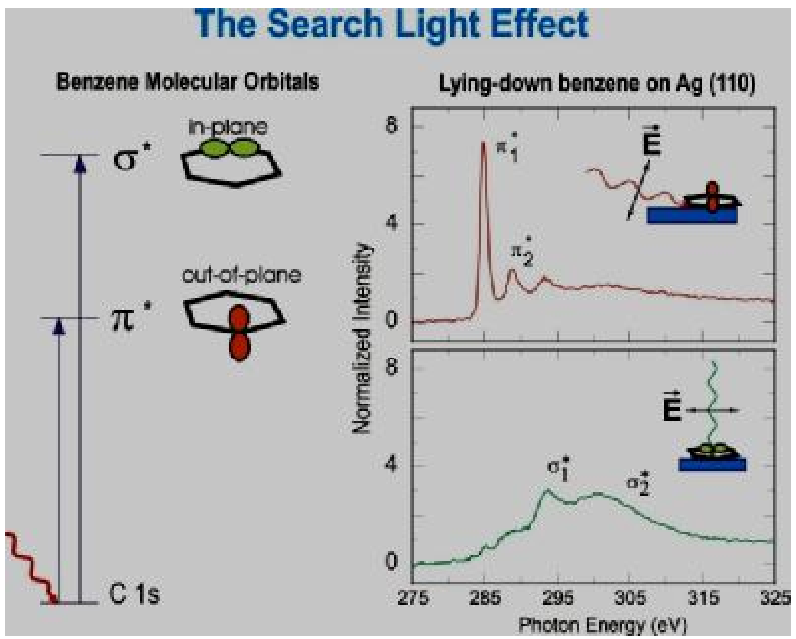
X射线吸收精细结构

- X射线吸收精细结构 (XAFS)
  - X射线近吸收边结构 (XANES) <50 eV
  - 广延X射线吸收边精细结构（EXAFS） >50 eV
- 透射法（TM）
- 全电子产额模式（TEY）
- X荧光模式


X-Ray Absorption Spectroscopy
Transmission
$I_t = I_0 e^{-\mu t}$
Sample
Polystyrene
聚苯乙烯
Absorption Length 1/μ (nm)
Photon Energy (eV)
Core
Electron Yield
$I_e = I_0 \mu L$
Picoammeter
Ground
X-Rays
sampling depth L
Auger electron
Core


XPS
NEXAFS
Secondary electrons (x 1/100)
Photon Energy 750 eV
Auger peaks
Valence Band
Intensity
Kinetic Energy (eV)
Photon Energy (eV)


Basic Building Blocks of Polymers
Carbon-Hydrogen Bonds
Polyethylene
Poly(ethylene oxide)
Unsaturated Bonds
Nylon
PMMA
Aromatic Rings
Polystyrene
Polyimide
Intensity
Photon Energy (eV)

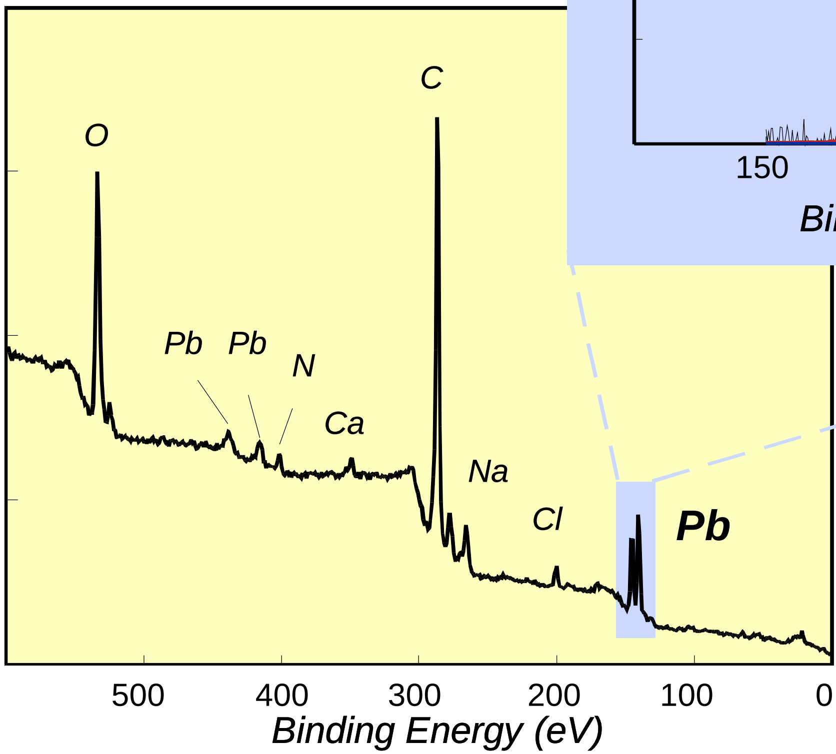

The Search Light Effect
Benzene Molecular Orbitals
Lying-down benzene on Ag (110)
in-plane
out-of-plane
C 1s
Normalized Intensity
Photon Energy (eV)

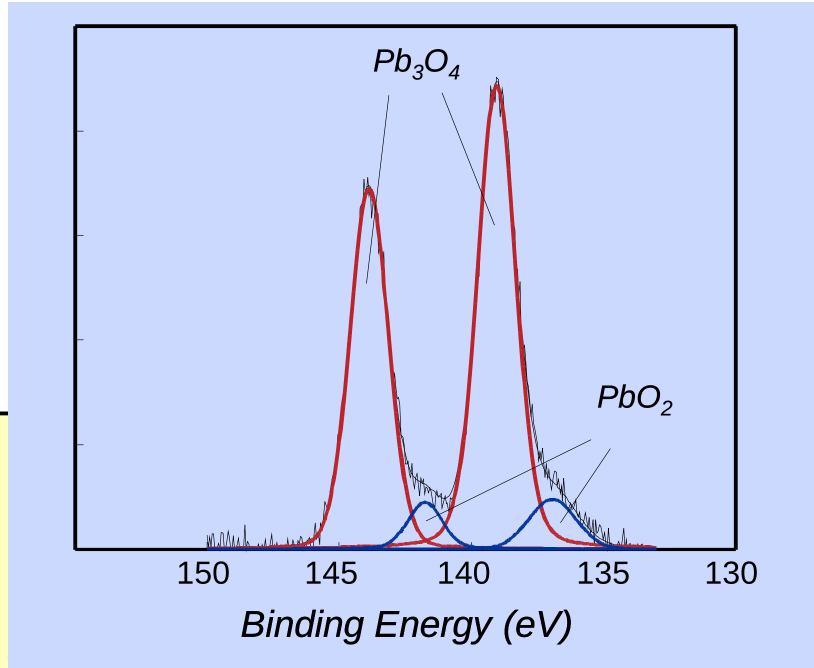
荷电效应

- 绝缘样品
- 中和电子枪
- 抹压柔软金属

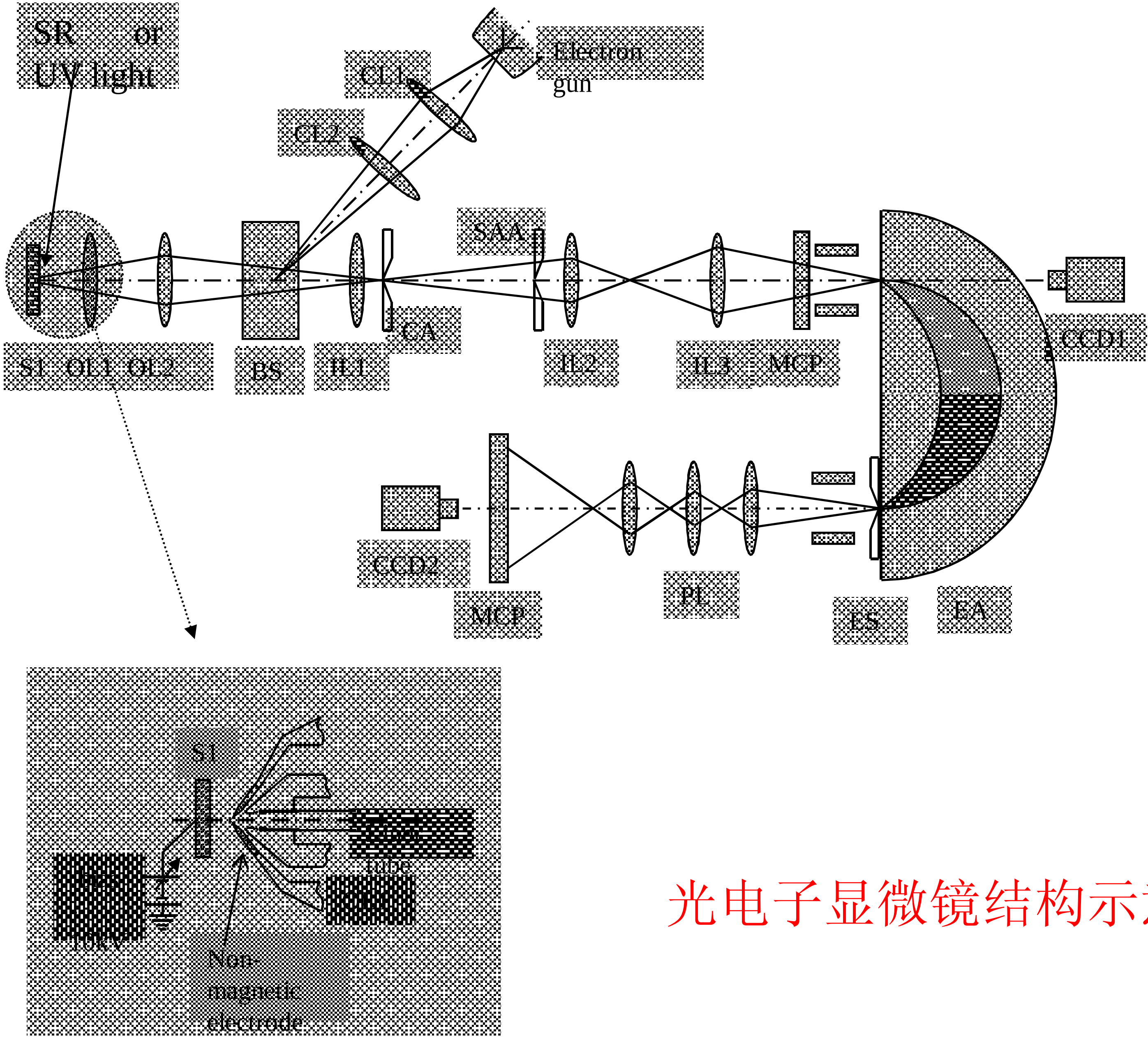
XPS Analysis of Pigment from Mummy Artwork

Egyptian Mummy
2nd Century AD
World Heritage Museum
University of Illinois

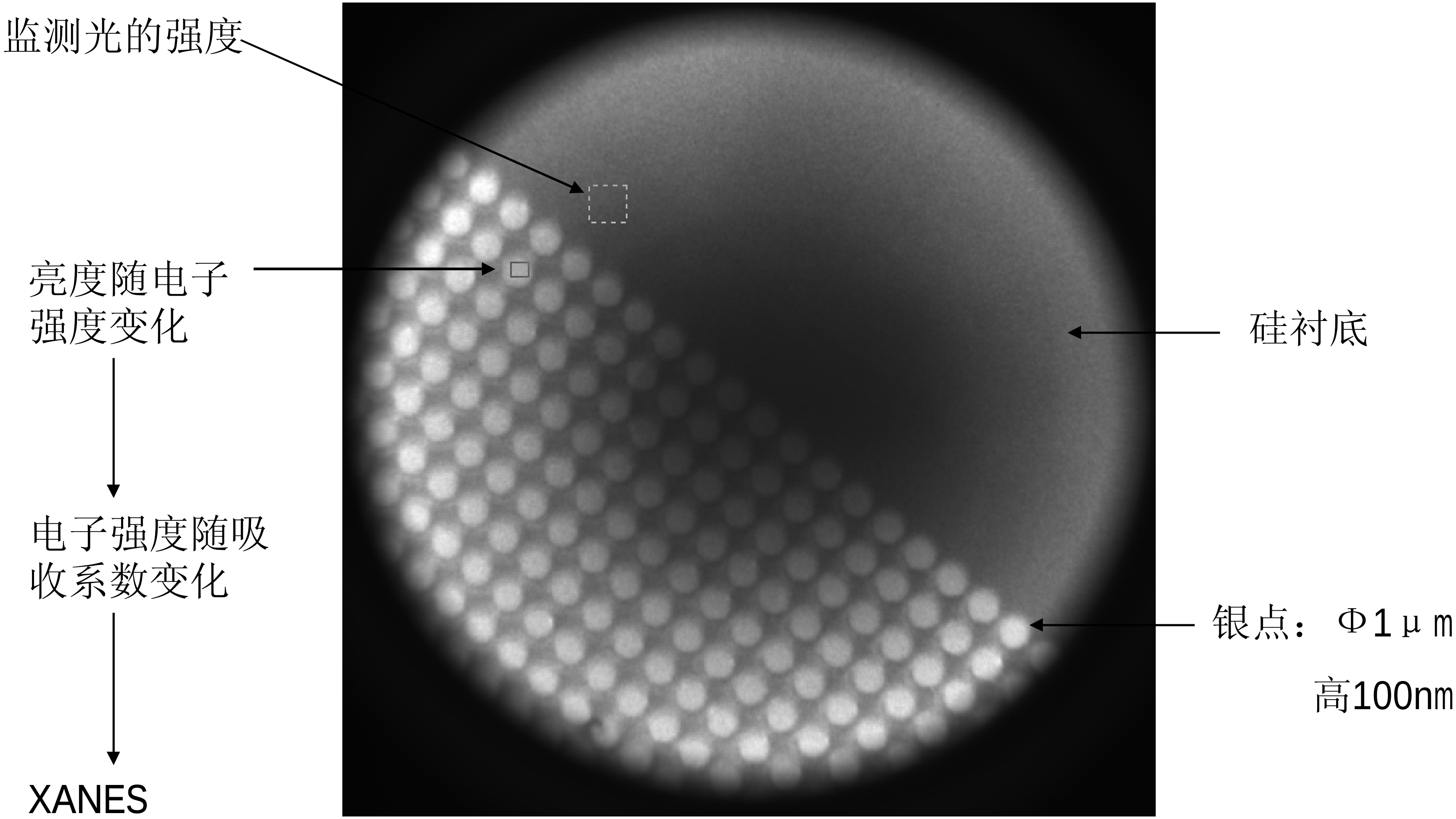




XPS analysis showed that the pigment used on the mummy wrapping was Pb_3O_4 rather than Fe_2O_3



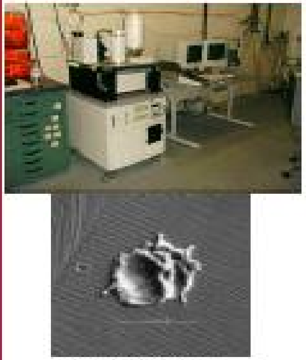
光电子显微镜结构示意图



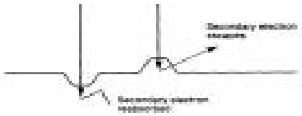
Ag/Si 光电子显微镜图像

X光能量：3390eV

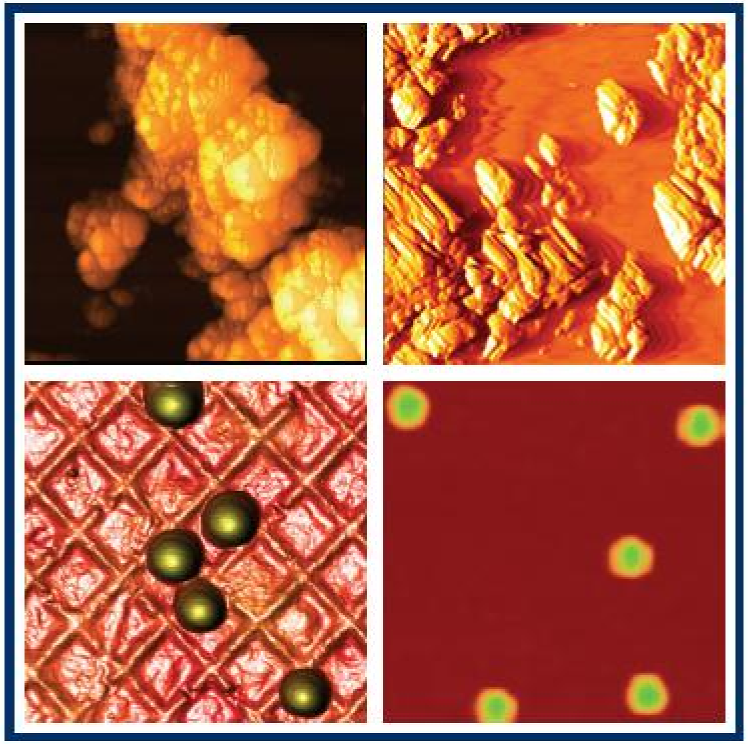
Scanning Electron Microscopy (SEM)



Breakdown-Damaged Copper Electrode



Scanning Electron Microscopy images surfaces at very high resolution (10 nanometers, depending on atomic number and surface finish). Images are made by scanning a high-energy primary electron beam onto the sample and collecting the low-energy secondary electrons, which are very surface sensitive. Images can be made more sensitive to sub-surface stress by selectively collecting only elastically-scattered ("backscatter mode") primary electrons.



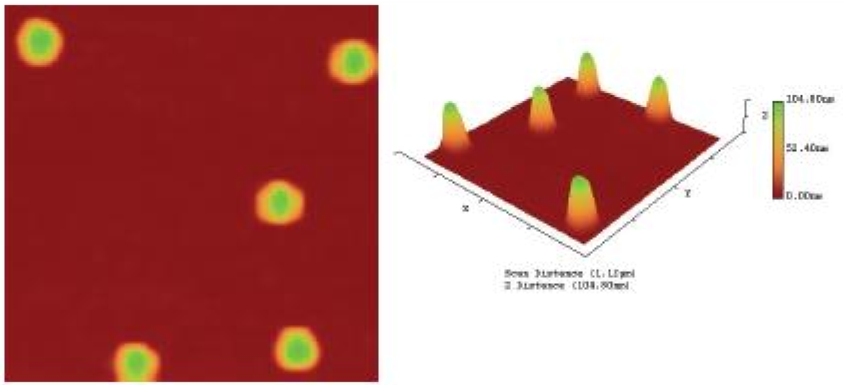
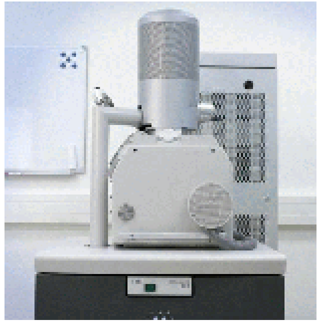


Figure 2: Left: NIST traceable polystyrene microspheres from Duke Scientific scanned with the NANO-RP™. Mean Ø of microspheres is 102nm. Scan size is 1µm x 1µm. Right: 3D view of 1x1µm scan of calibrated spheres.

Modern high resolution FE SEM

Zeiss Ultra 60



FEI Nova 600

JEOL JSM-7700F

Hitachi S5500

Instrument	Source	Resolution
Zeiss Ultra 60	TFE	1.0 nm @ 15 kV 1.7 nm @ 1 kV 4.0 nm @ 0.1 kV
FEI Nova 600	TFE	1.0 nm @ 15 kV 1.8 nm @ 1 kV
JEOL JSM-7700F	CFE	0.6 nm @ 5 kV 1.0 nm @ 1 kV
Hitachi S5500	CFE	0.4 nm @ 30 kV 1.6 nm @ 1 kV

From
www.smt.zeiss.com www.fei.com www.jeol.co.jp www.hitachi-hitec.com

其它分析手段

- STM
- AFM
- AES
- REELS

谢谢大家!