Nano Materials

Contents

- ☐ **Introduction**
- ☐ **Basics**
- ☐ **Synthesis of Nano Materials**
- ☐ **Fabrication of Nano Structure**
- ☐ **Nano Characterization**
- ☐ **Properties and Applications**

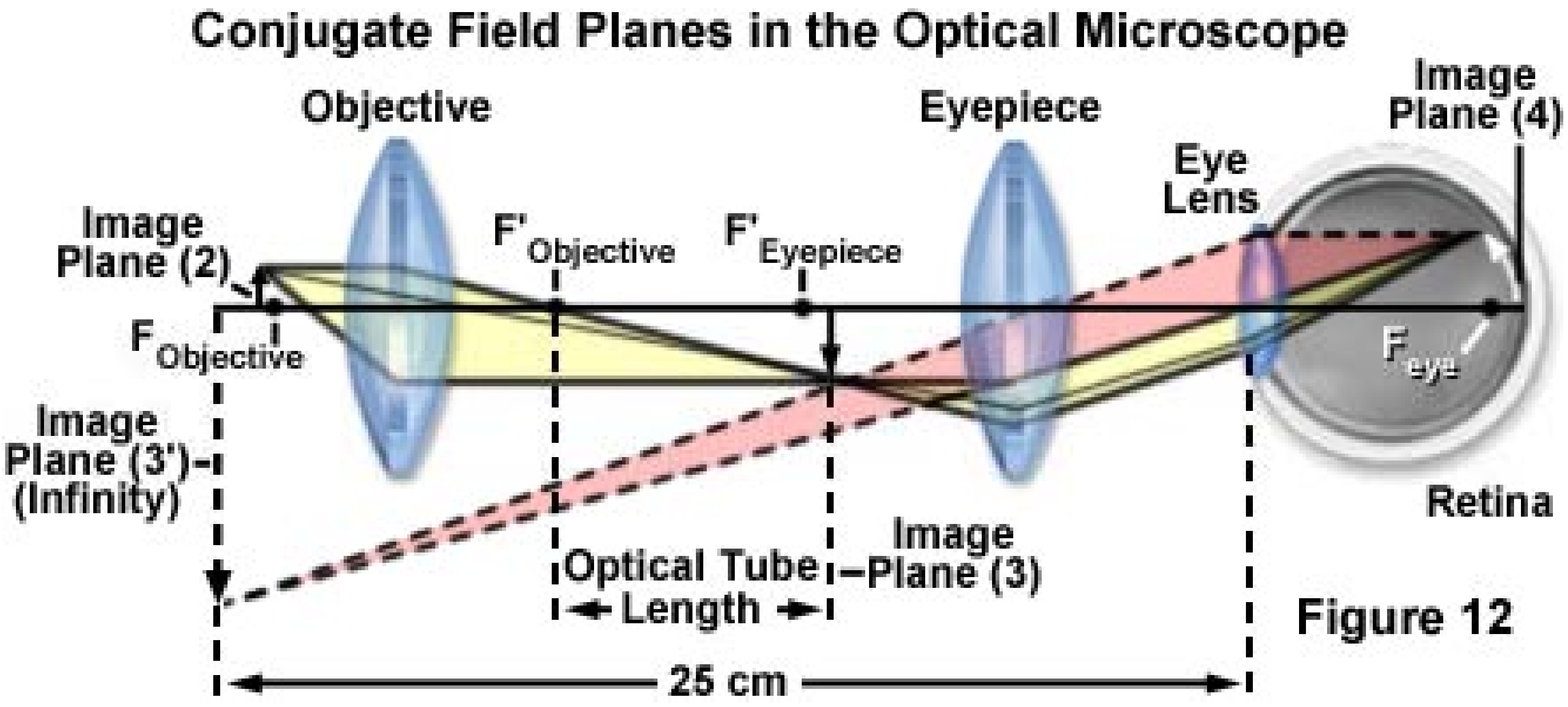
Nano Characterization

- Microscopy Analysis (Image Analysis)
  - Electron Microscopy
    - SEM
    - TEM
  - Scanning Probe Microscopy
    - AFM
    - STM
  - Optical Microscopy
    - NSOM
- Diffraction Analysis
  - X-Ray Diffraction
  - Electron Diffraction
- Spectroscopy Analysis
  - Optical spectroscopy
  - Electron spectroscopy

Nano Characterization

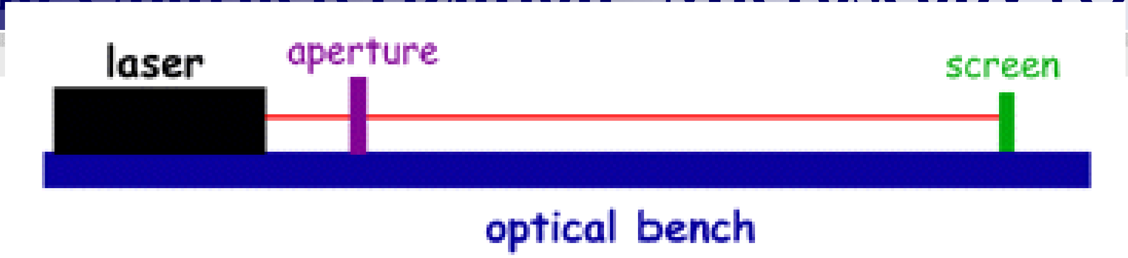
- ❑Structural analysis
  - ❑ SEM, TEM, XRD, SAM, SPM, PEEM, LEEM, STXM
- ❑Chemical analysis
  - ❑ AES, XPS, TPD, SIMS, EDX, SPM
- ❑Electronic, optical analysis
  - ❑ UV/VIS, UPS, SPM
- ❑Magnetic analysis
  - ❑ SQUID, SMOKE, SEMPA, SPM
- ❑Vibrational analysis
  - ❑ IR, HREELS, Raman, SPM
- ❑Local physico-chemical analysis
  - ❑ SPM

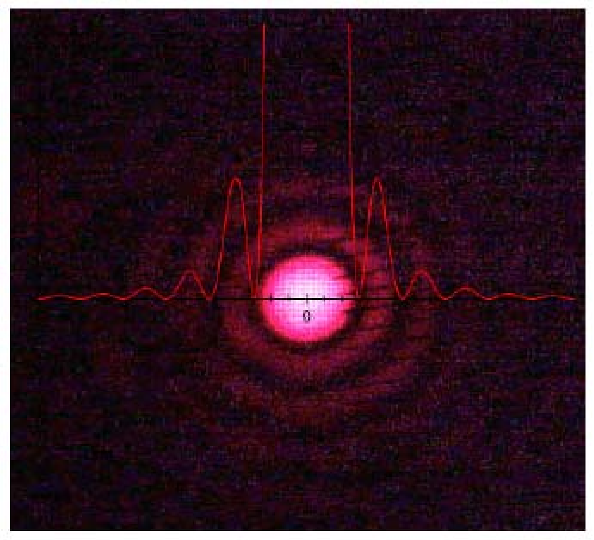
Nano Characterization- Microscopy (OM)

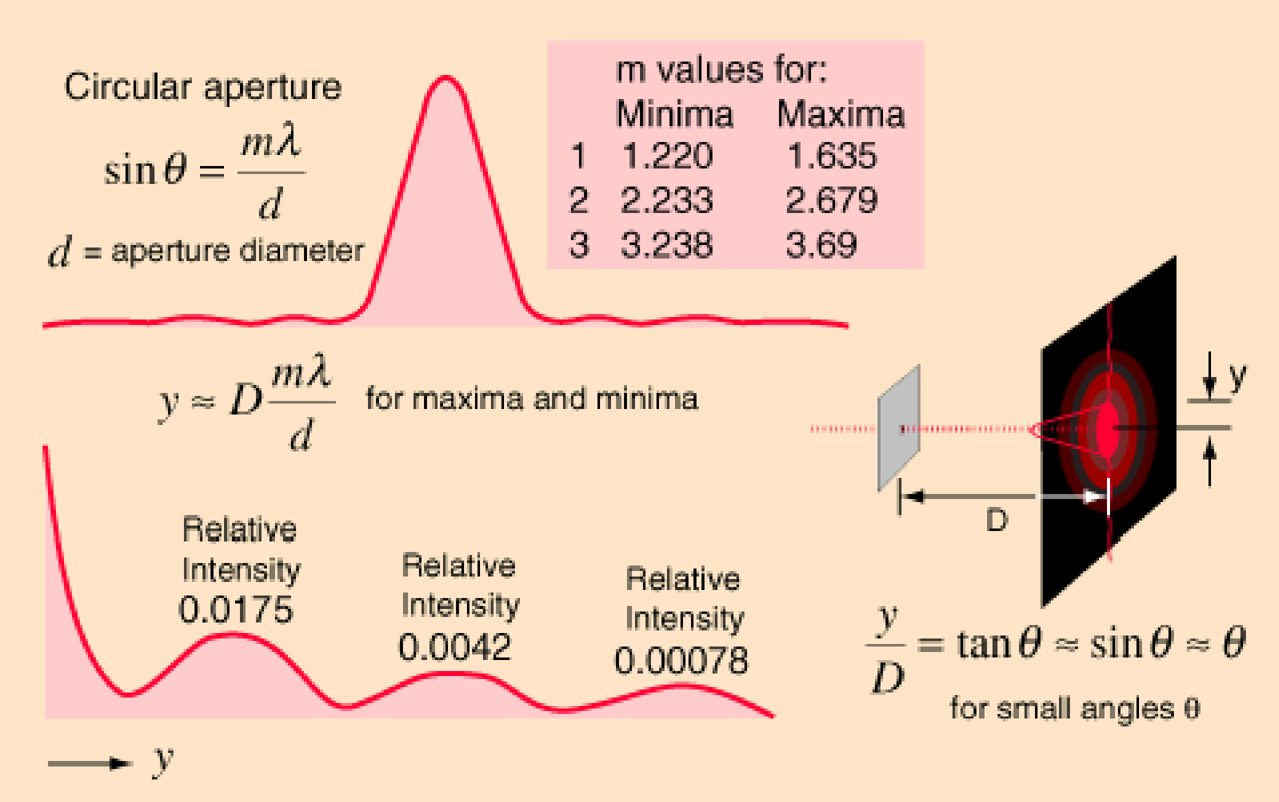


http://www.microscopyu.com/articles/optics/components.html

Nano Characterization- Microscopy (OM)






Circular aperture

$$\sin\theta = \frac{m\lambda}{d}$$

d = aperture diameter

m values for:

	Minima	Maxima
1	1.220	1.635
2	2.233	2.679
3	3.238	3.69

$$y \approx D\frac{m\lambda}{d}$$ for maxima and minima

$$\frac{y}{D} = \tan\theta \approx \sin\theta \approx \theta$$

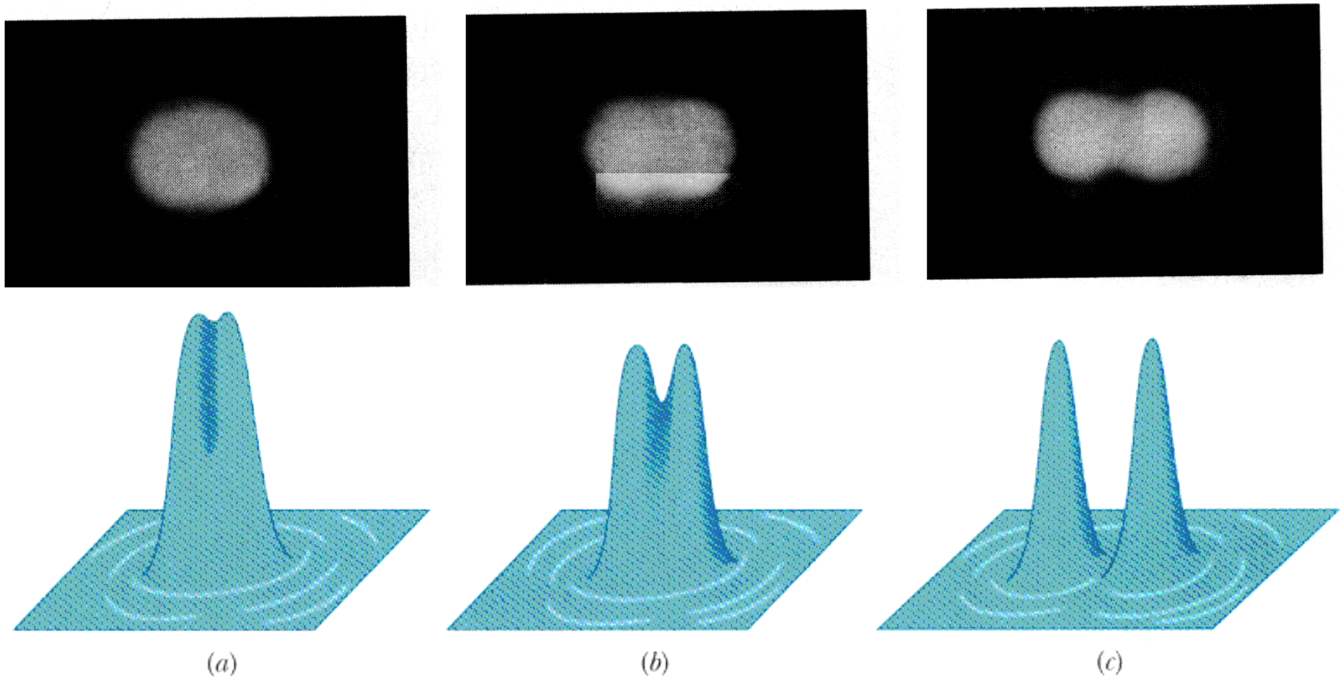
for small angles θ

http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/cirapp2.html

Nano Characterization- Microscopy (OM)

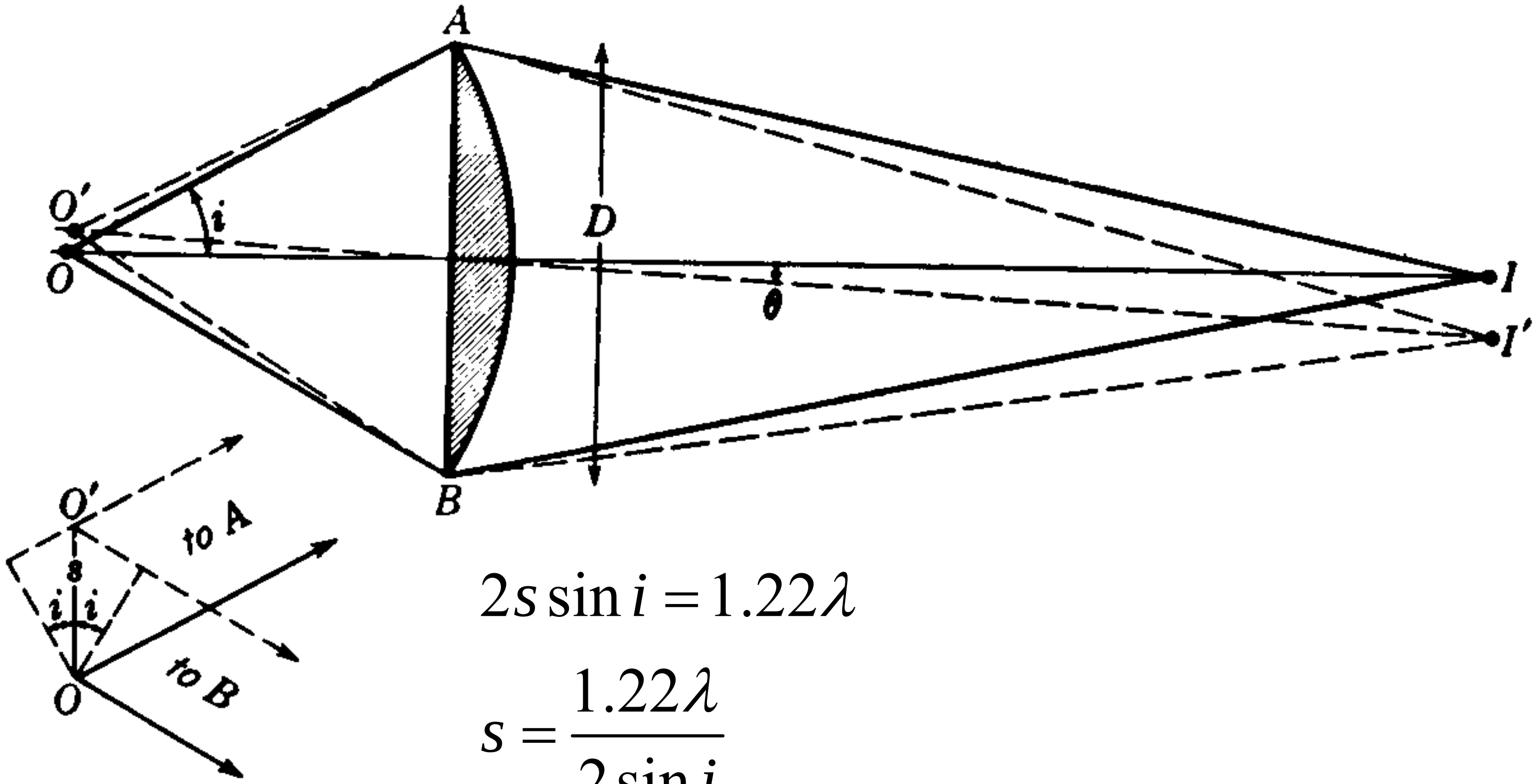
- resolved when the central maximum of one falls on the first dark ring of the other

$$\sin\theta \approx \theta = 1.22\frac{\lambda}{d}$$



(a) (b) (c)

Nano Characterization- Microscopy (OM)



$$2s\sin i = 1.22\lambda$$

$$s = \frac{1.22\lambda}{2\sin i}$$

corrections: self luminous, refractive index

$$s = \frac{\lambda}{2n\sin i}$$ $n\sin i$: numerical aperture (<1.6)

ex) λ=500 nm s=180 nm

7.1 Detection Limit

Physical Detection Limit

1. Optical microscopy (λ~0.55µm):

-Diffraction limited optical microscopy resolution:

RL=0.61λ/NA(=nsinθ)

Ex) w/ 40x objective, sin θ =0.65, n=1, thus, RL=0.52 µm

2. Electron microscopy:Particle-wave duality, λ=h/(mv)~ 1Å

- Transmission Electron Microscopy (TEM)
- Scanning Electron Microscopy (SEM)

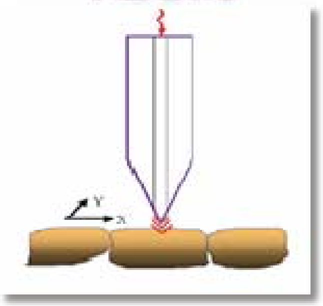
3. Beyond diffraction Limit

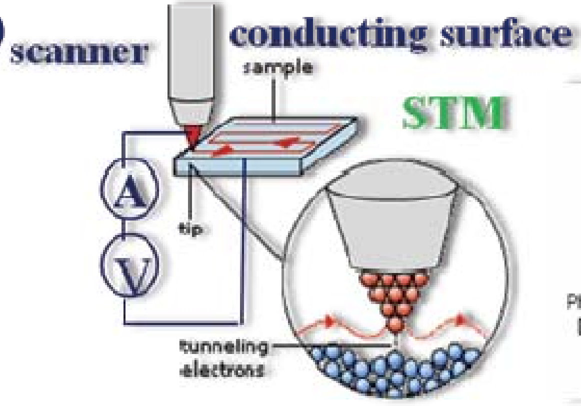
- Near field scanning optical microscopy(NSOM)
- Scanning tunneling microscopy(STM): conductive surface
- Atomic Force Microscopy(AFM)

NSOM

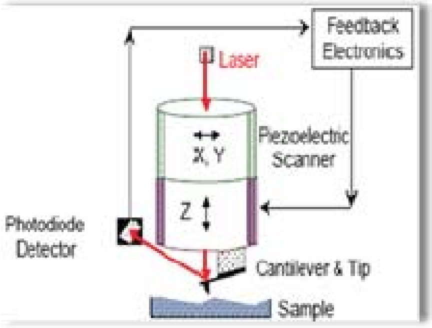
-tip aperture
Diameter:
100nm
-µm Grain

Nano chemistry





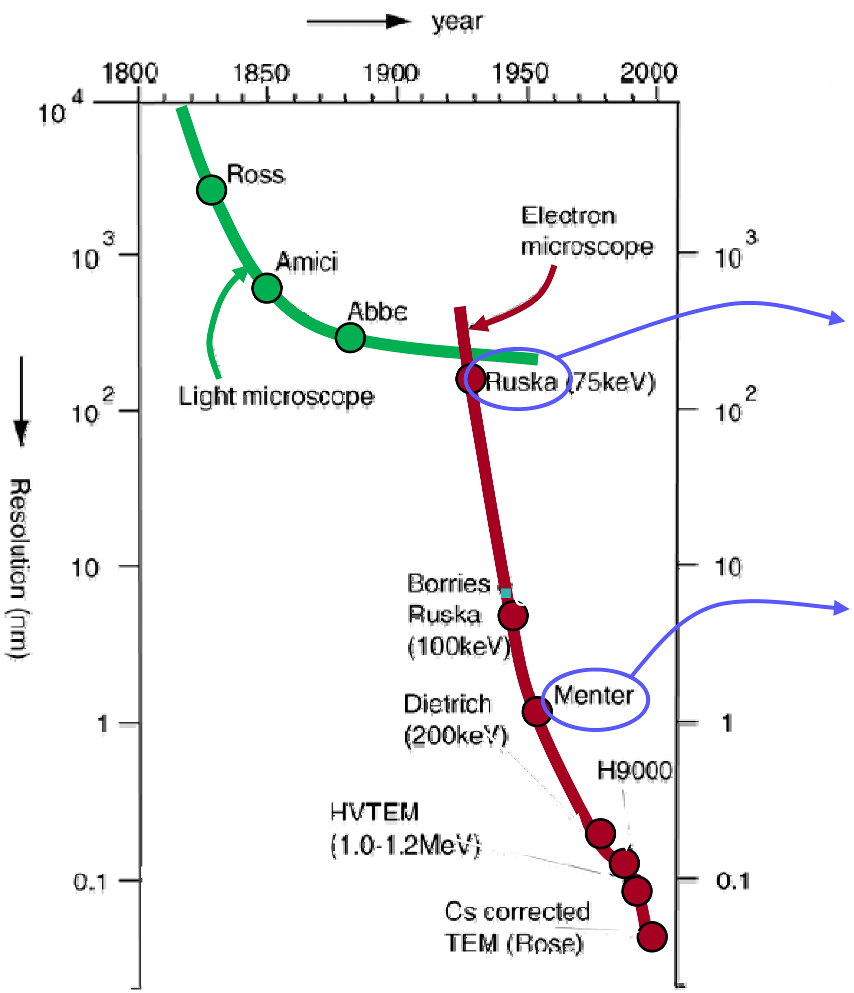
AFM



Nano Characterization- Microscopy

	Optical microscope	Electron microscope	Scanning probe microscope
Operation	Air, Liquid	Vacuum	Air, Liquid, UH
Depth of field	Small	Large	Medium
Lateral resolution	1μm	SEM : 1~5nm TEM : 0.1nm	AFM : 2~10nm STM : 0.1nm
Vertical resolution	N/A	N/A	AFM : 0.1nm STM : 0.01nm
Magnification	1~2×10^3	10~10^6	5×10^2~10^8
Sample	Not completely transparent	Un-chargeable TEM : vacuum compatible thin film	Surface height < 10mm
Contrast	Absorption Reflection	Scattering Diffraction	Tunneling

Nano Characterization- Microscopy



- 1926, Schrodinger, Schrodinger equation
- 1928, Bethe, Dynamical diffraction theory
- 1931, Ruska & Knoll, Invented TEM
- 1936, 1st Commercial TEM (Siemens, Germany)
- 1939, Mollenstedt, CBED theory
- 1956, Menter, first observed lattice image
- (High Resolution)
- 1961, Howie & Whelan,
- Kinematical diffraction theory
- 1986, Ruska, Nobel prize winner

Nano Characterization- Microscopy

- de Broglie relationship

$$\lambda = \frac{h}{m_e v} = \frac{h}{\sqrt{2m_e eV}} = \frac{h}{\sqrt{2m_o eV(1+\frac{eV}{2m_o c^2})}}$$

$$= \frac{12.26}{V^{1/2}(1+0.9788\times10^{-6}V)^{1/2}} \quad \text{(A)}$$

- 1kV → 0.3785 A

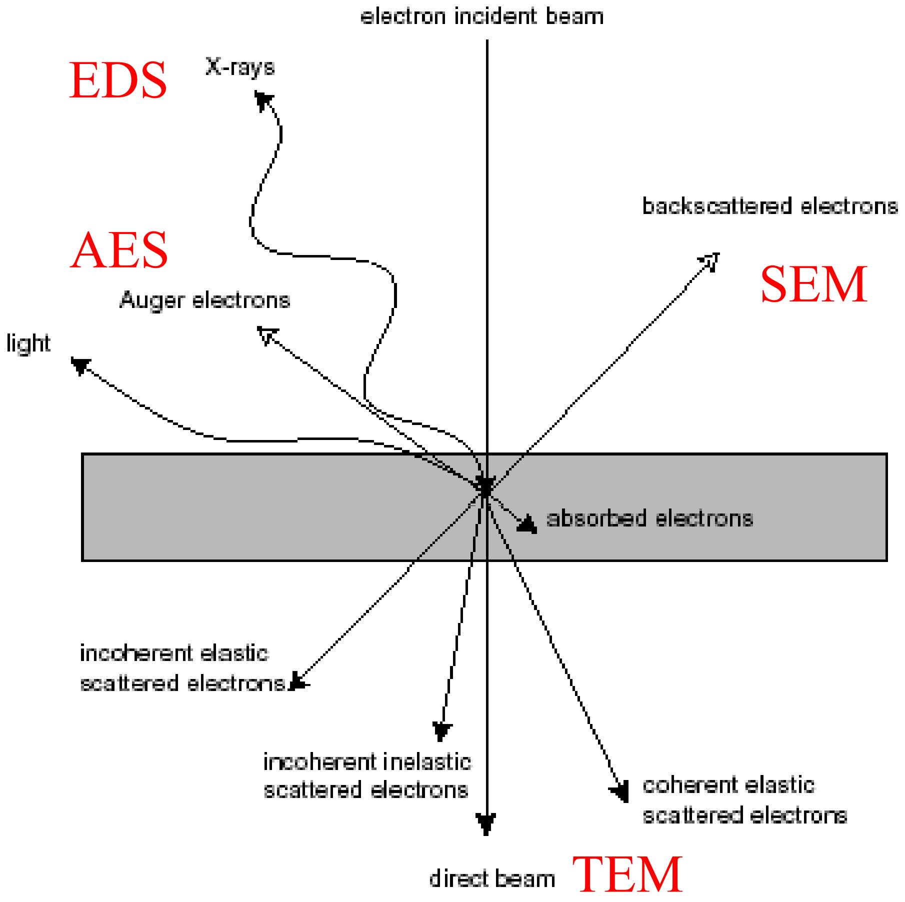
10 kV → 0.1220 A

100 kV → 0.037 A, 200 kV → 0.0251 A

- $R = \frac{0.61\lambda}{n\sin\alpha} \approx 0.3$ nm (n=1, $\sin\alpha = \alpha = 5\times10^{-3}$ rad)

Nano Characterization- Electron microscopy

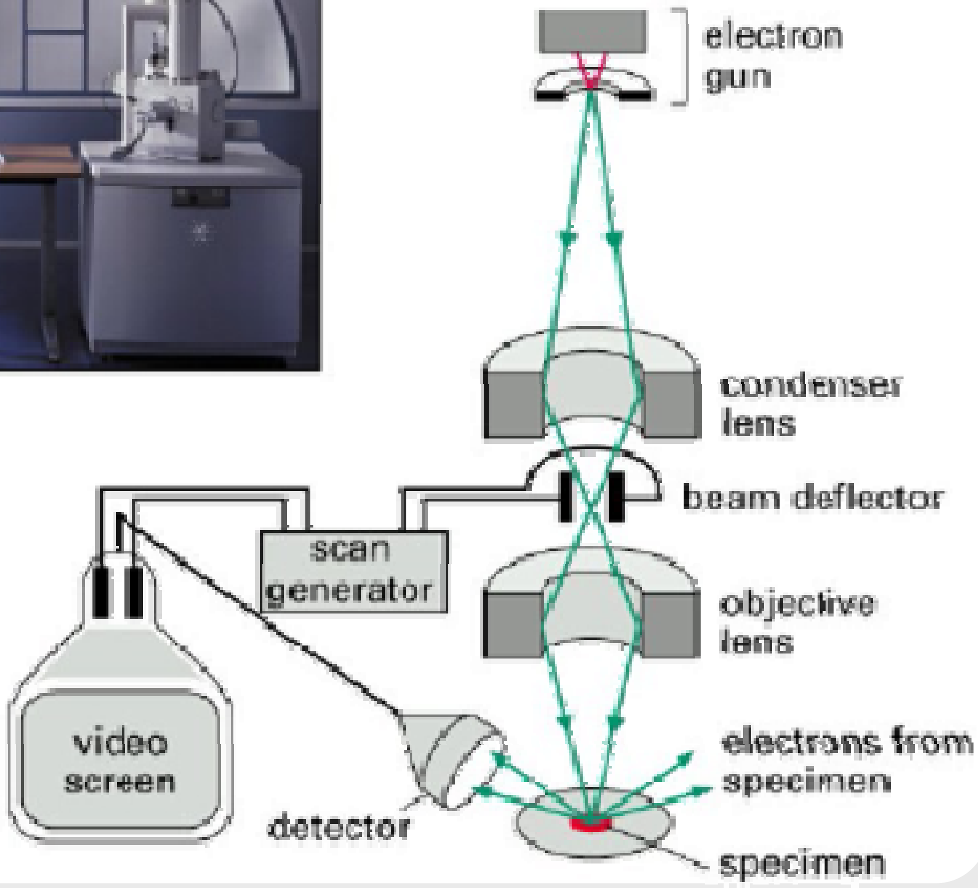
☐Interaction between electrons and materials



Nano Characterization- Microscopy (SEM)

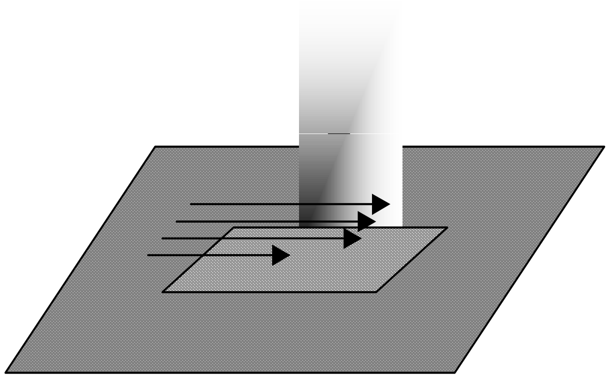
SEM (Scanning Electron Microscopy)

- Beam size : a few~30 Å
- Beam voltage : 20~40kV
- Resolution : 10~100 Å
- Magnification : 20~650000 times
- Imaging radiations : secondary electrons, backscattering electrons
- Topographic contrast : inclination effect, shadowing, edge contrast
- Composition contrast : backscattering, yield-bulk composition
- Detections
  - Secondary electrons : topography
  - Backscattering electrons : atomic # and topography
  - X-ray fluorescence : composition

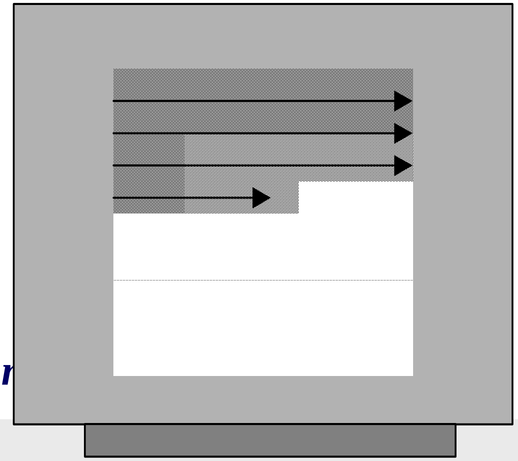


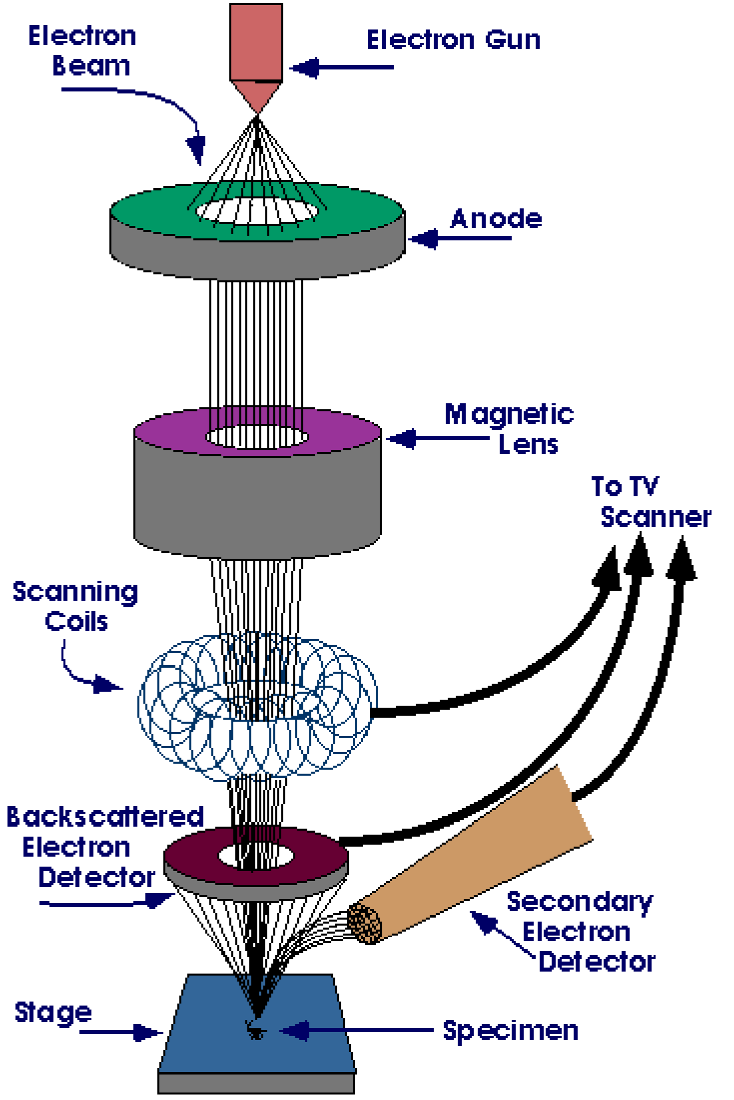
Nano Characterization- Microscopy (SEM)

Focused Electron Beam



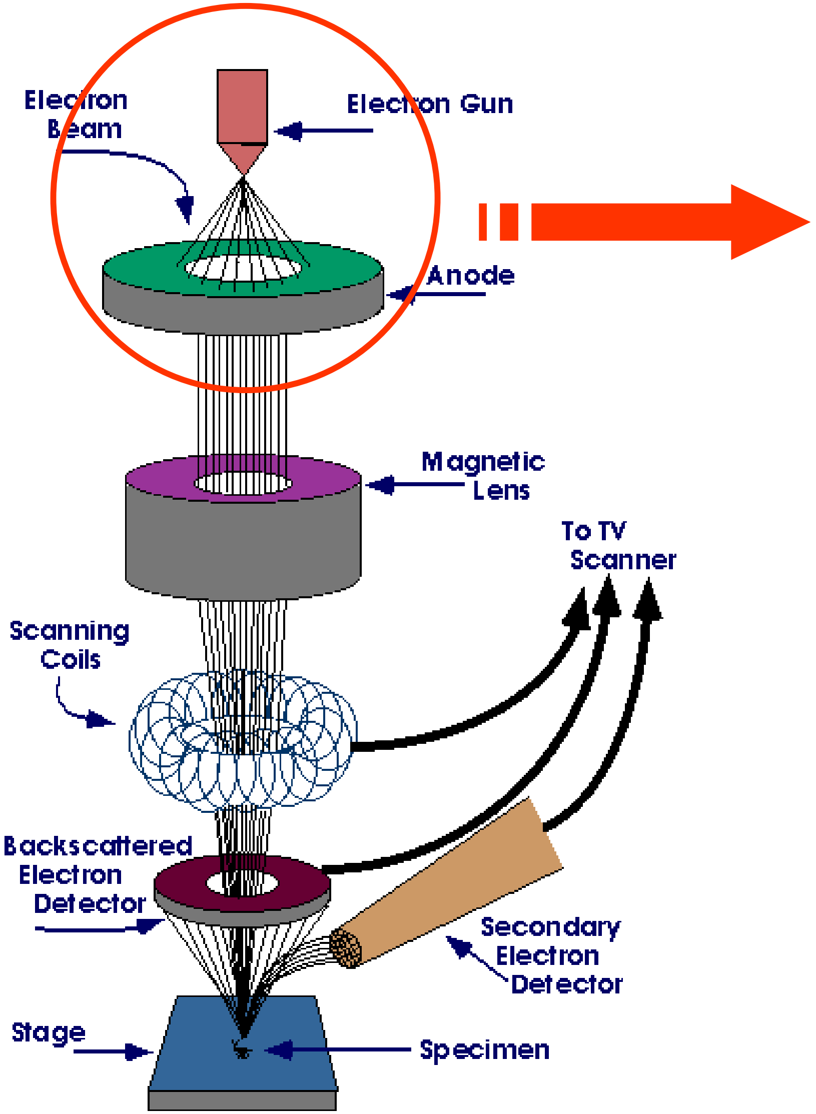
CRT

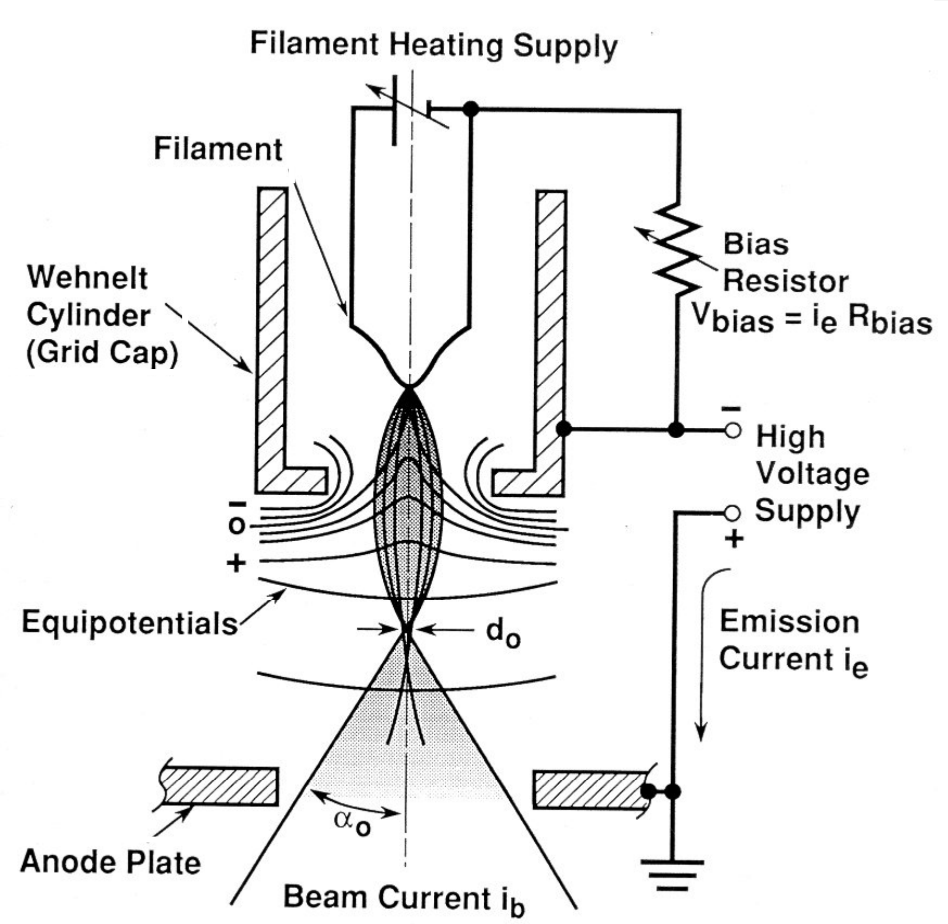




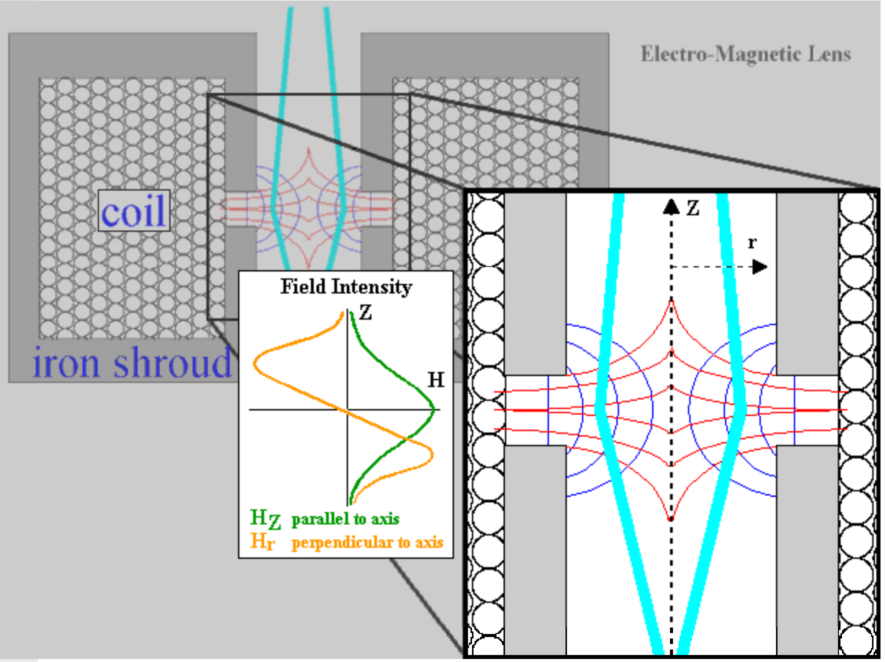
Nano Characterization- Microscopy (SEM)

- tungsten hairpin
  LaB_6
  field Emission





Nano Characterization- Microscopy (SEM)



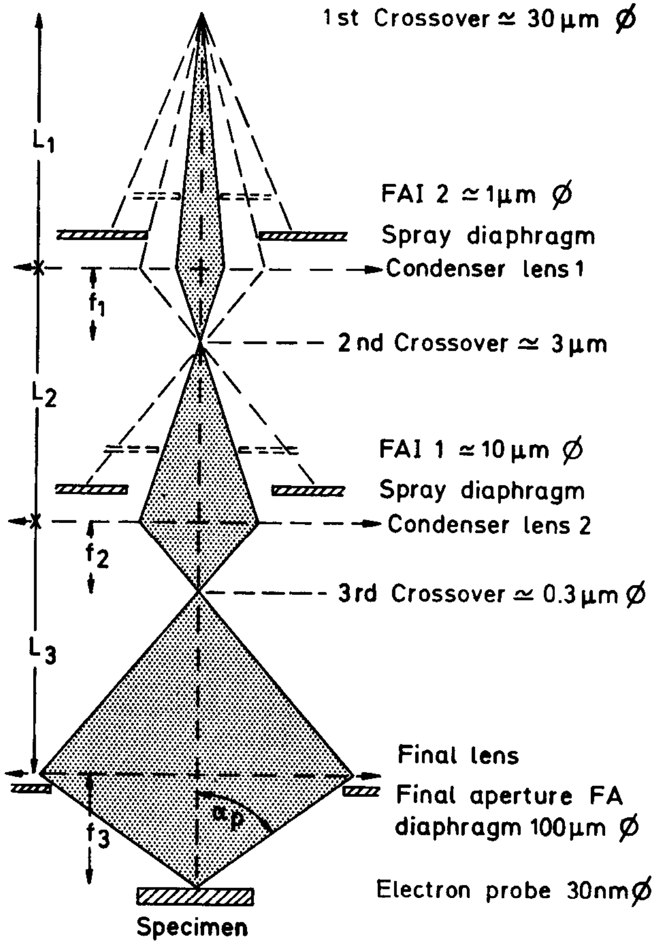
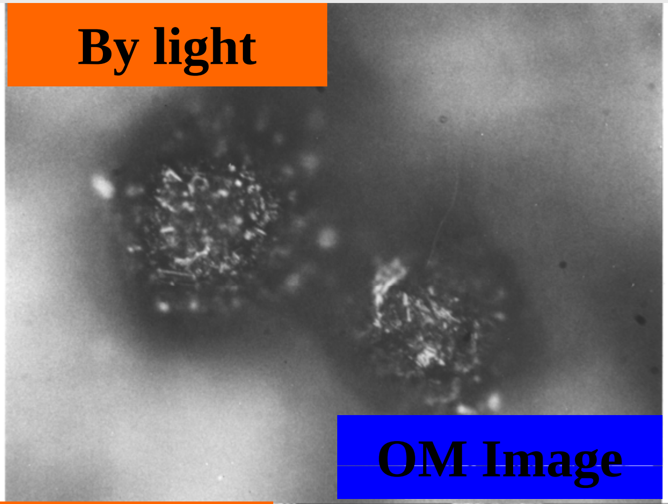


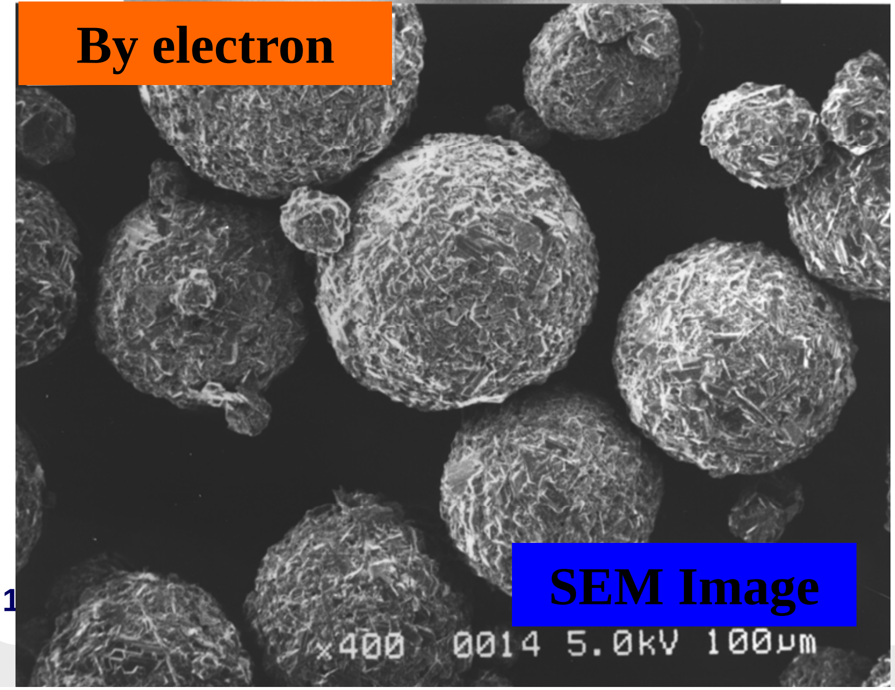
Fig. 2.13. Schematic ray in the electron-optical column of a SEM (FAI = final aperture image)

Nano Characterization- Microscopy (SEM)



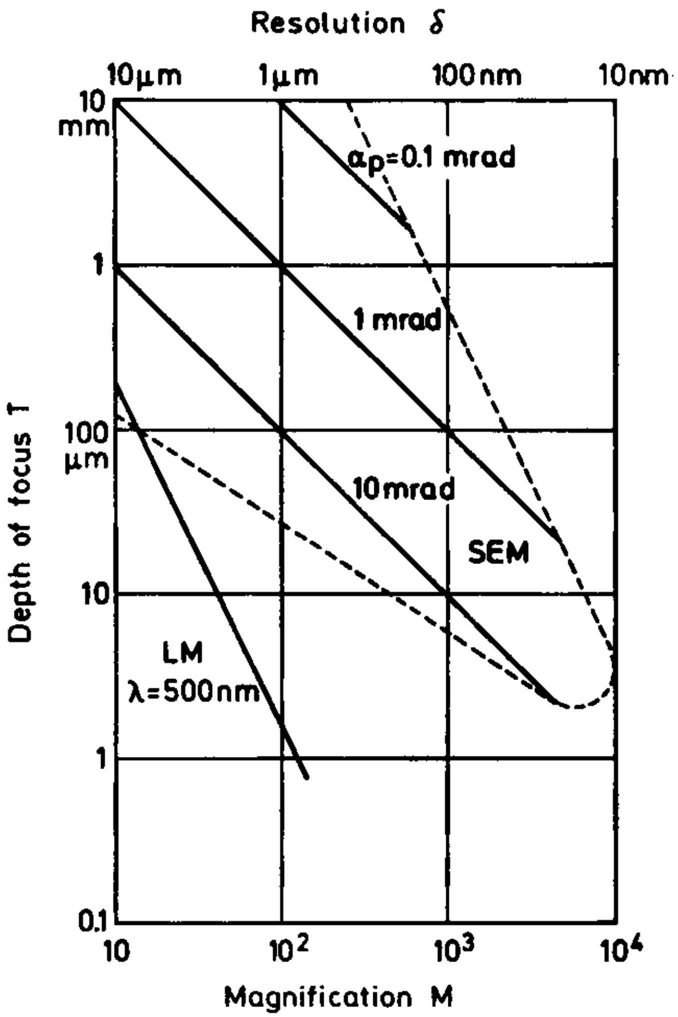
By light

OM Image

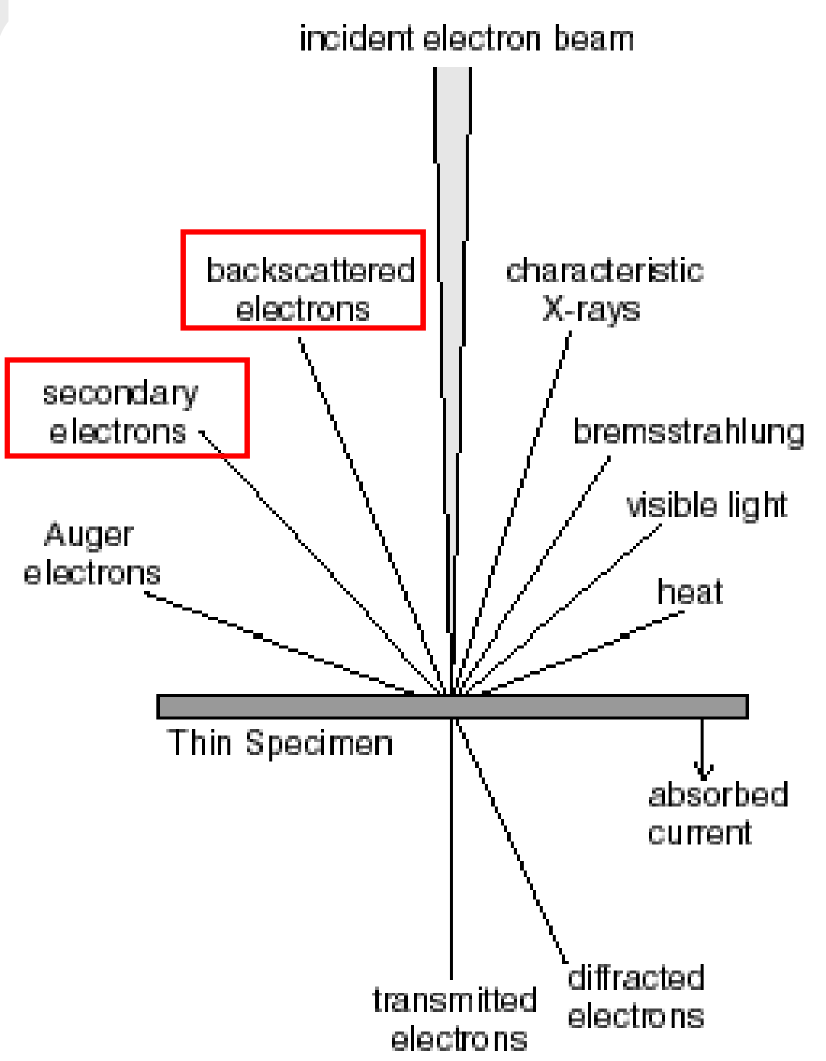


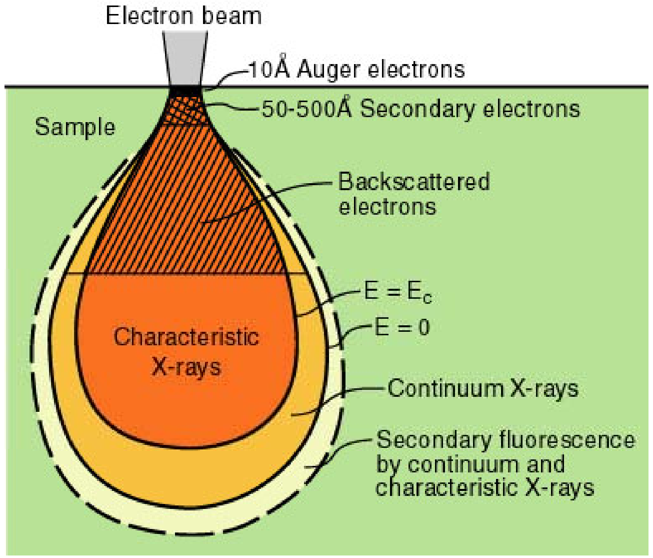
By electron

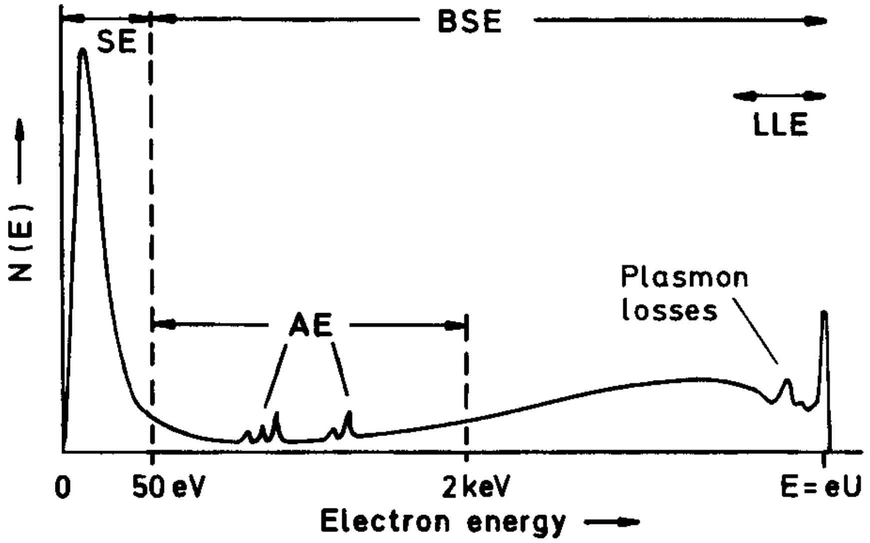
SEM Image



Nano Characterization- Microscopy (SEM)







Nano Characterization- Microscopy (SEM)

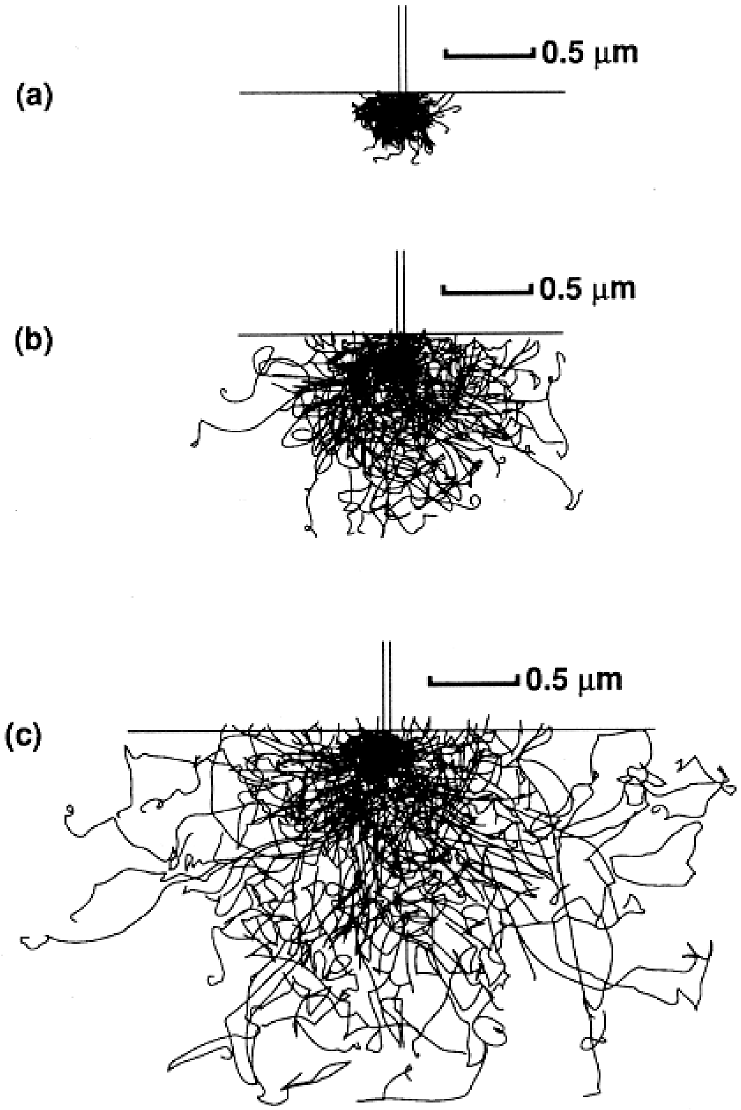
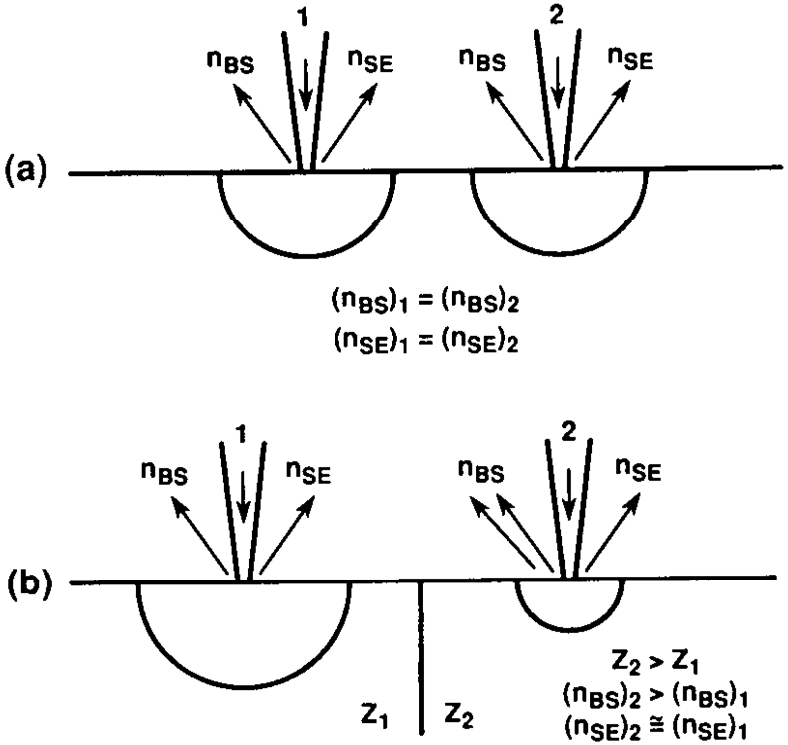


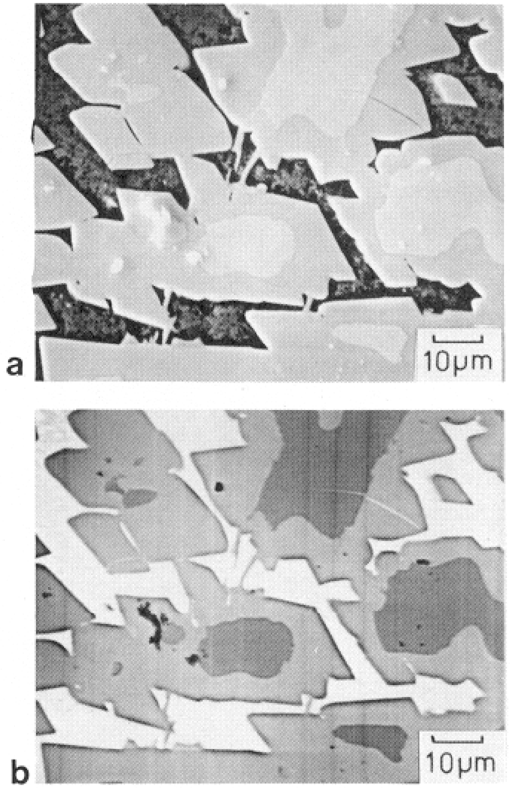
Figure 3.8. Monte Carlo electron-trajectory simulations of the interaction volume in iron as a function of beam energy: (a) 10 keV, (b) 20 keV, (c) 30 keV.

Nano Characterization- Microscopy (SEM)

Image Contrast

- contrast $C = \dfrac{S_{\max} - S_{\min}}{S_{\max}}$
- compositional (atomic number) contrast





BSE

Al-Ni alloy

direct current

Nano Characterization- Microscopy (SEM)

Image Contrast

- topogr

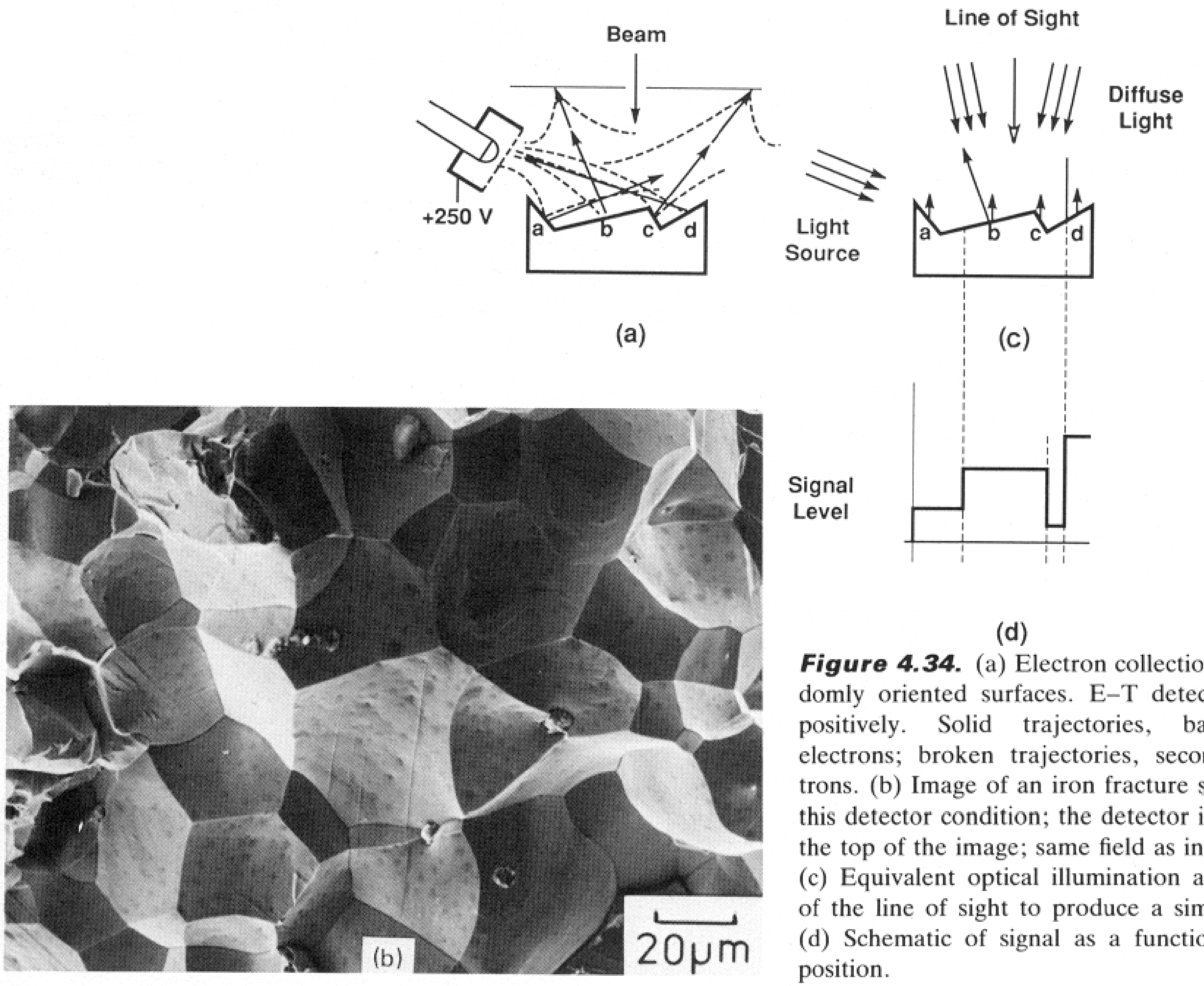
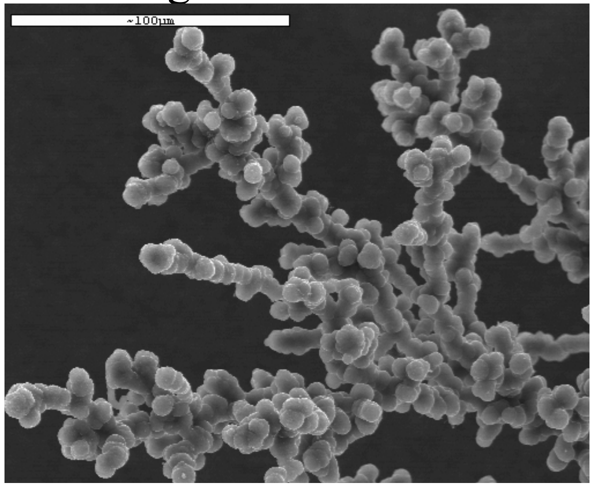


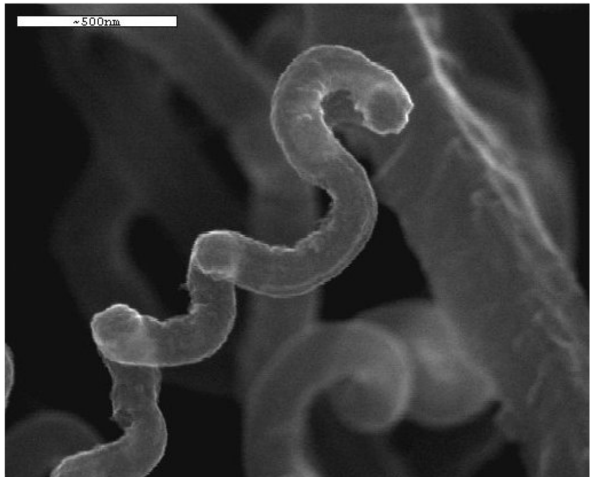
Figure 4.34. (a) Electron collection from randomly oriented surfaces. E–T detector, biased positively. Solid trajectories, backscattered electrons; broken trajectories, secondary electrons. (b) Image of an iron fracture surface with this detector condition; the detector is located at the top of the image; same field as in Fig. 4.33b. (c) Equivalent optical illumination and position of the line of sight to produce a similar image. (d) Schematic of signal as a function of beam position.

Nano Characterization- Microscopy (SEM)

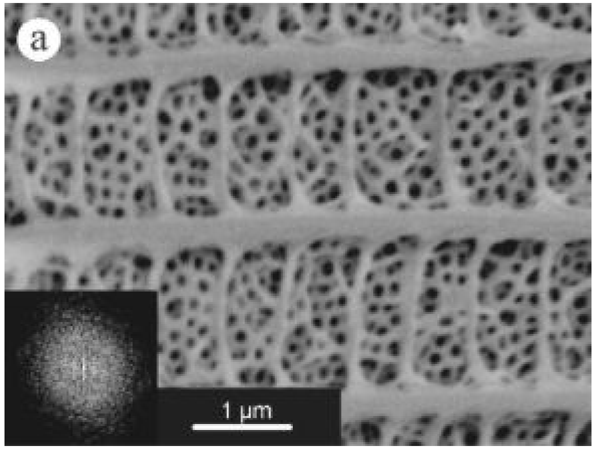
❑ SEM image of carbon tree



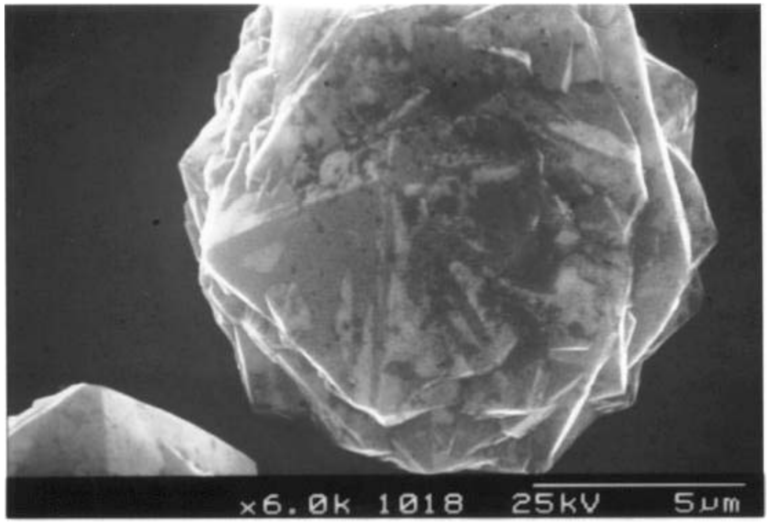
❑ SEM image of single wall CNT



❑ SEM image of butterfly



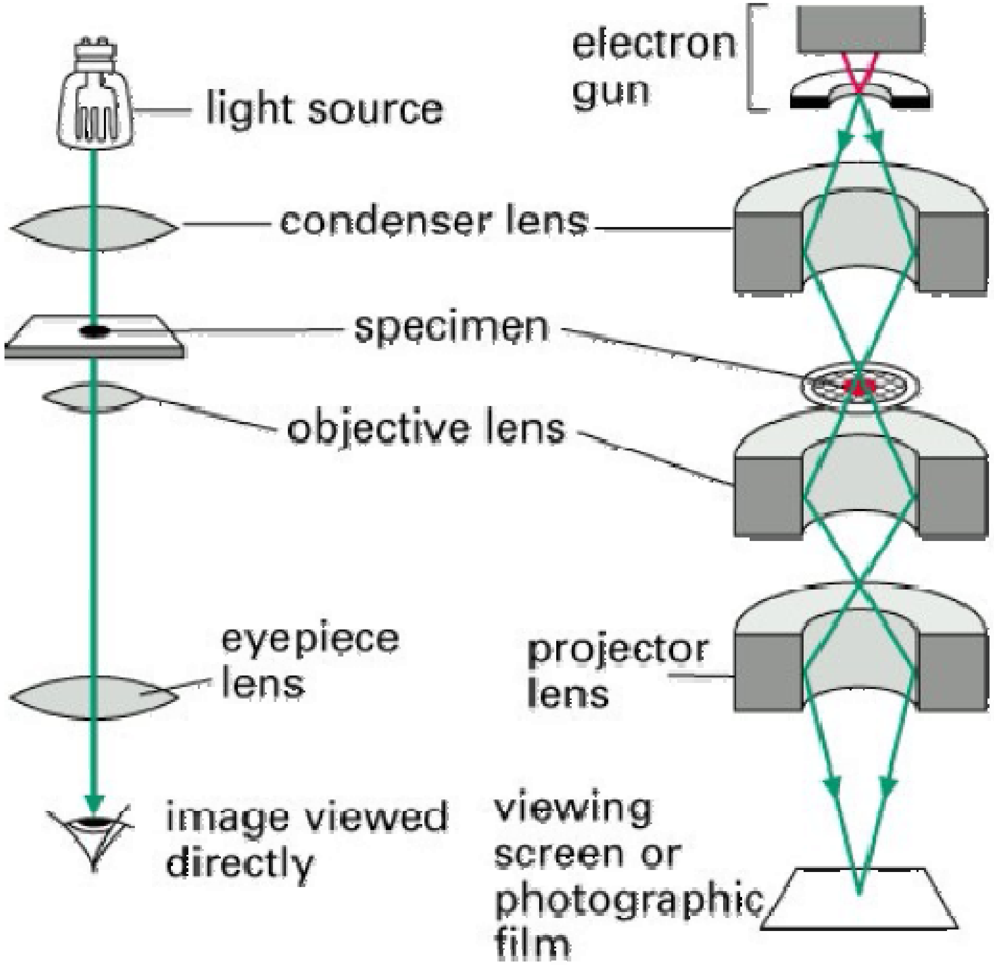
❑ SEM image of nano diamond crystal



Nano Characterization- Microscopy (TEM)

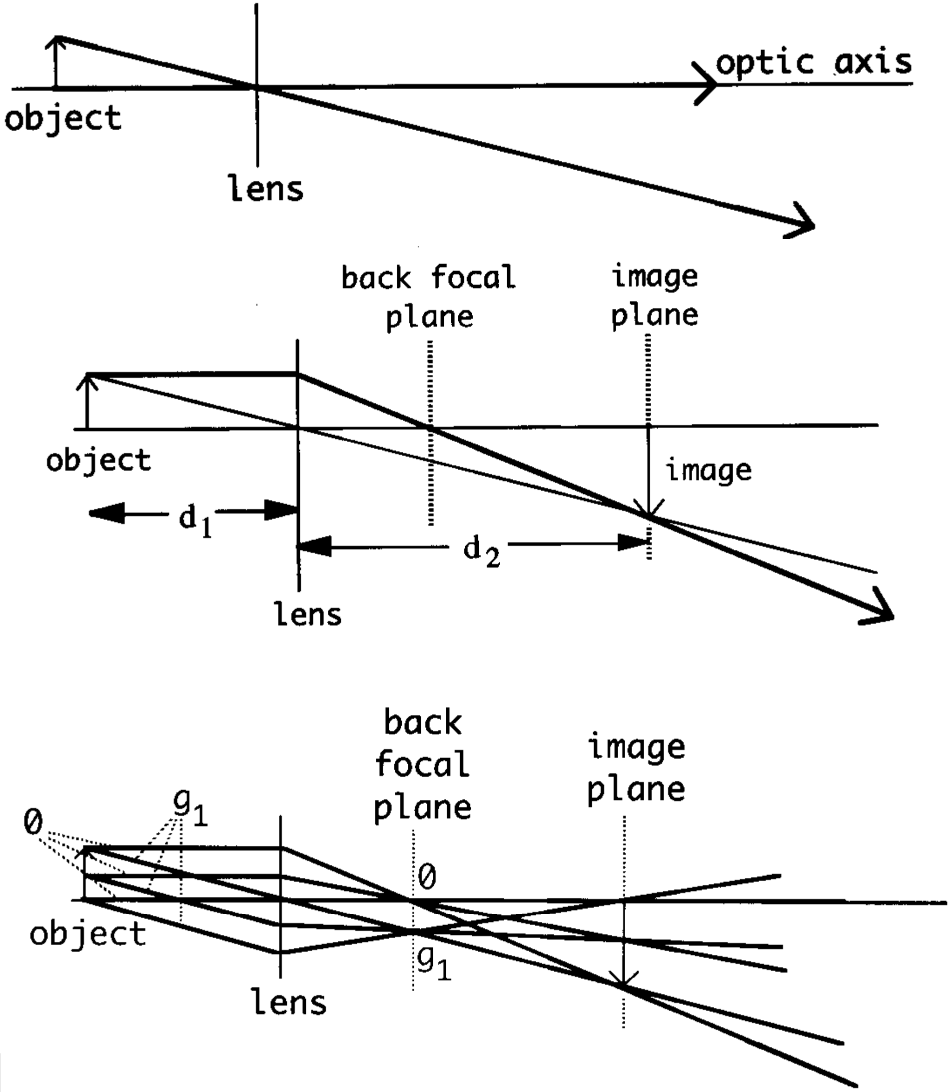
- TEM (Transmission Electron Microscopy)
  - Beam voltage : 40kV~1MV
  - Resoultion : 1~2 Å
  - Imaging radiations : transmitted electrons
  - Imaging contrast : Scattering effect
  - Magnification : 60~15,000,000 times
  - Image contrast
    - Amplitude (scattering) contrast
      - Transmitted beam only (bright field image)
      - Diffraction beam only (dark field image)
    - Phase (interference) contrast
      - Combination of transmitted and diffraction beam
      - Multi-beam lattice image : atomic resolution (HRTEM)

Nano Characterization- Microscopy (TEM)



Nano Characterization- Microscopy (TEM)

Ray Diagram



Nano Characterization- Microscopy (TEM)

Ray Diagram

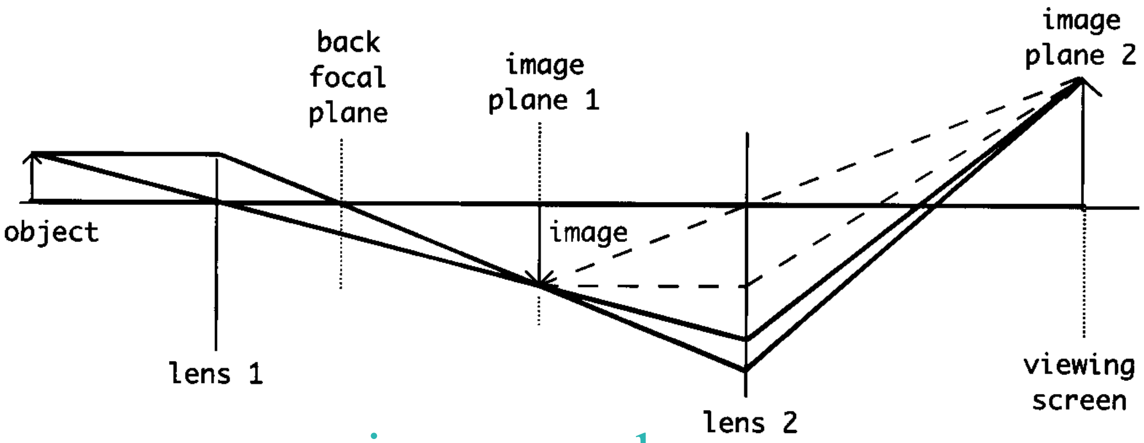
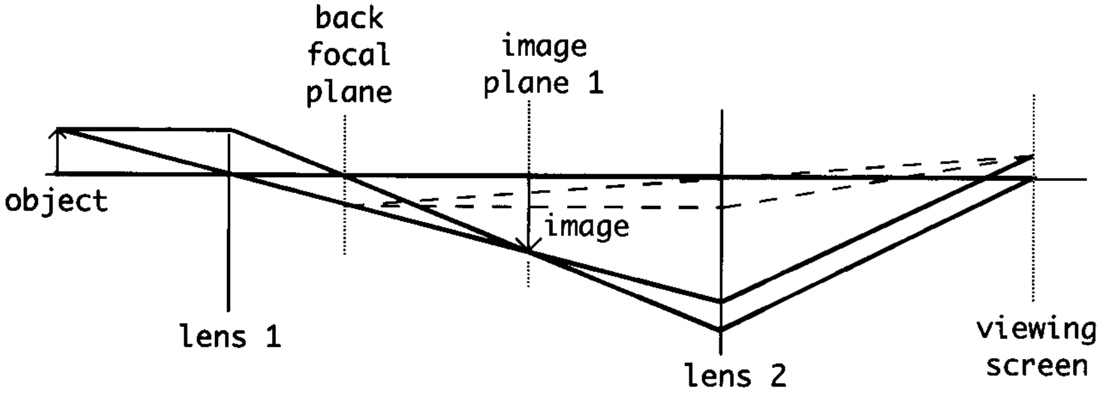
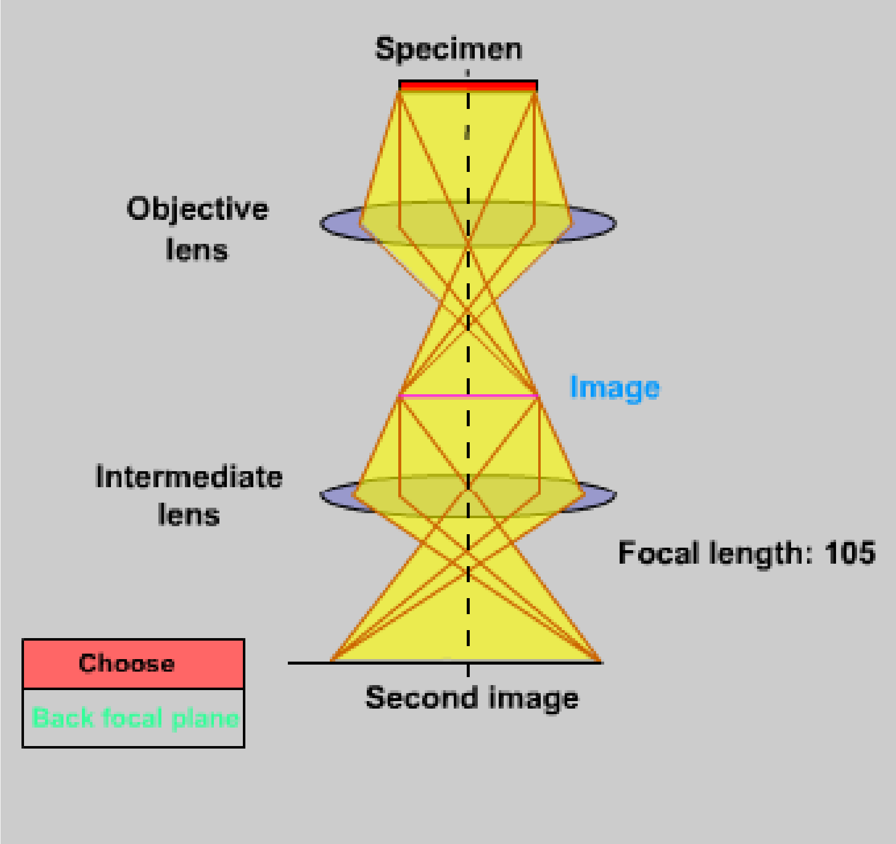


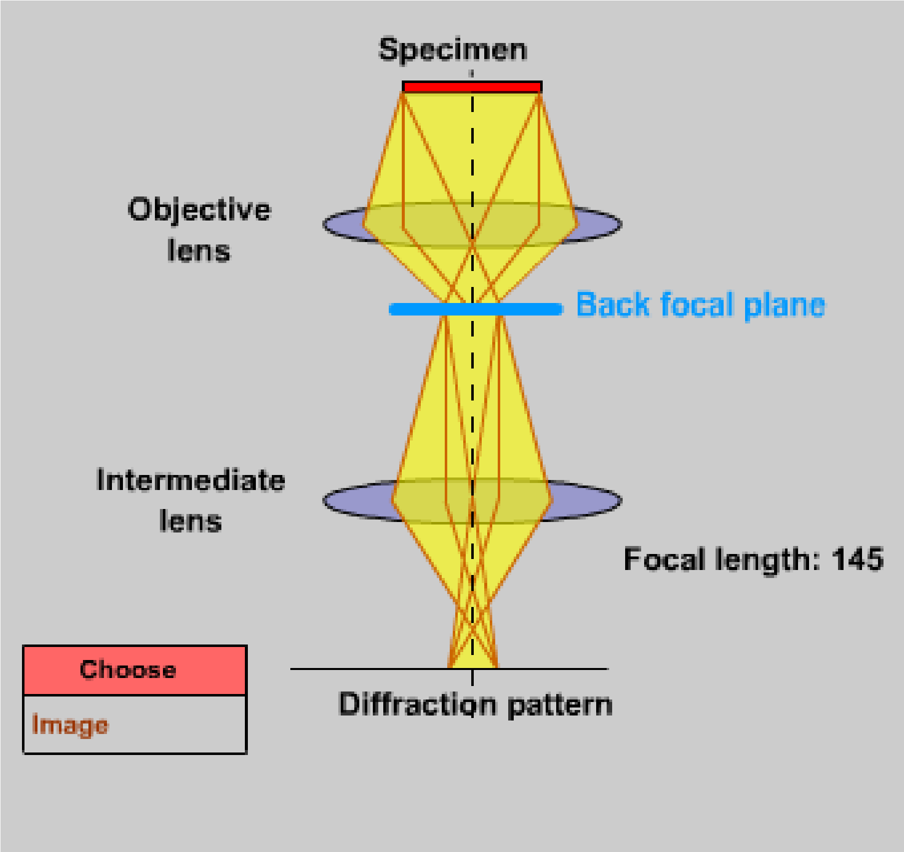
image mode



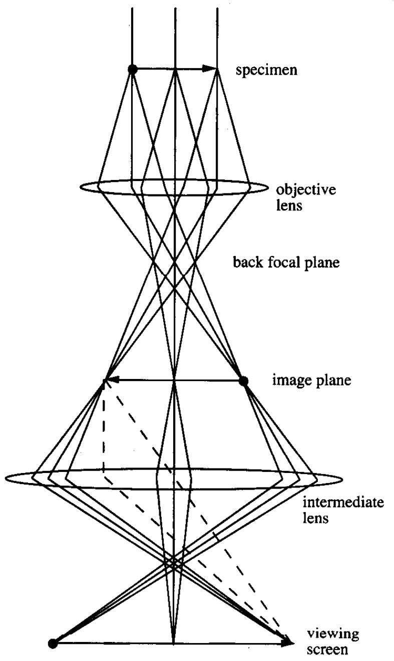
diffraction mode

Nano Characterization- Microscopy (TEM)





Nano Characterization- Microscopy (TEM)



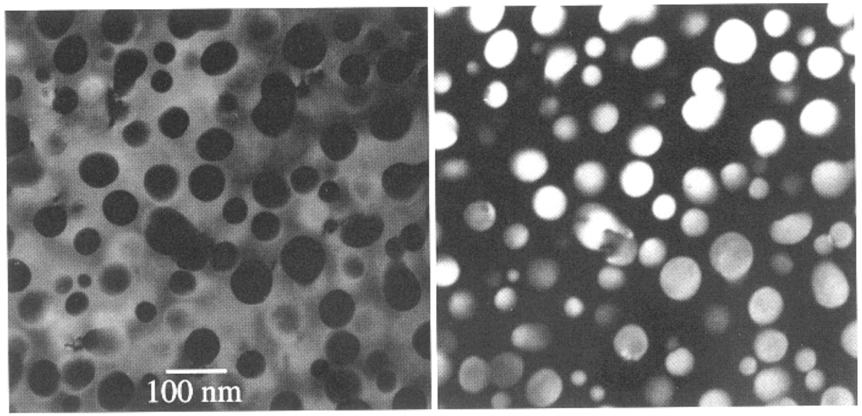
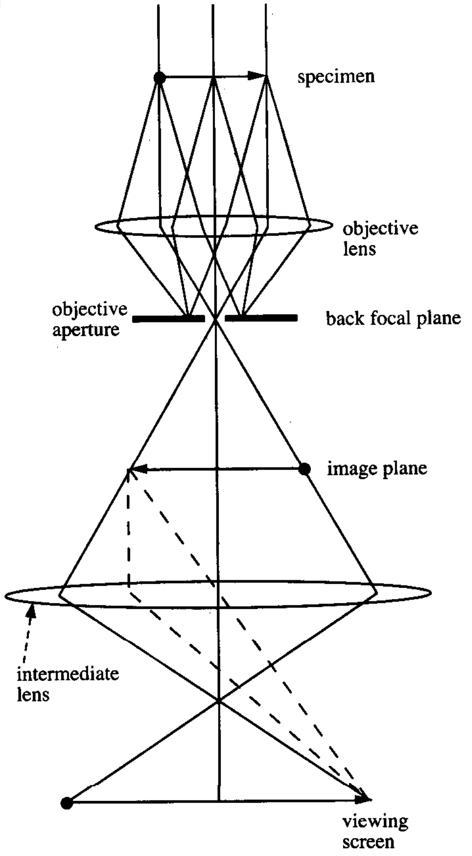
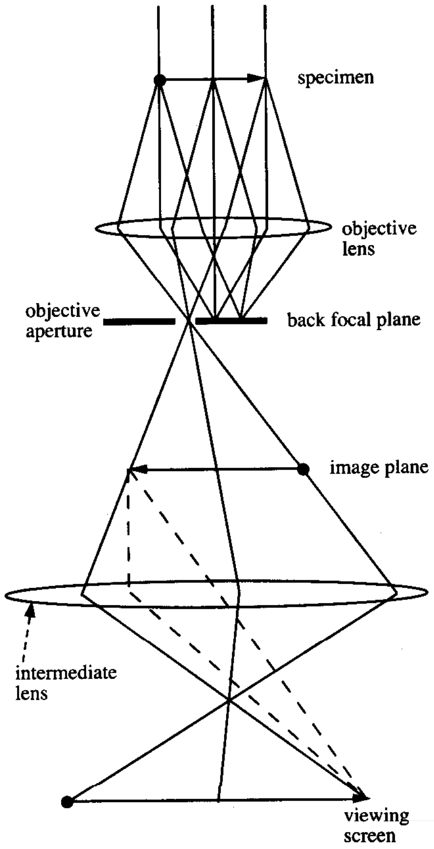


Fig. 2.14. Spherical δ' precipitates in an Al-Li alloy at 80,000 X magnification. Left: BF image. Right: DF image from (100) diffraction spot, unique to δ' precipitates.

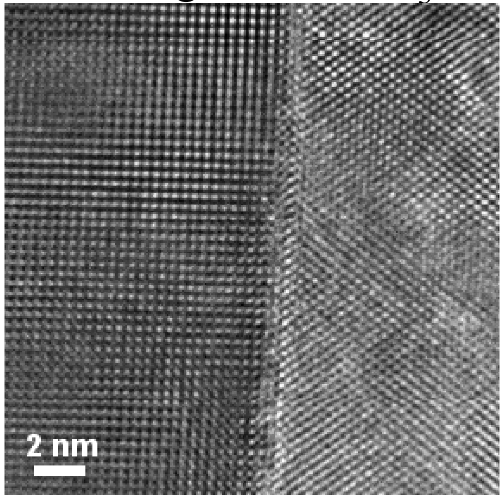




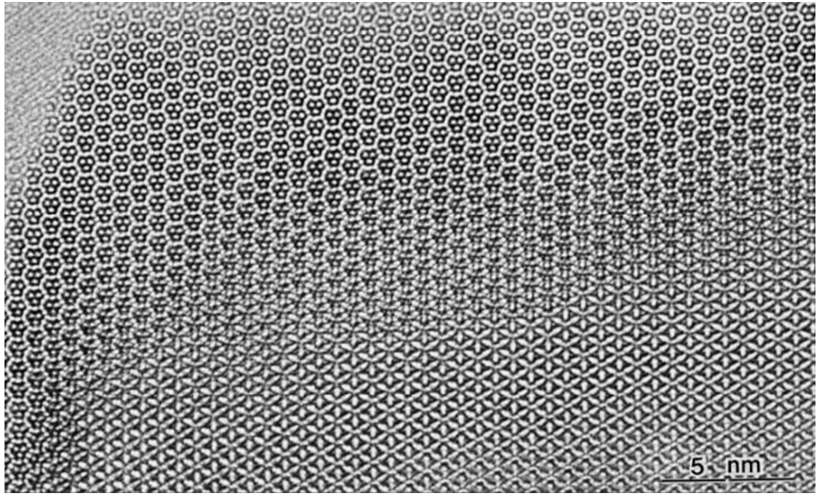
BF (bright field) DF (dark field)

Nano Characterization- Microscopy (TEM)

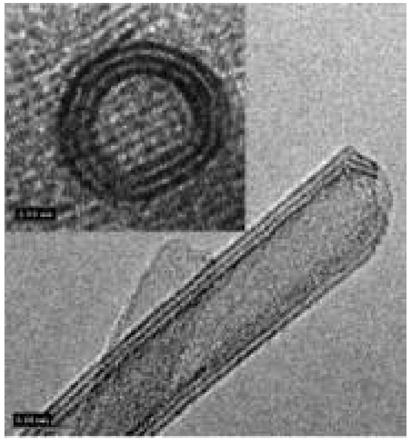
- HRTEM image of $LaAlO_3/Si$



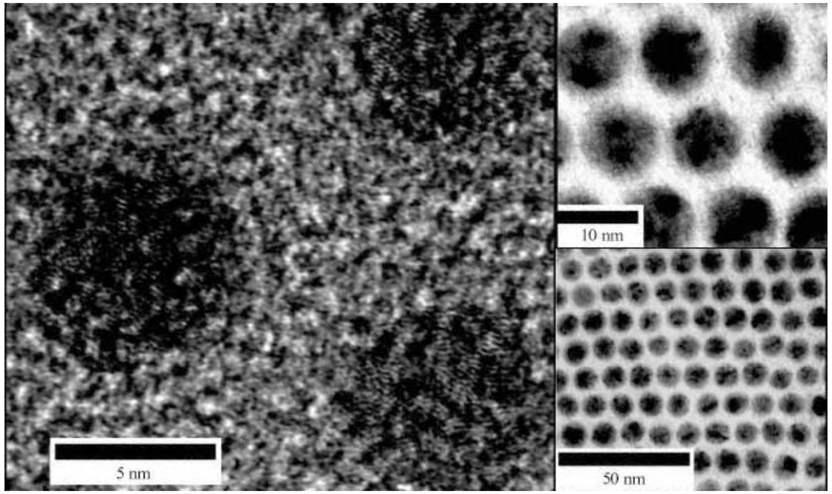
- HRTEM image of Si_3N_4



- HRTEM image of single wall CNT



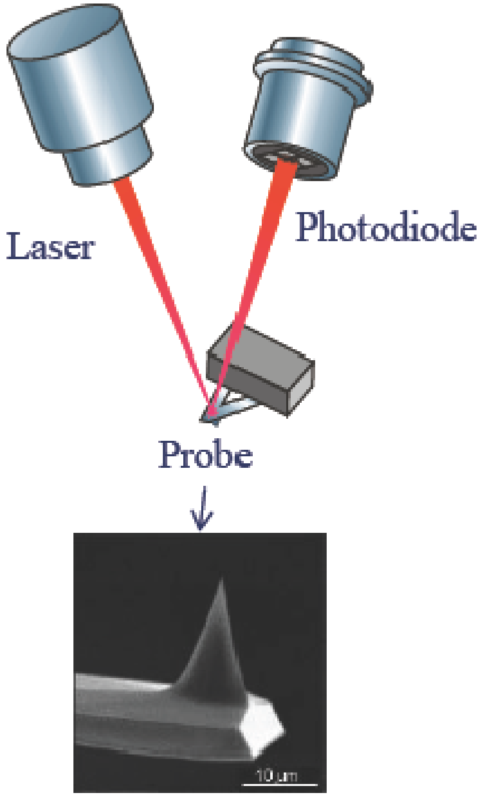
- HRTEM image of Co nano particle



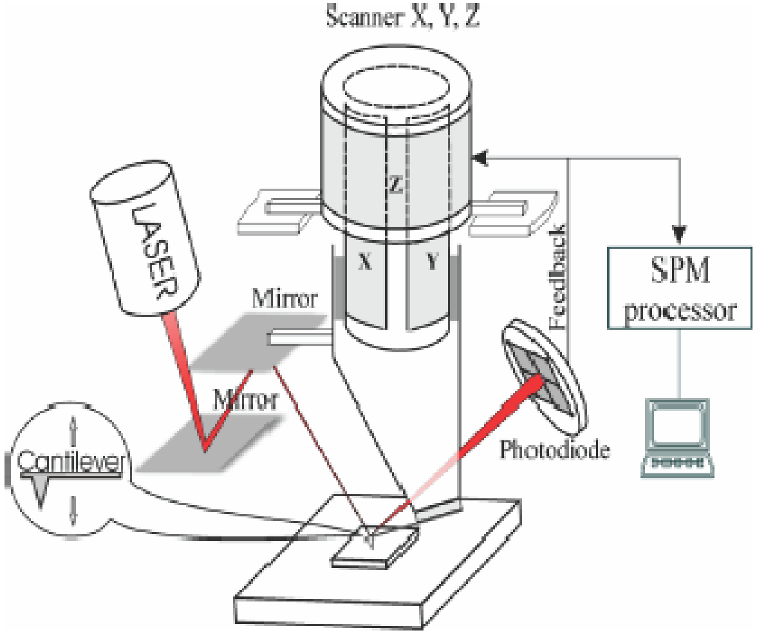
Nano Characterization- Microscopy (AFM)

❑ AFM (Atomic Force Microscopy)

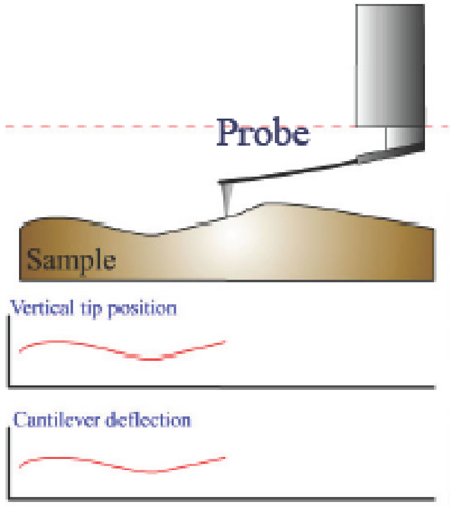
Detecting Systems



Basic working scheme



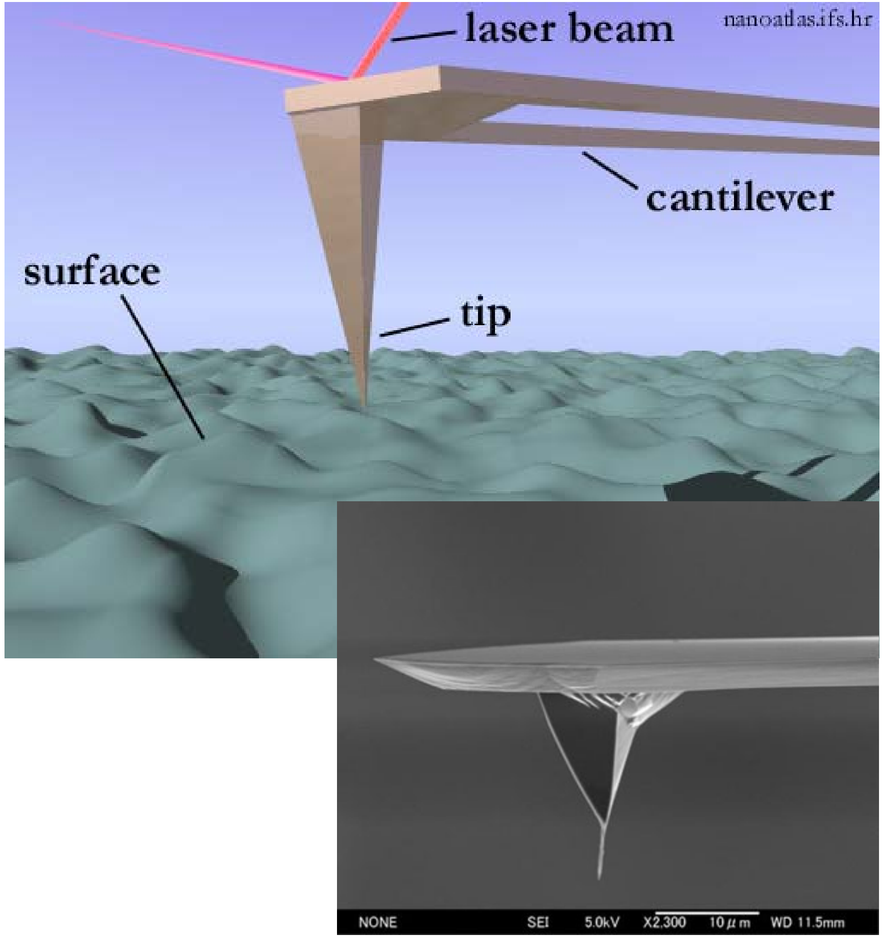
Basic scanning scheme



Nano Characterization- Microscopy (AFM)

AFM (Atomic Force Microscopy

Schematic diagram of AFM.



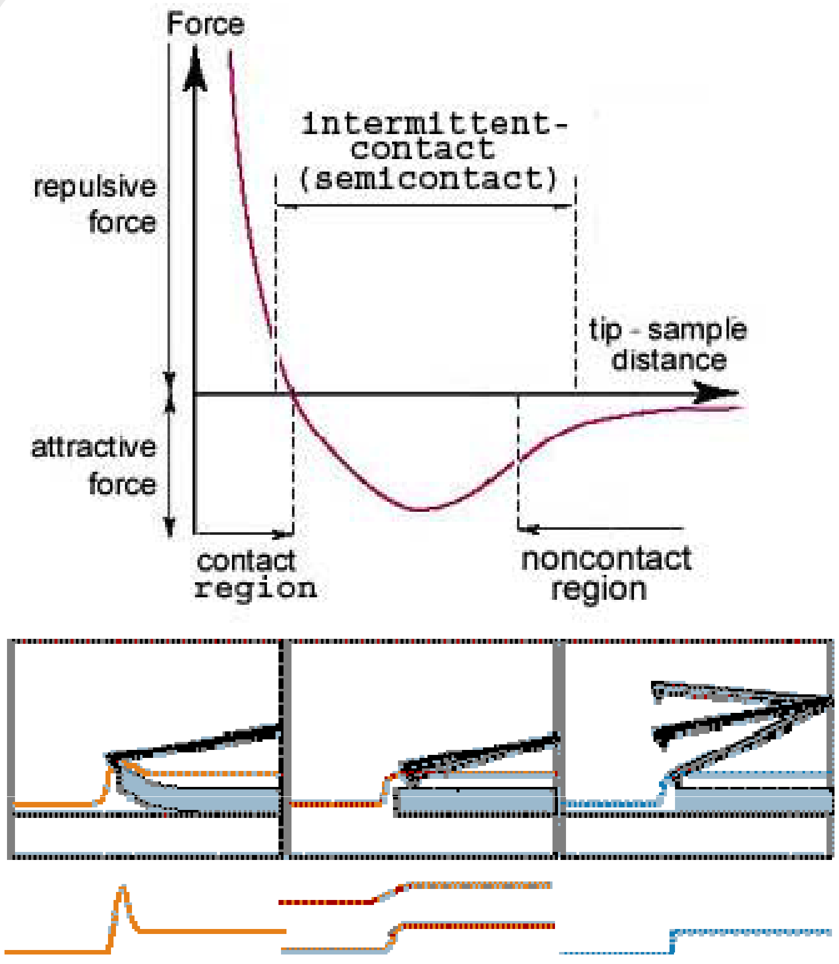
Advantage

- extraordinary topographic contrast direct height measurements and unobscured views of surface features (no coating is necessary)
- Conductors and insulators
- Three dimensional AFM images

Disadvantage

- The image size that it provides is much smaller than what electron microscopes can create
- It is slow in scanning an image, unlike an electron microscope which does it in almost real-time.

Nano Characterization- Microscopy (AFM)



(a) (b) (c)

(a) Contact Mode :

Repulsive force (1-10nN)

A feedback loop maintains a constant deflection between the cantilever and the sample by vertically moving the scanner.

(b) Non-contact Mode :

Attractive Van der Waals Force (0.1-0.01nN)

The cantilever's resonant frequency decreased by the van der Waals forces causes the amplitude of oscillation to decrease.

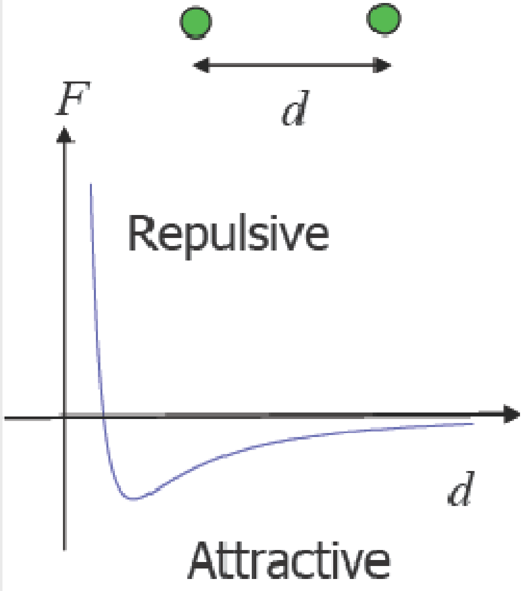
AC detection methods can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase, or frequency of the oscillating cantilever.

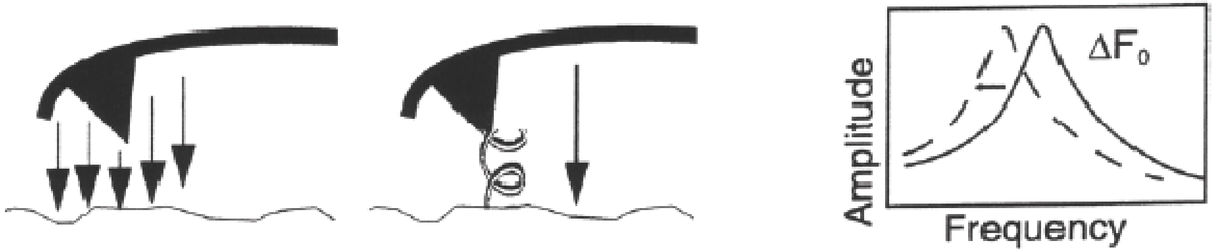
(c)Tapping Mode :

It is obtained by placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface

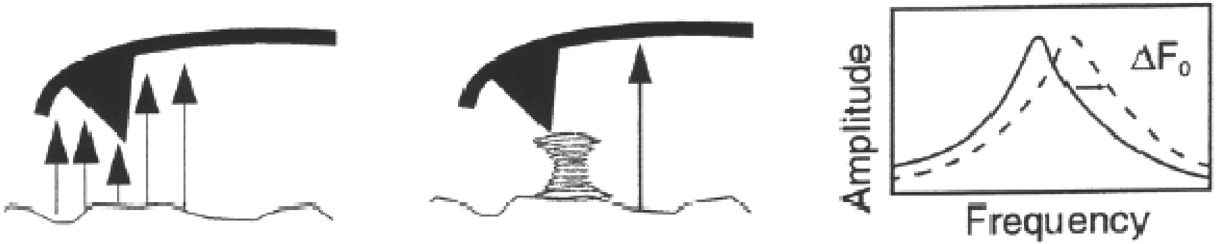
Nano Characterization- Microscopy (AFM)

- The cantilever's resonant frequency is decreased by the van der Waals forces.
- The decrease in resonant frequency causes the amplitude of oscillation to decrease.





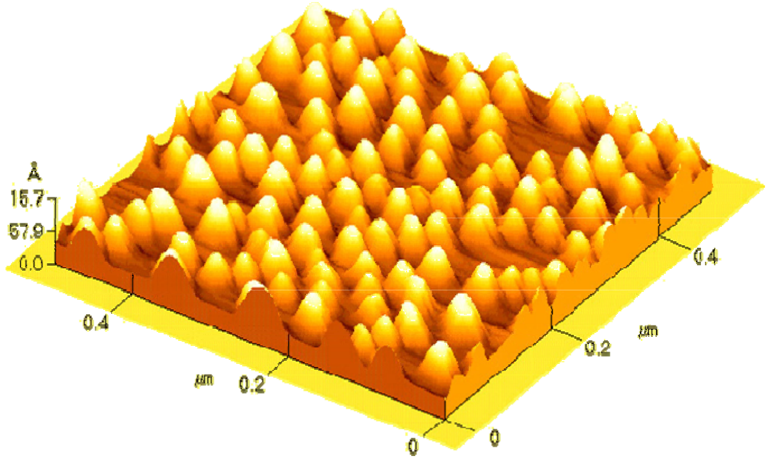
Attractive gradient equivalent to additional spring in tension attached to tip, reducing the cantilever resonance frequency.



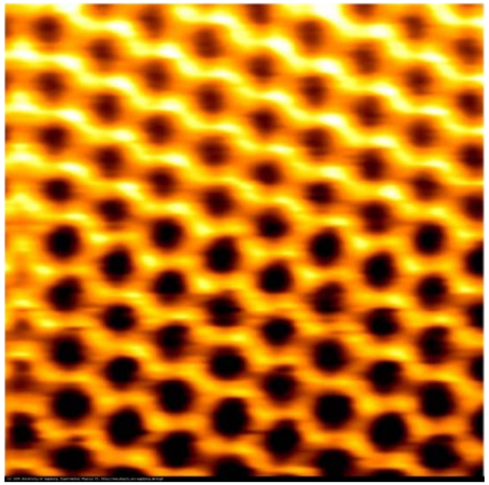
Repulsive gradient equivalent to additional spring in compression attached to tip, increasing the cantilever resonance frequency.

Nano Characterization- Microscopy (AFM)

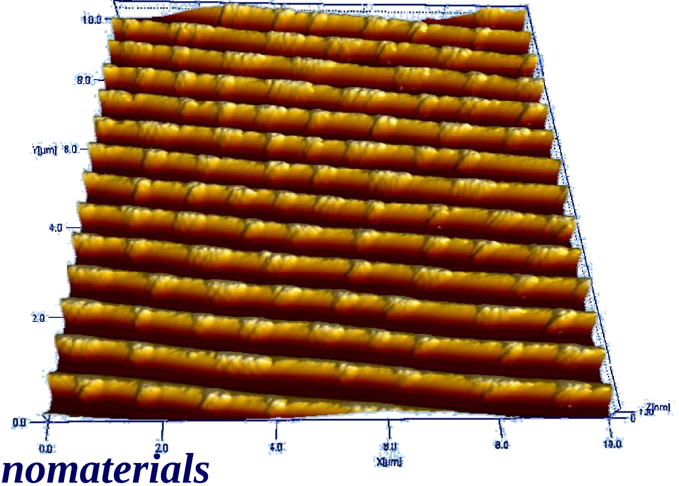
❑ AFM image of QD



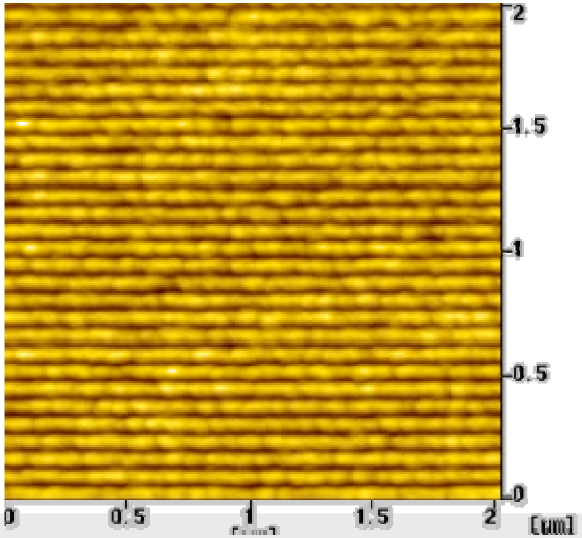
❑ AFM image of graphene



❑ AFM image of DVD+R

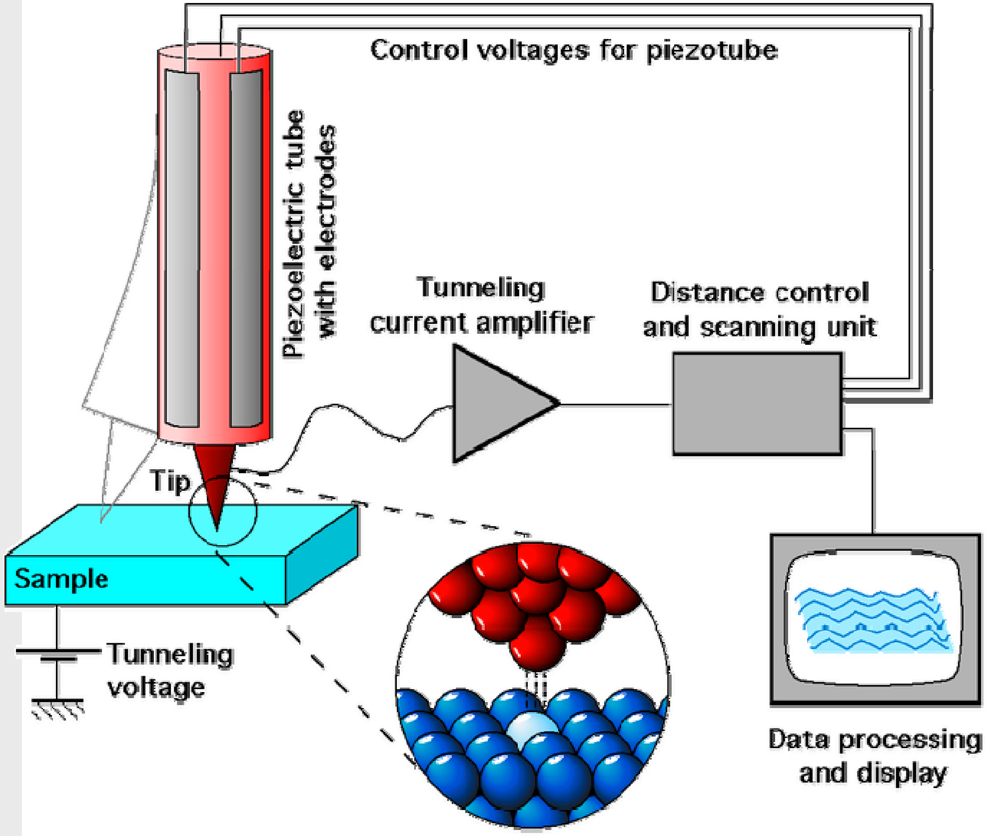


❑ AFM image of Si Nano wire by AIPEL



Nano Characterization- Microscopy (STM)

❑ STM (Scanning Tunneling Microscope)



- ❑ To form image, tip is raster-scanned (using x-y motion piezoelectric) across surface and tunneling current is measured

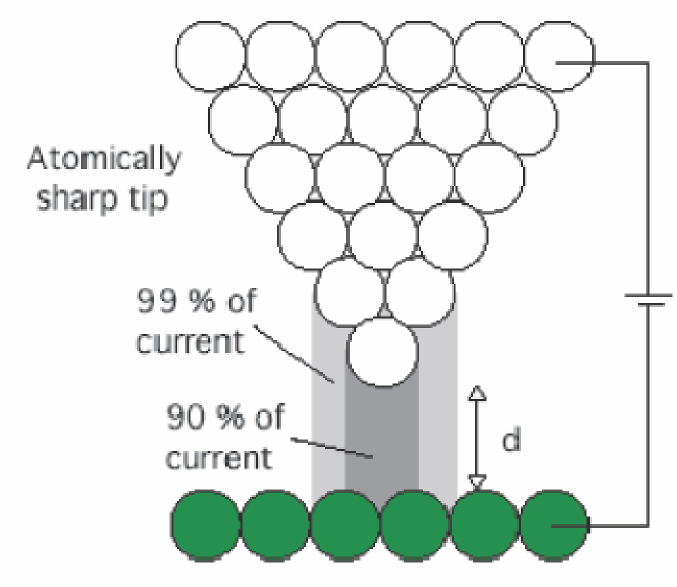
- ❑ Topology image formed by displacing feedback voltage (to z- motion piezoelectric) necessary to maintain constant tunneling current

Nano Characterization- Microscopy (STM)

❑Quantum tunneling

Based on Quantum mechanical tunneling of electrons between an atomically sharp tip and the surface of interest.

The tunneling current depends strongly on the amount of overlap between the samp and tip wave function.



$$I \propto \exp(-A\sqrt{\Phi}Z)$$

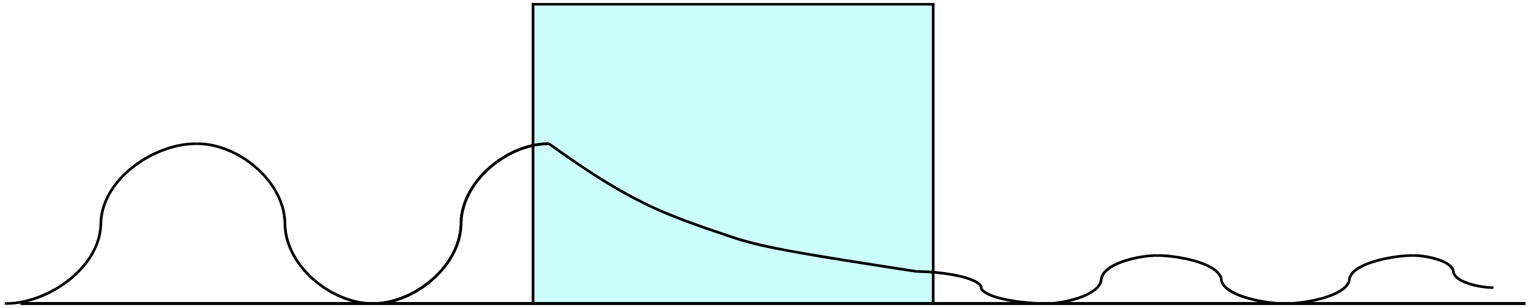
Φ : work function

Z : distance

$$A = 2\sqrt{2m}/\eta = 1.025eV^{-1/2}\,\overset{o}{A}^{-1}$$

Nano Characterization- Microscopy (STM)

- Quantum tunneling
  - The size of the gap in practice is on the order of a couple of Angstroms (10^{-10} m), so the current is VERY sensitive to the gap distance.



Outside Barrier:
$V(x) = 0$

$\psi''(x) = -k_1^2\psi(x)$ where $k_1^2 = \left(\frac{2m}{\hbar^2}\right)E$

$\Rightarrow \Psi(x)$ is oscillatory

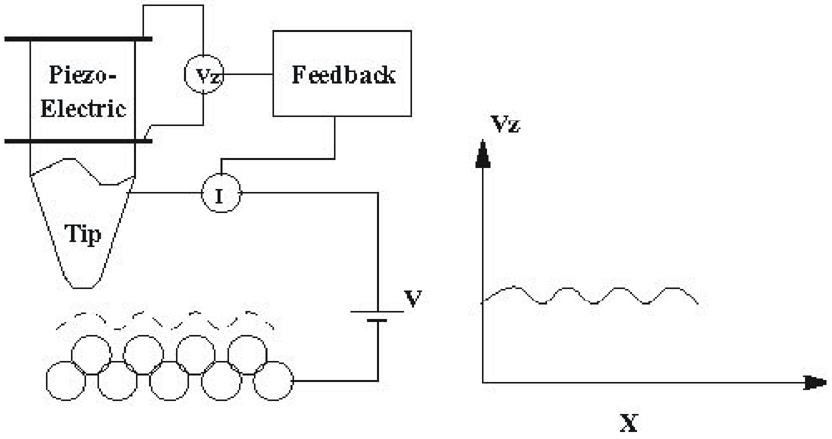
Inside Barrier:
$V(x) = V_0$

$\psi''(x) = k_2^2\psi(x)$ where $k_2^2 = \frac{2m}{\hbar^2}(V_o - E) > 0$

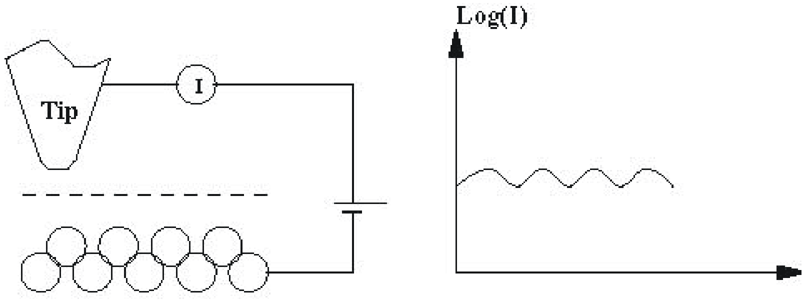
$\Rightarrow \Psi(x)$ is decaying

Nano Characterization- Microscopy (STM)

☐STM scanning modes



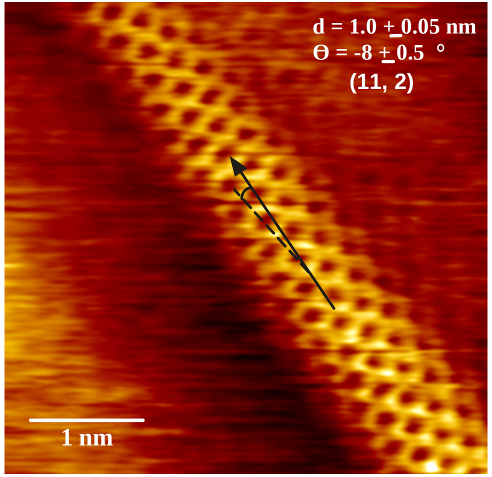
- ☐Constant current mode
  - ☐Constant Current Mode
  - ☐Measure Z-location for topography imaging.
  - ☐Low speed
  - ☐Irregular surfaces with high precision



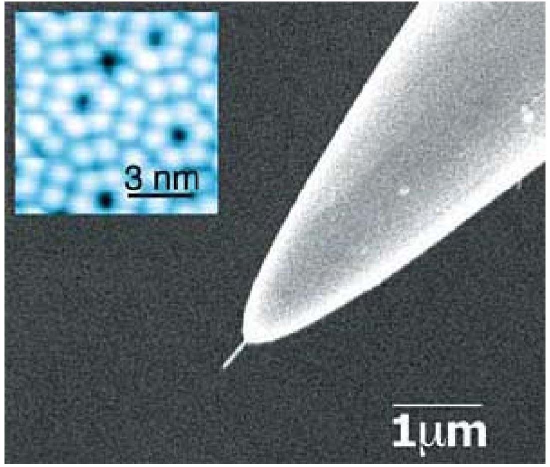
- ☐Constant Height Mode
  - ☐ Measure tunneling current for imaging
  - ☐ Fast speed
  - ☐ Relatively smooth surfaces

Nano Characterization- Microscopy (STM)

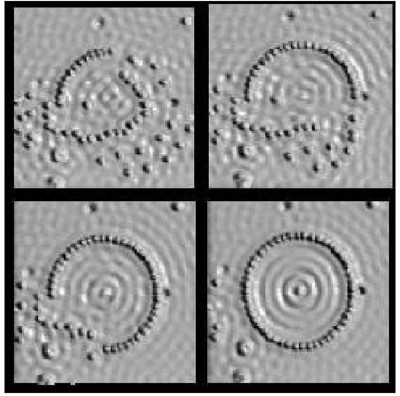
- STM image of Single wall CNT

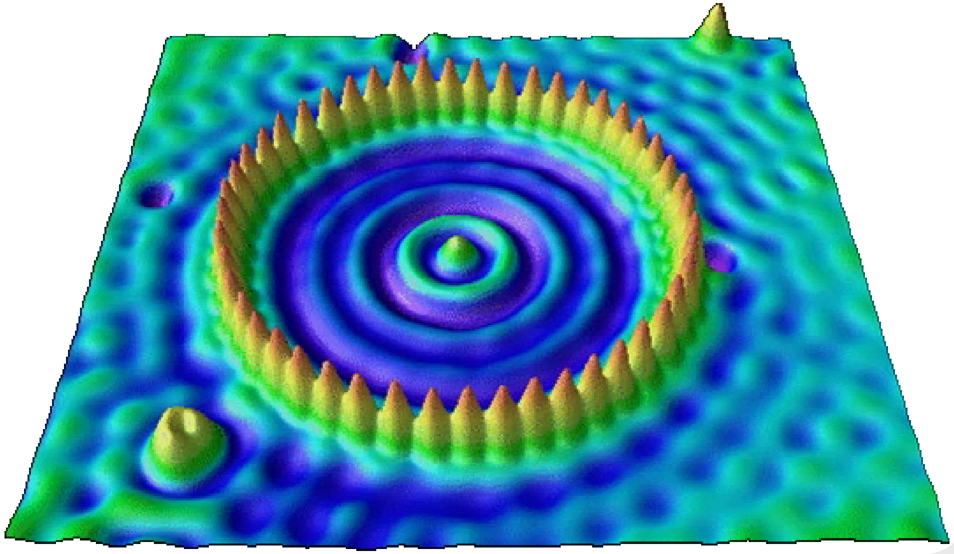


- STM image of Si and STM probe



- Manipulation of atoms by STM
  - Fe atoms on Cu(111) surface

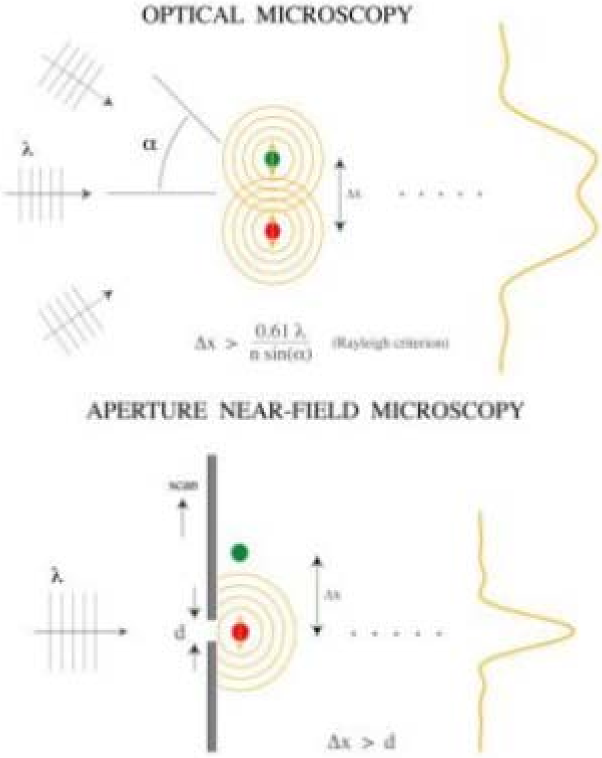




Nano Characterization- Microscopy (NSOM)

NSOM (Near field Scanning Optical Microscopy)

- Conventional OM: resolution limited by interference and diffraction of light, 200~300nm at best
- Rayleigh criterion: separation of two objects must be greater than 0.61λ/(n sinα) to be distinguishable. λ: wavelength of illuminating light, n: refractive index of medium, α: half angle of aperture. (EM:nanoscale λ)
- Far field: distance between aperture & specimen >> λ → interference & diffraction come into play; near field: < λ → interference & diffraction cannot occur yet → resolution limited by aperture size instead of light wavelength → much better resolution, 20-50 nm.



Nano Characterization- Microscopy (NSOM)

❑ NSOM (Near field Scanning Optical Microscopy)

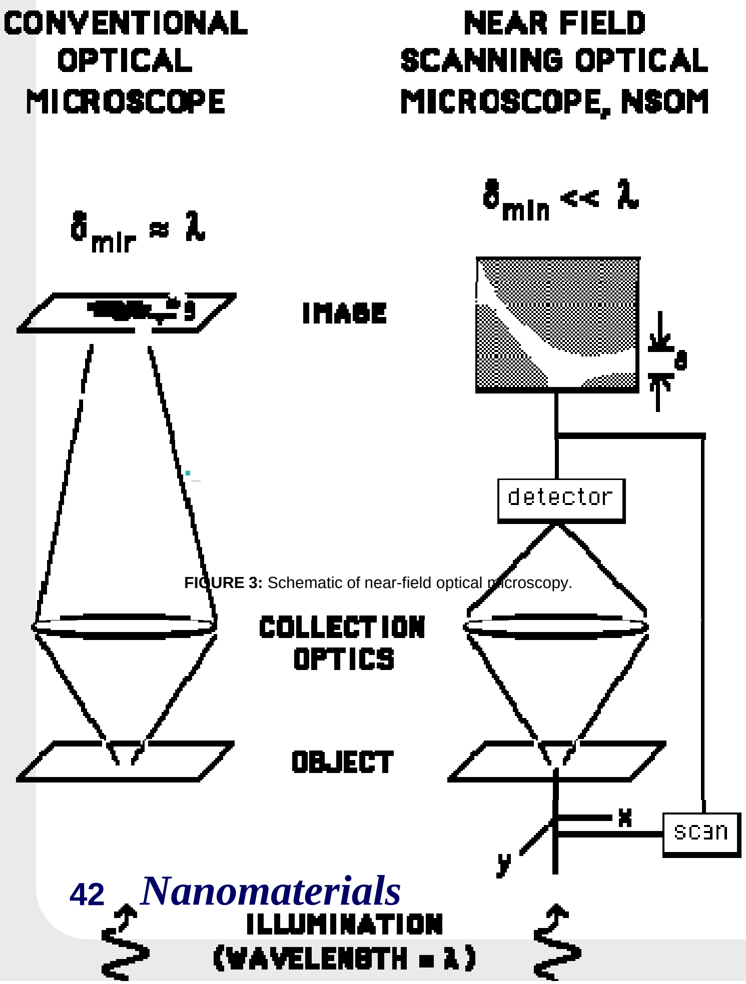
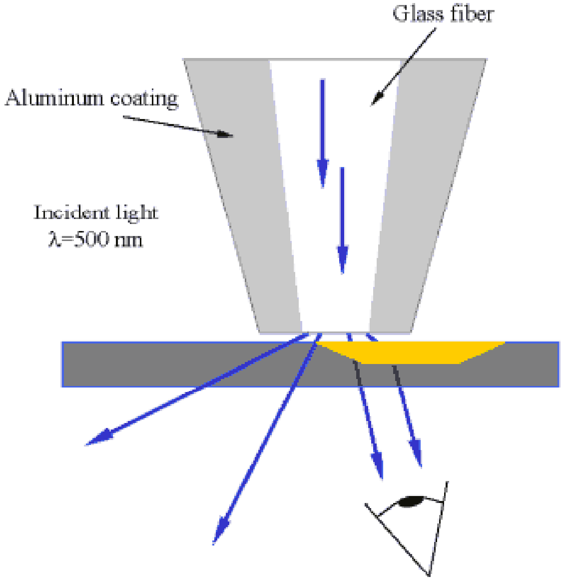
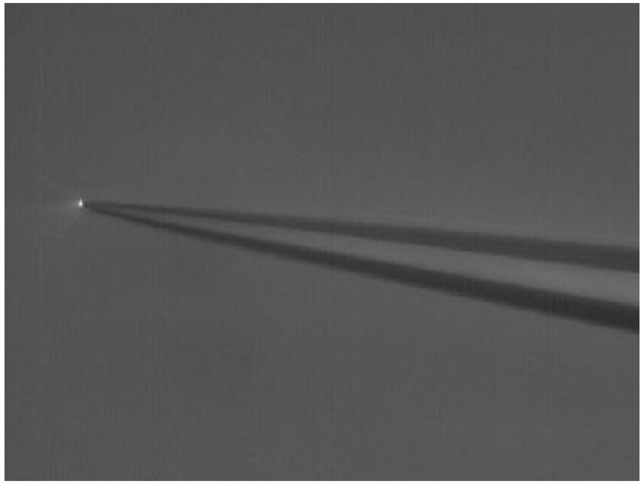


FIGURE 3: Schematic of near-field optical microscopy.



Light wavelength (λ) 500 nm	
Probe:	
aperture size (a)	25-100 nm
evanescent field	a/π
tip-sample gap	5-50 nm
Sample:	
feature size	< λ
skin depth	0- ∞
Optics:	
Far-field detector	1-100 mm
Interference effects	λ/4

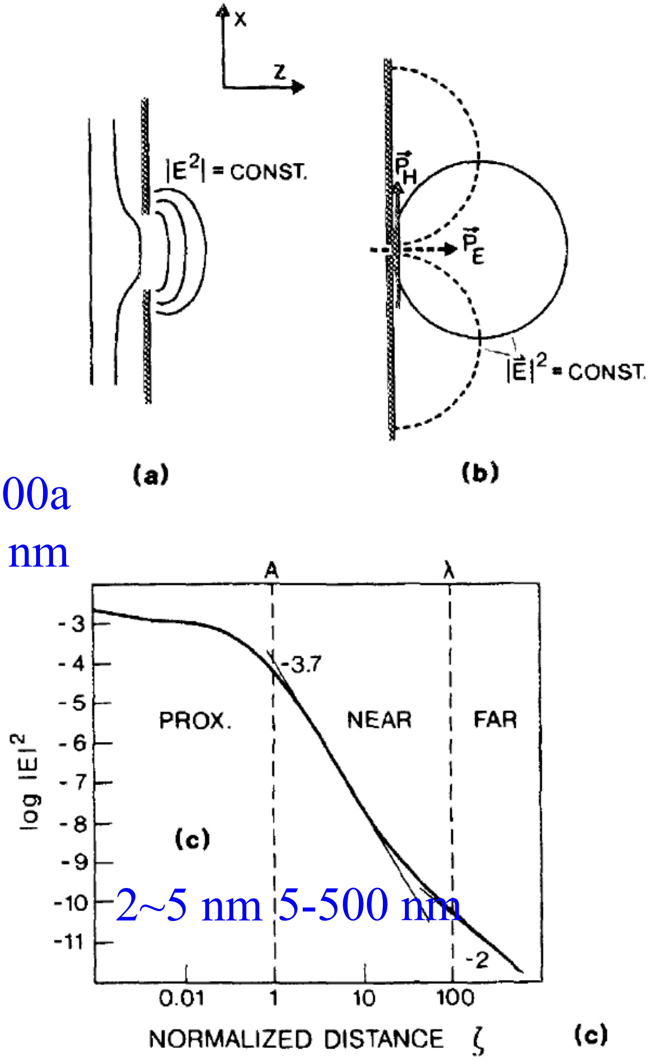


http://physics.nist.gov/Divisions/Div844/facilities/nsom/nsom.html

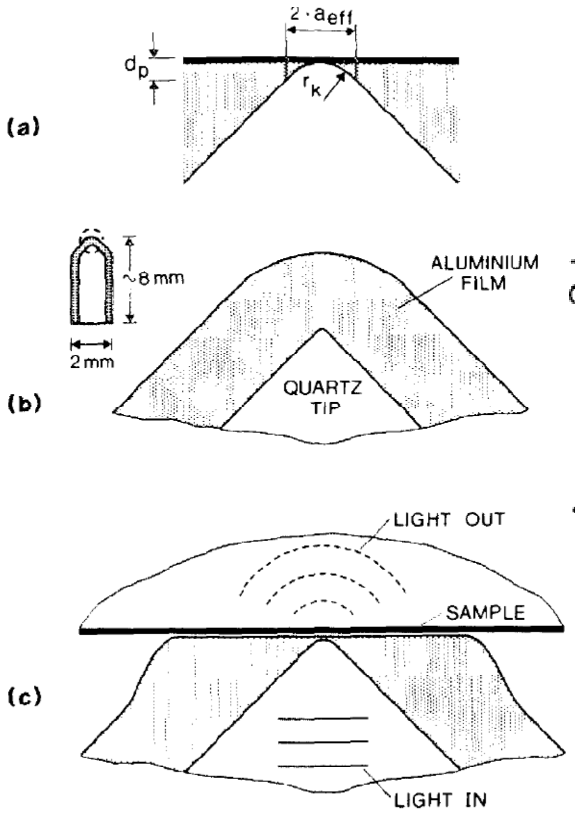
Nano Characterization- Microscopy (NSOM)

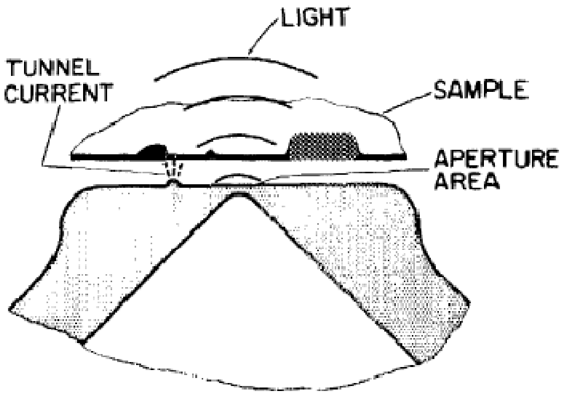
❑ NSOM (Near field Scanning Optical Microscopy)

λ=100a
a=5 nm



2~5 nm 5-500 nm





U. Dung, J. Appl. Phys. 59 (1986) 3318

Nano Characterization- Microscopy (NSOM)

❑ NSOM (Near field Scanning Optical Microscopy)

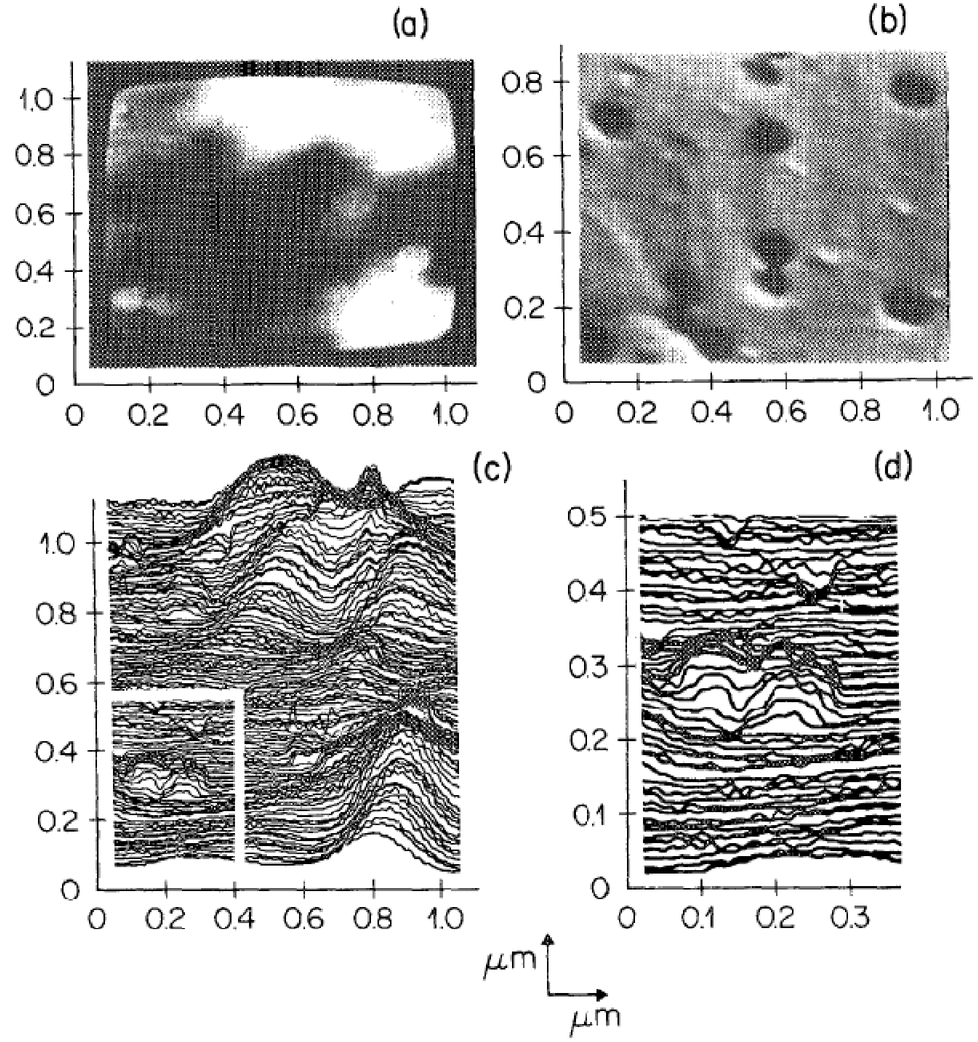


FIG. 6. (a) High-resolution NFOS micrograph of a 30-nm Ta film with 100-nm holes. (b) SEM micrograph of the same sample. (c) Line-scan record of the transmitted intensity corresponding to (a). (d) Magnification of the inset. From Ref. 18.

U. Dung, J. Appl. Phys. 59 (1986) 3318

Nano Characterization- Microscopy (NSOM)

❑ NSOM (Near field Scanning Optical Microscopy)

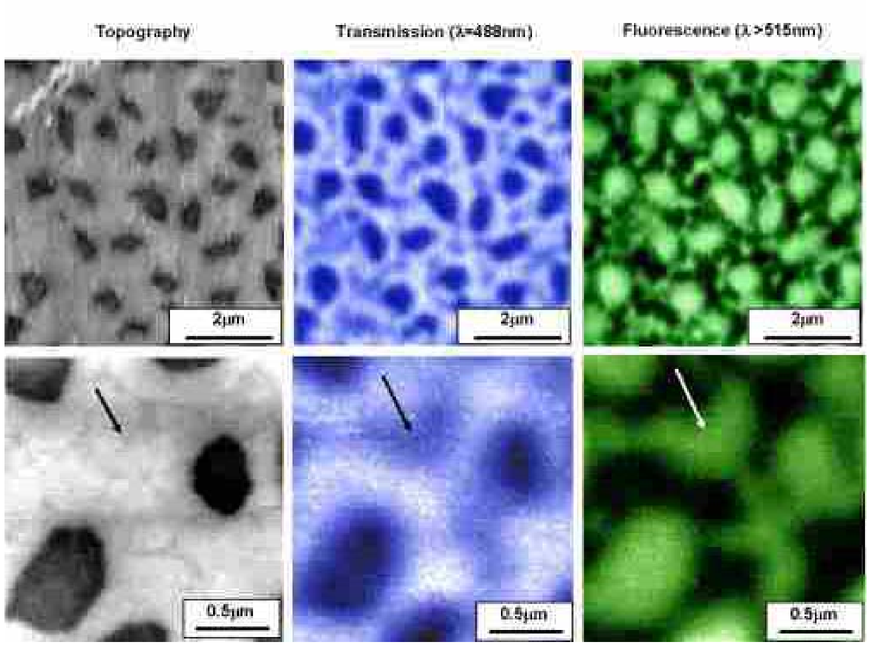


FIGURE 5: Shear force (topography), transmission NSOM, and fluorescence NSOM images of a phase separated polymer blend sample [enlarged 2 MB (800×600 pixels)].

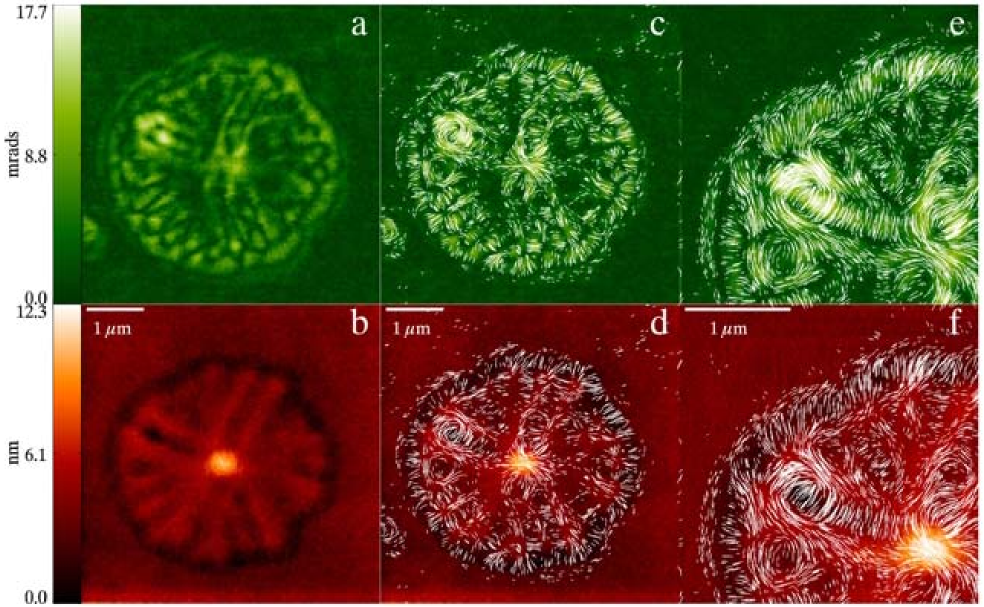


FIGURE 6: Shear force (topography), transmission NSOM, and fluorescence NSOM images of a phase separated polymer blend sample [enlarged 2 MB (2084×1292 pixels)].

http://physics.nist.gov/Divisions/Div844/facilities/nsom/nsom.html

Nano Characterization- Microscopy (NSOM)

❑ NSOM (Near field Scanning Optical Microscopy)

Limitations of NSOM

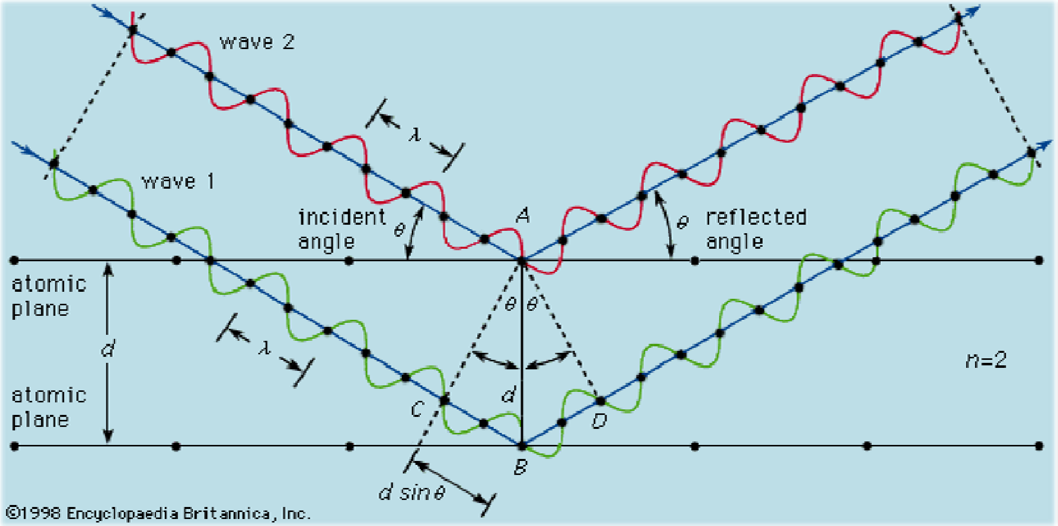
- Very low working distance and extremely shallow depth of field.
- Limited to study of surfaces.
- Not conducive for studying soft materials, especially under shear force mode.
- Long scan times for large sample areas or high resolution imaging.

http://en.wikipedia.org/wiki/Near-field_scanning_optical_microscope

Nano Characterization- Diffraction

☐ Basics in diffraction

- Bragg equation



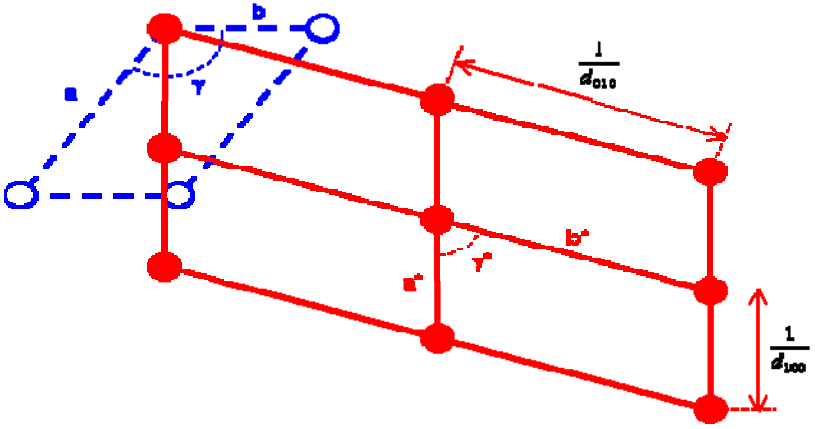
Coherent phase!

$$n\lambda = 2d\sin\theta$$

- ☐ Braggs equation tells how to reflect the incident beam
- ☐ The angle depends on the incident wavelength λ, and atomic spacing d
- ☐ We can find atomic spacing d by Bragg diffraction row

Nano Characterization- Diffraction

❑ Reciprocal lattice



Reciprocal lattice is a geometrical construction which gives a physical picture of the diffraction geometries. It is a lattice constructed in momentum space k, which is the space of electron

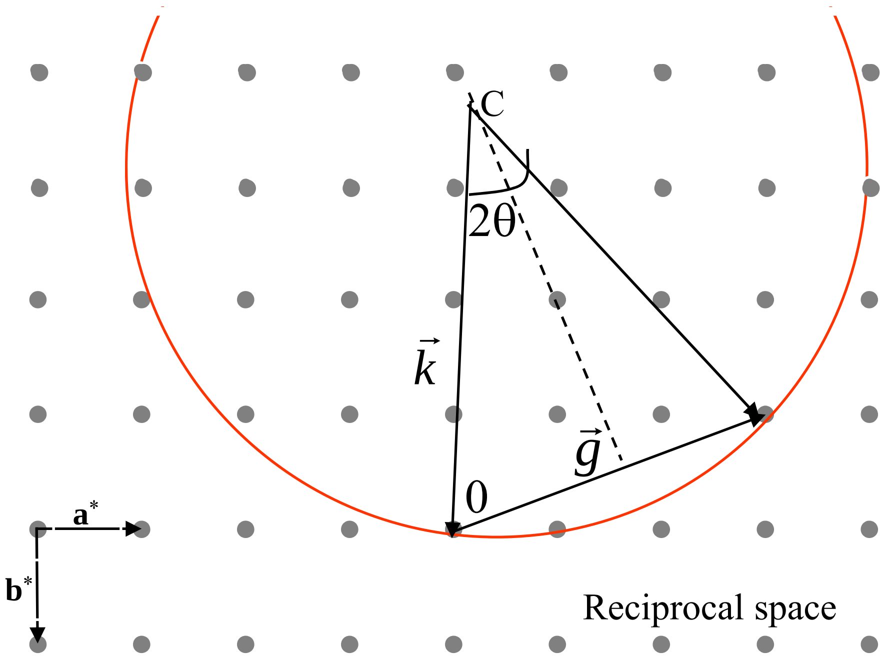
$$\vec{g}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$

$$\left|\vec{g}_{hkl}\right| = g_{hkl} = 1/d_{hkl}$$

The dimension of reciprocal space is $1/d_{hkl}$ where d_{hkl} is the spacing between (hkl) crystal plane.

Nano Characterization- Diffraction

☐ Ewald’s sphere



The Ewald’s sphere is a geometrical construction for interpreting diffraction patterns. When a beam hits a crystal, Ewald's sphere shows which sets of planes are at (or close to) the Bragg angle for diffraction to occur.
In electron diffraction, we see many diffraction spots at the same time because the Ewald’s sphere is very flat (λ is small and k is large). For thin samples the reciprocal lattice points are stretched (relrods) and we see even more diffraction spots.

Nano Characterization- Diffraction

Average diffraction properties of X-rays, electrons, and neutron

	X-rays	Electrons	Neutrons
1) Charge	0	-1 e	0
2) Rest mass	0	9.11×10^{-31} kg	1.67×10^{-27} kg
3) Energy	10 keV	100 keV	0.03 eV
4) Wavelength	1.5 Å	0.04 Å	1.2 Å
5) Bragg angles	Large	1°	Large
6) Extingtion lenrth	10 μm	0.03 μm	100 μm
7) Absorption length	100 μm	1 μm	5 cm
8) Width of rocking curve	5”	0.6°	5”
9) Refractive index $n=1+\delta$	$n < 1$ $\delta \approx -1 \times 10^{-5}$	$n > 1$ $\delta \approx +1 \times 10^{-4}$	$n \geq 1$, $n \leq 1$ $\delta \approx \pm 1\times 10^{-6}$
10) Atomic scattering amplitudes *f*	10^{-3} Å	10 Å	10^{-4} Å
11) Dependence of *f* on the atomic number Z	$\sim Z$	$\sim Z^{2/3}$	Nonmonotonic
12) Anomalous dispersion	Common	-	Rare
13) Spectral length	1 eV $\Delta\lambda/\lambda \approx 10^{-4}$	3 eV $\Delta\lambda/\lambda \approx 10^{-5}$	500 eV $\Delta\lambda/\lambda \approx 2$

Nano Characterization- Diffraction

❑ Compared to Diffraction Source

	X-ray	Neutron	Electron
scattering center	electrons	nucleus	both electrons and nucleus
intensity	depends on Z	week (irregular dependence on Z)	very high (multiple scattering)
sample thickness	1-20 μm	1-10 cm	10-1000 Å
special consideration	fluorescence (absorption)	need nuclear reactor	high vacuum
unique abilities	can be portable structure det.	mapping vibrational modes low Z elements	surface and thin film characterization

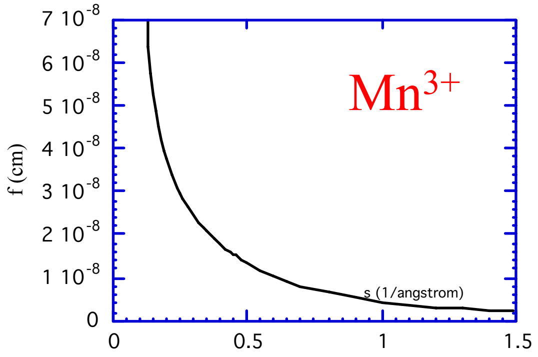
Nano Characterization- Diffraction

❑ Compared to Diffraction Source

Electrons

$$f(s)=\int v(\mathbf{r})\exp(4\pi i\mathbf{s}\cdot\mathbf{r})d\mathbf{r}$$

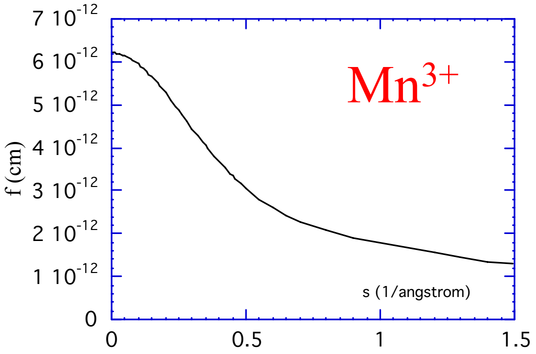
$$=2.38\times10^{-10}\left(\frac{\lambda}{\sin\theta}\right)^2\left(Z-f^x\right)$$



X-ray

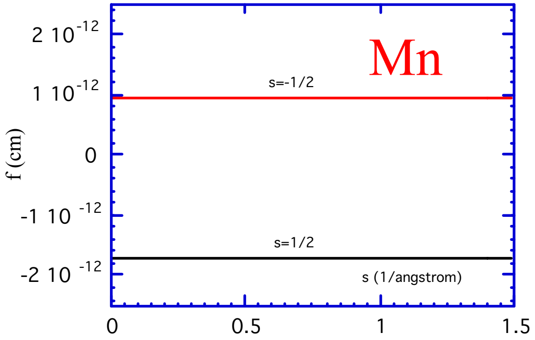
$$f^x(s)=\frac{e^2}{m_oc^2}\int\rho(\mathbf{r})\exp(4\pi i\mathbf{s}\cdot\mathbf{r})d\mathbf{r}$$

$$=2.82\times10^{-13}f^x$$



Neutrons

$$b=b_c+2b_i\left[I(I+1)\right]^{-1/2}\mathbf{s}\cdot\mathbf{I}$$

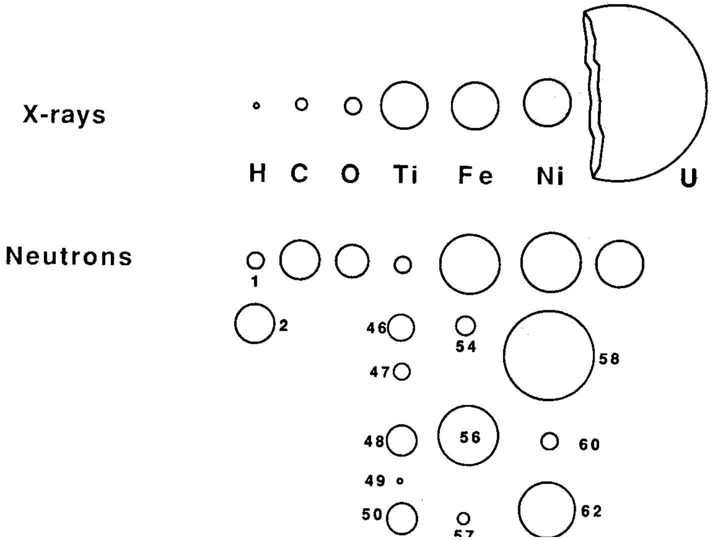


❑Compared to X-rays and Neutrons, Electrons

- ❑ Interact strongly with matter
- ❑ Bright source
- ❑ Very sensitive to charge states at small scattering angles
- ❑ Scattered predominantly by nuclei at high scattering angles
- ❑ Have the smallest probe ~1 Å

Nano Characterization- Diffraction

Neutron Diffraction



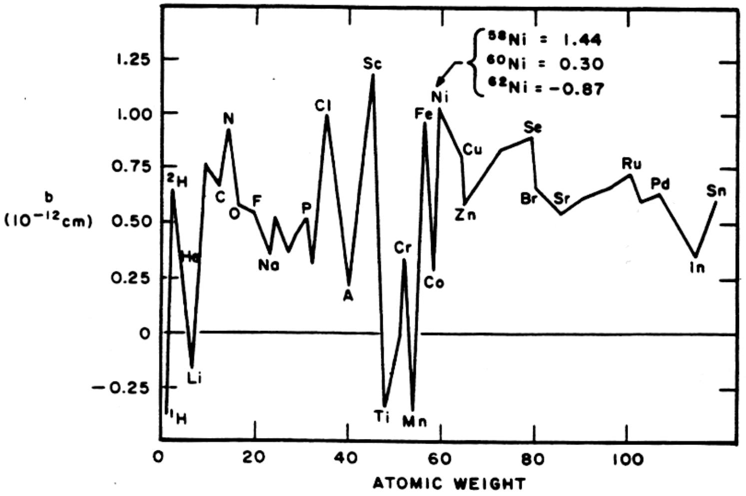


Fig. 3. Distribution of neutron scattering amplitudes (Williams and Peterson, 1971, p.

Table 1 Comparison of neutron and x-ray scattering and absorption characteristics(a)

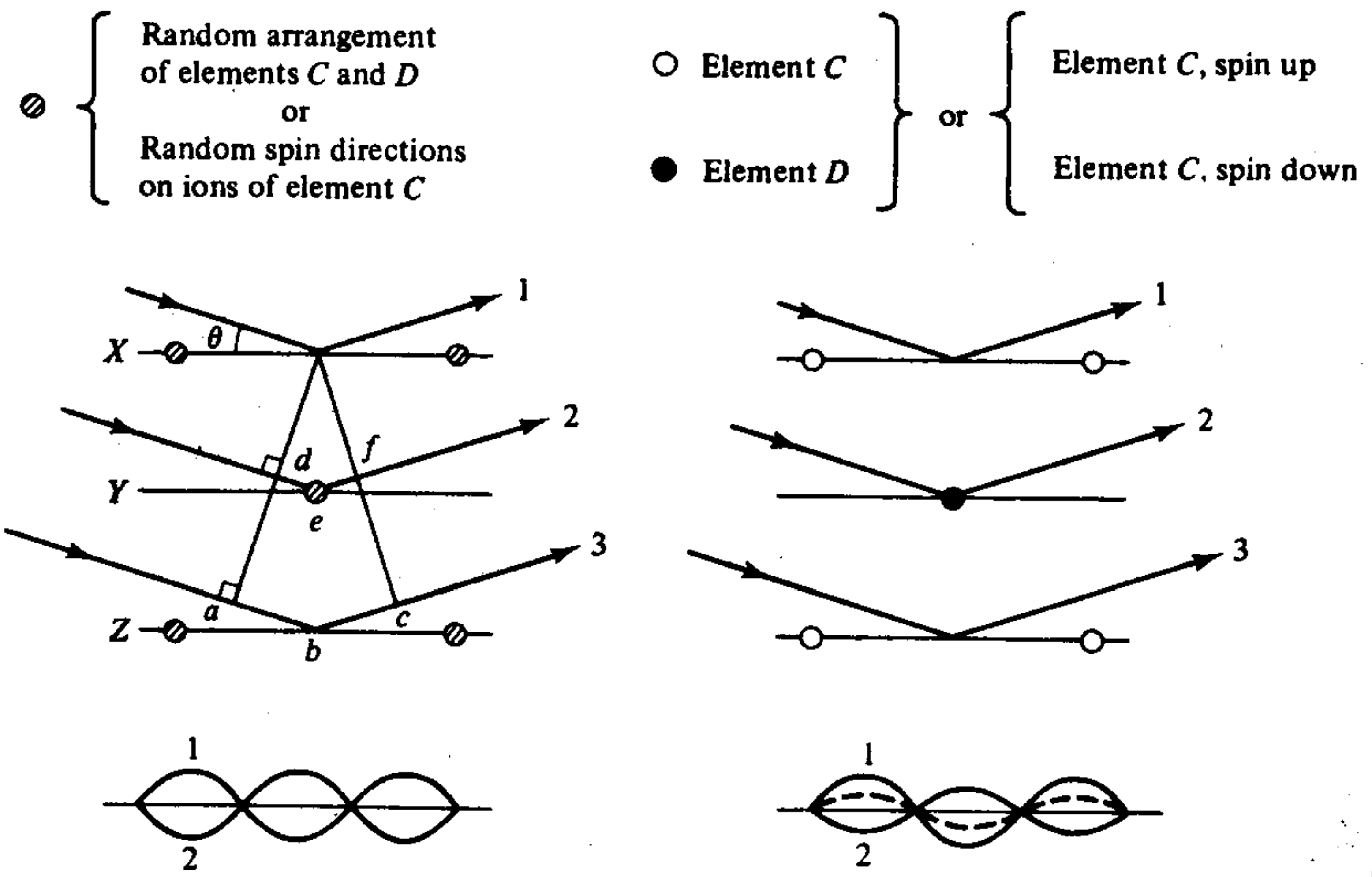
Element	Neutrons			X-rays		
	b, 10^{-12} cm	μ, cm^{-1}	$t_{50\%}$, cm	f, 10^{-12} cm	μ, cm^{-1}	$t_{50\%}$, cm
$C_{Graphite}$	0.66	0.62	1.11	1.69	9.6	0.72×10^{-1}
Al	0.35	0.10	7.05	5.69	131	0.53×10^{-2}
Ti	−0.34	0.45	1.55	9.12	938	0.74×10^{-3}
V	−0.05	0.56	1.25	9.63	1356	0.51×10^{-3}
Cr	0.35	0.47	1.47	10.1	1814	0.38×10^{-3}
Fe	0.96	1.12	0.62	11.5	2424	0.29×10^{-3}
Co	0.25	2.40	0.29	12.2	2980	0.23×10^{-3}
Ni	1.03	1.86	0.37	12.9	407	0.17×10^{-2}
Mo	0.69	0.48	1.44	21.6	1618	0.43×10^{-3}
W	0.47	1.05	0.66	42.3	3311	0.21×10^{-3}

Note: b is the neutron scattering length; μ is the linear absorption coefficient; $t_{50\%}$ represents the thickness required to absorb 50% of a thermal neutron beam; and f is the x-ray form factor.

(a) X-ray f and μ values calculated for CuKα at $\sin \theta/\lambda = 0.5$.

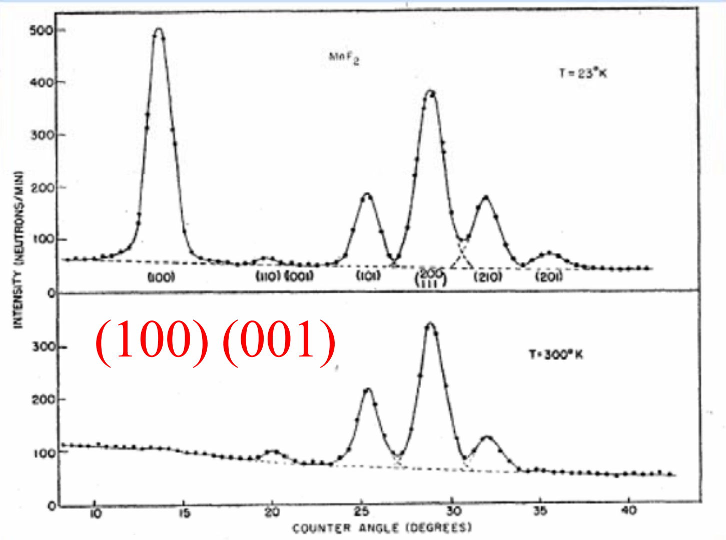
Nano Characterization- Diffraction

Neutron Diffraction



Nano Characterization- Diffraction

Magnetic Ordering in Antiferromagnet MnF$_2$



(100) (001)

FIG. 1. Neutron diffraction patterns for MnF$_2$ in the paramagnetic state (295°K) and in the antiferromagnetic state (23°K). The unit cells for antiferromagnetic and nuclear scattering are of the same size.

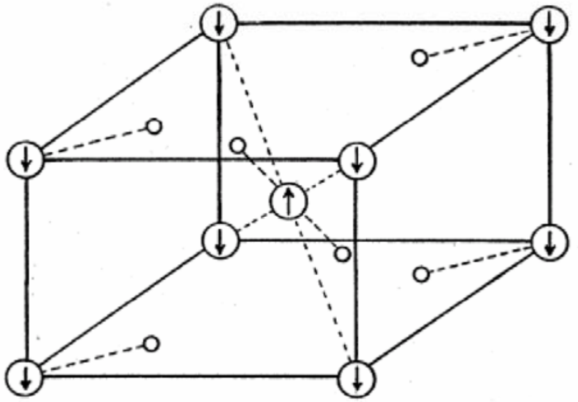
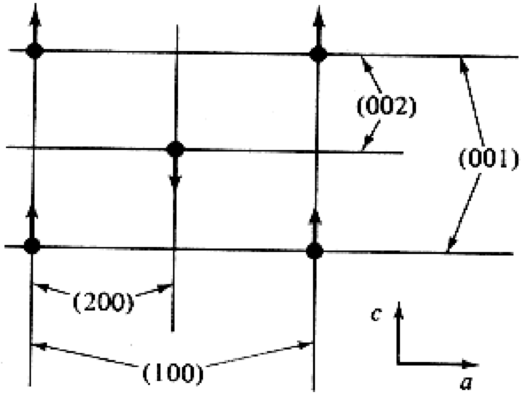


FIG. 4. Magnetic structure of MnF$_2$ showing the order and orientation of the Mn^{++} magnetic moments. The small circles correspond to fluorine sites.

after R. A. Erickson, *Phys. Rev.* **90**, 779 – 785 (1953)

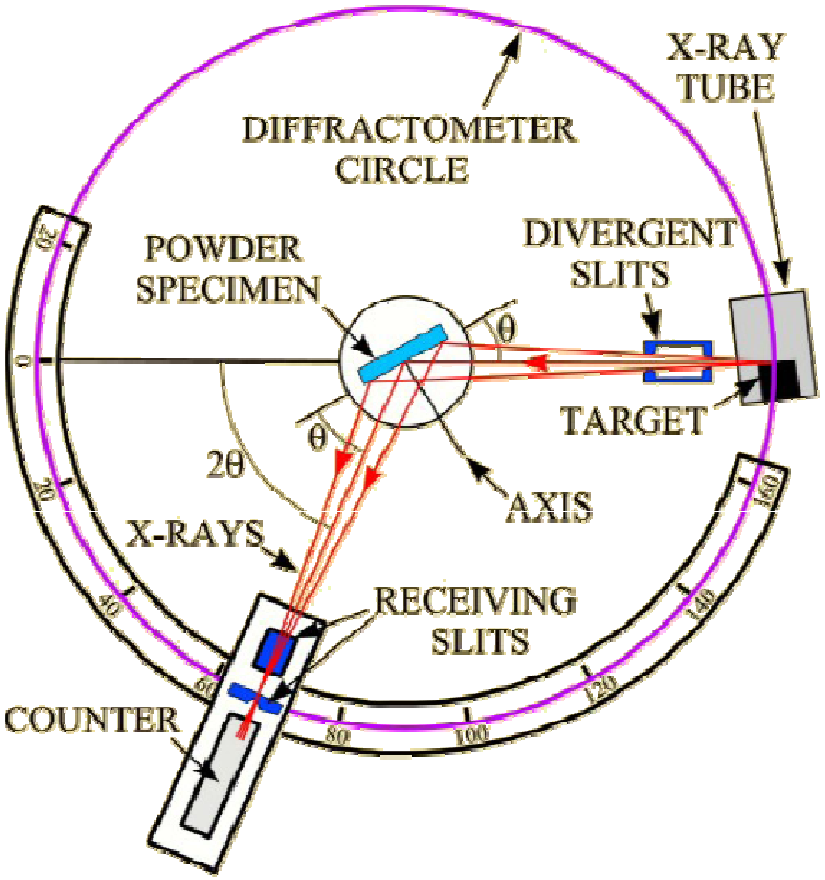


Nano Characterization- Diffraction (XRD)

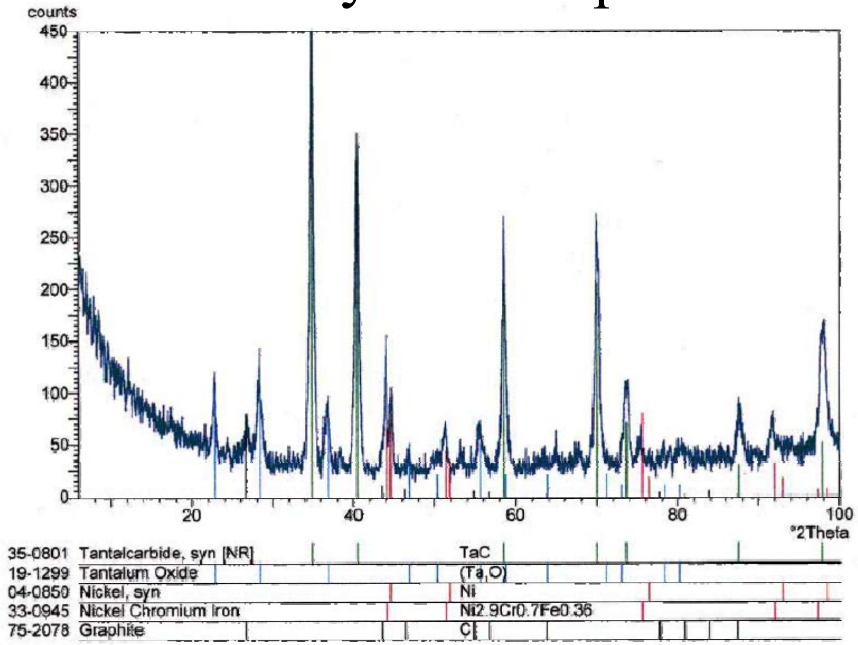
- Uniquely identify the crystalline phase present in material
- The structural properties
  - Strain state
  - Grain size
  - Epitaxy
  - Phase composition
  - Preferred orientation
  - Defect structure
- Determine the thickness of thin films
- Atomic arrangement in amorphous material (including polymer) and at interfaces

Nano Characterization- Diffraction (XRD)

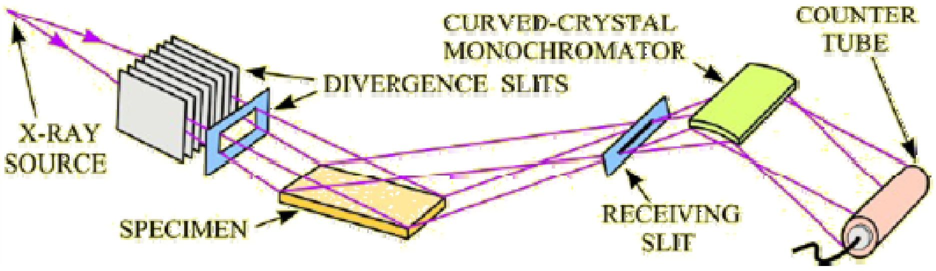
☐Schematic diagram of XRD



☐XRD analysis example

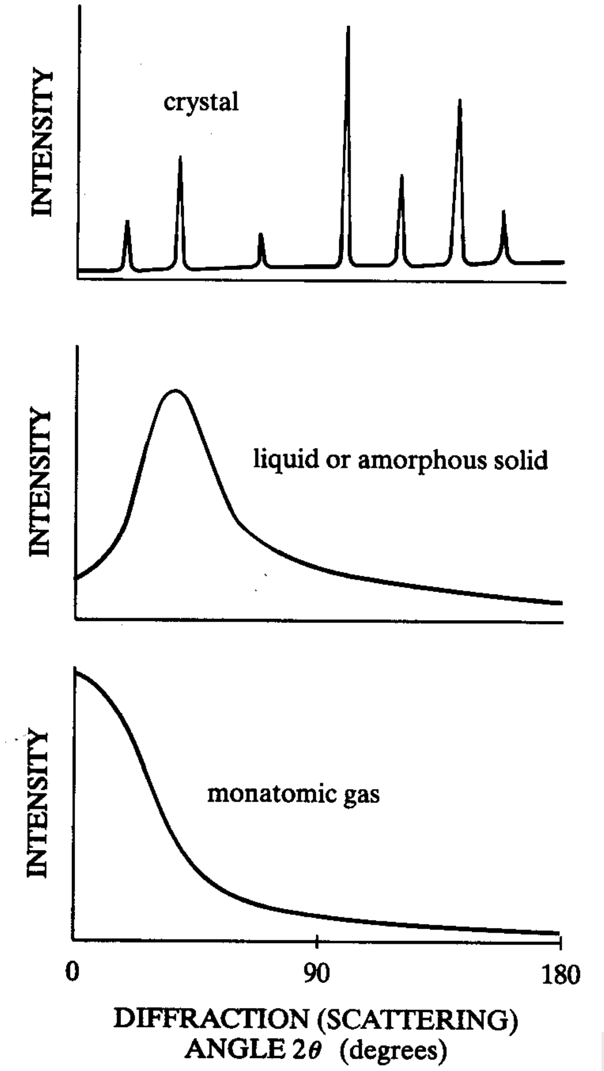


☐X-rays path way in XRD



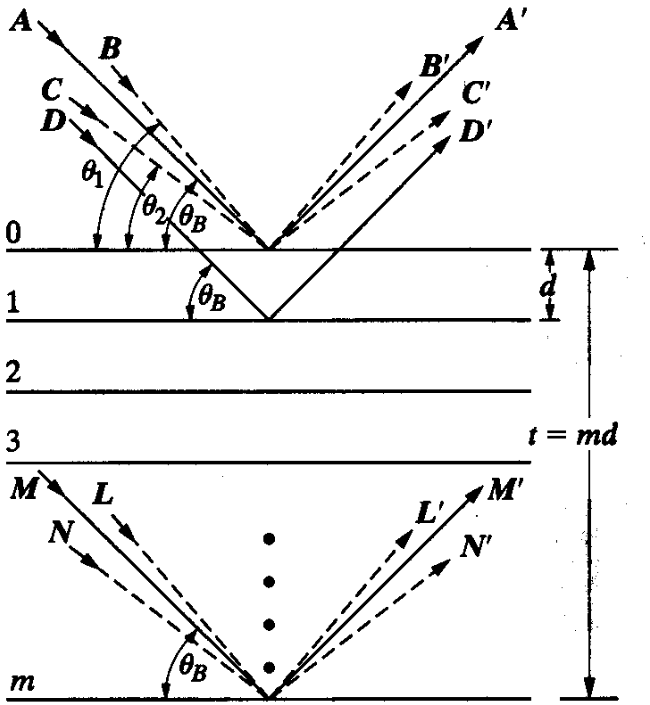
Nano Characterization- Diffraction (XRD)

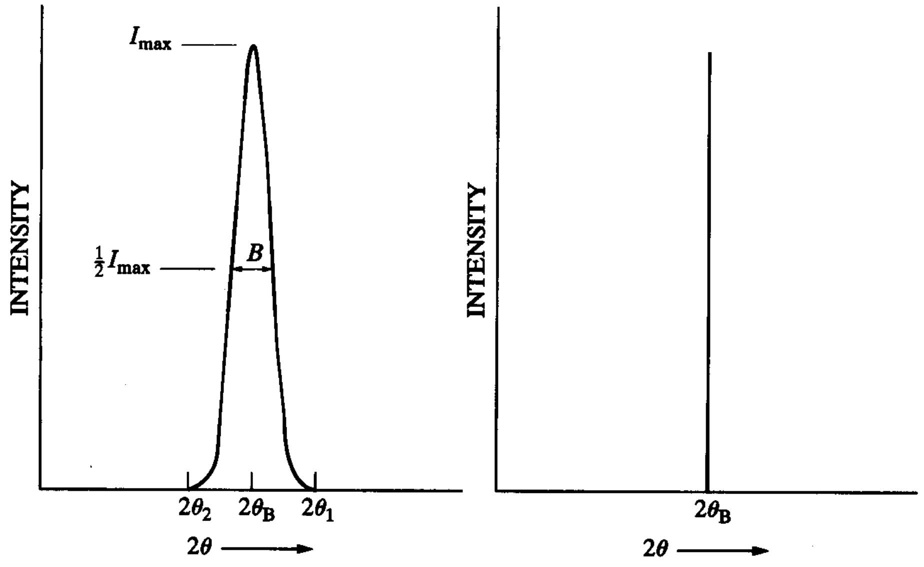
Amorphous and Partially Crystalline



Nano Characterization- Diffraction (XRD)

Crystallite Size





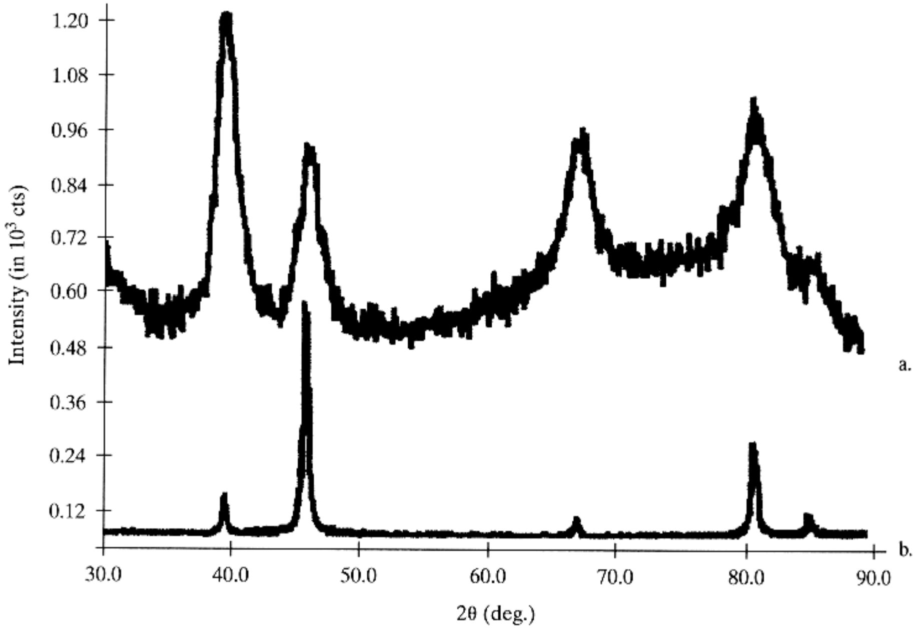
Scherrer's formula

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

$$B_{total}^2 = B_{inst}^2 + B_{crystal\ size}^2$$

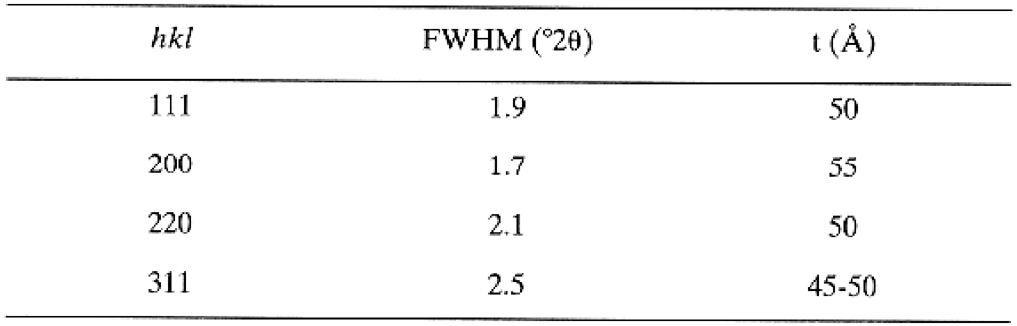
Nano Characterization- Diffraction (XRD)

Crystallite Size



-platinum nano-particle in a matrix of amorphous carbon

- rolled platinum sheet



hkl	FWHM (°2θ)	t (Å)
111	1.9	50
200	1.7	55
220	2.1	50
311	2.5	45-50

Nano Characterization- Diffraction (XRD)

Crystallite Size

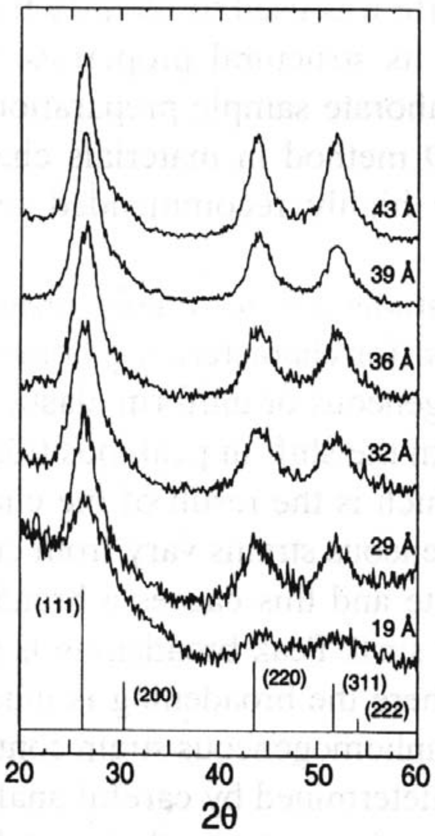
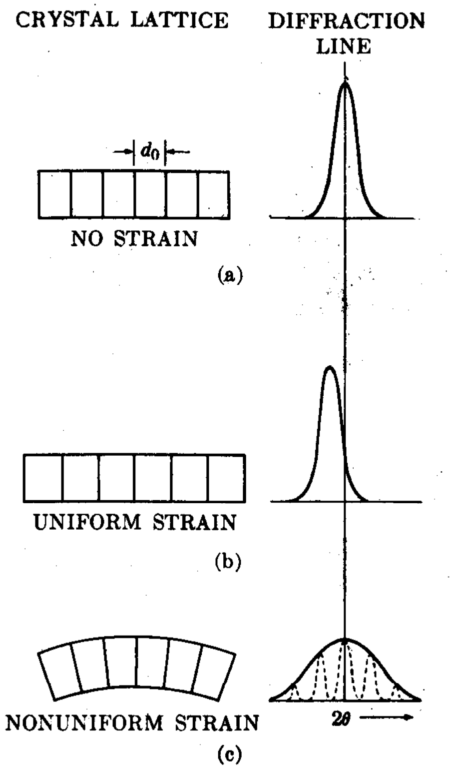


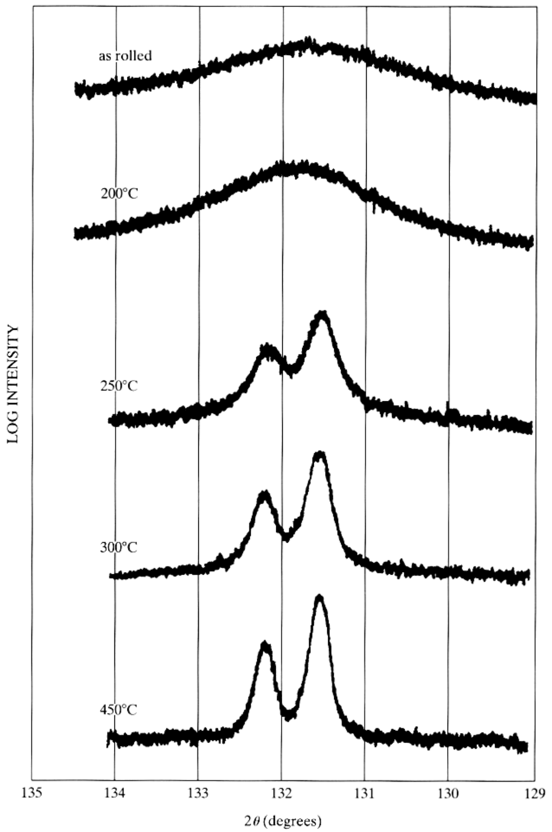
Fig. 8.1. Powder X-ray diffraction of a series of InP nanocrystal sizes. The stick spectrum gives the bulk reflections with relative intensities. [A.A. Guzelian, J.E.B. Katari, A.V. Kadavanich, U. Banin, K. Hamad, E. Juban, A.P. Alivisatos, R.H. Wolters, C.C. Arnold, and J.R. Heath, *J. Phys. Chem.* **100**, 7212 (1996).]

Nano Characterization- Diffraction (XRD)

Strain



70Cu30Zn



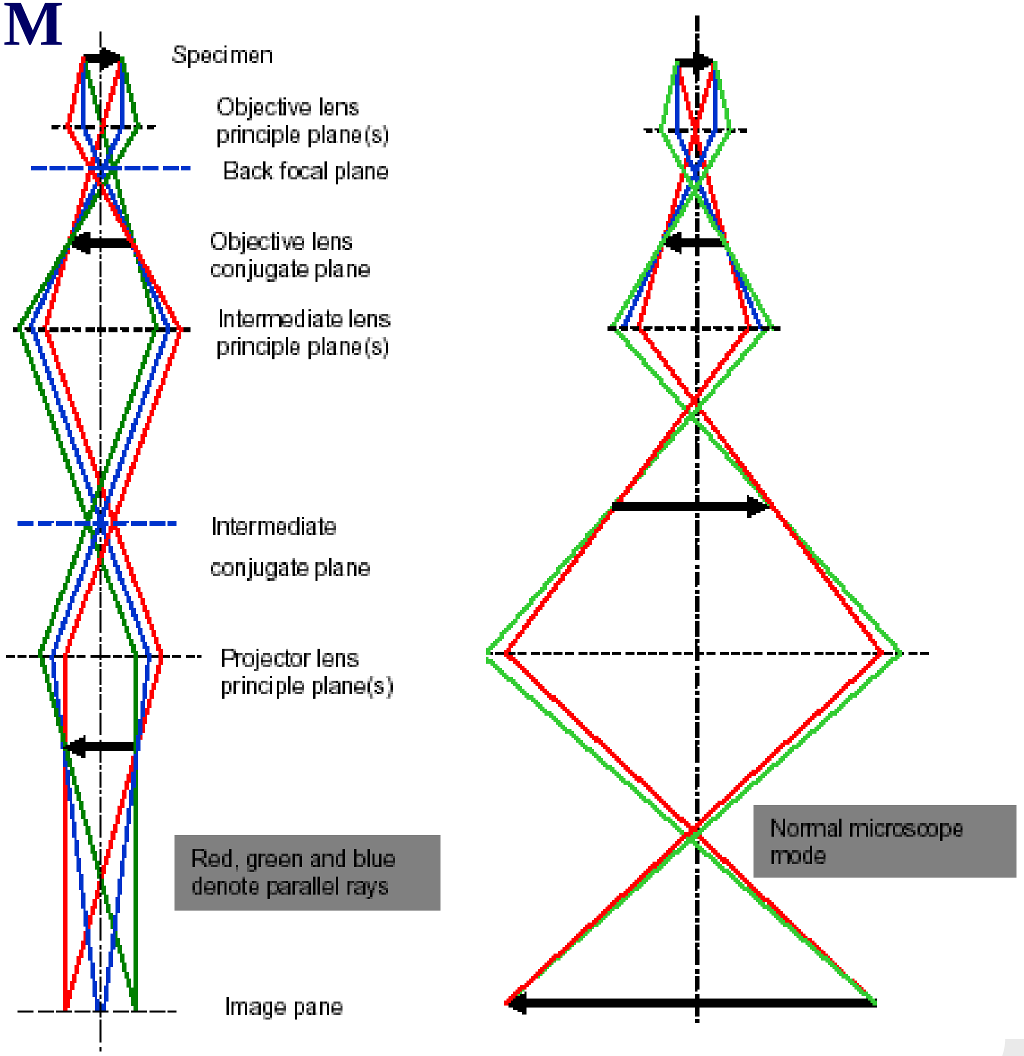
$$B = \Delta 2\theta = -2\frac{\Delta d}{d}\tan\theta$$

Nano Characterization- Diffraction (TEM)

❑ Electron Diffraction in TEM

- Diffraction mode

Optional Objective and Selected area metal apertures can restrict the beam; the Objective aperture enhancing contrast by blocking out high-angle diffracted electrons, the selected area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample



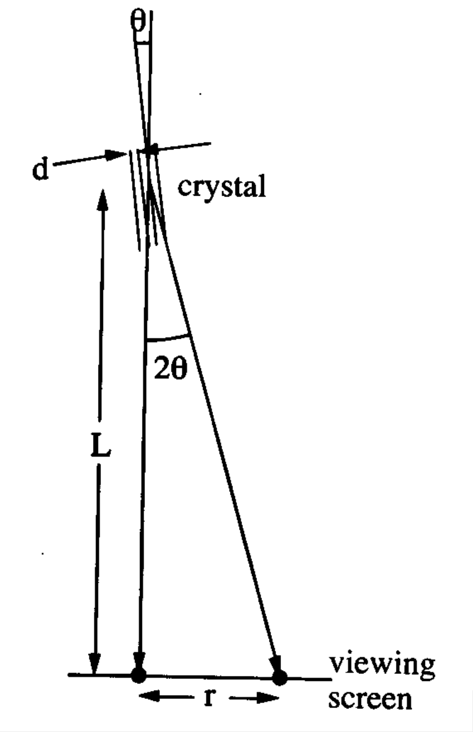
Red, green and blue denote parallel rays

Normal microscope mode

Nano Characterization- Diffraction (TEM)

❑ Electron Diffraction in TEM

Electron energy / keV	Wavelength / pm	Diffracting planes	θ_B
50	5.355	Cu_{111}	0.75
100	3.701	Al_{200}	0.54
300	1.969	Si_{200}	0.32



Bragg's law $2d\sin\theta = \lambda$

$$\theta \sim 1^o \quad \sin\theta = \tan\theta = \frac{1}{2}\tan 2\theta$$

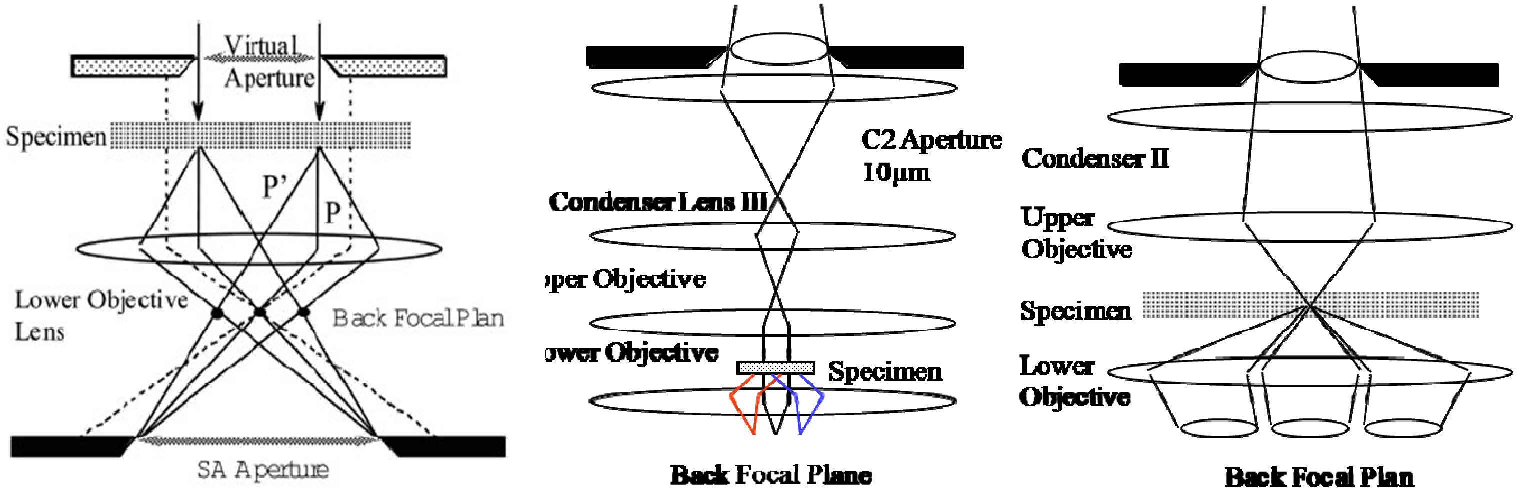
$$\tan 2\theta = \frac{r}{L}$$

$$2d\frac{1}{2}\frac{r}{L} = \lambda \;\Rightarrow\; rd = L\lambda$$

camera constant

Nano Characterization- Diffraction (TEM)

❑ Electron diffraction mode

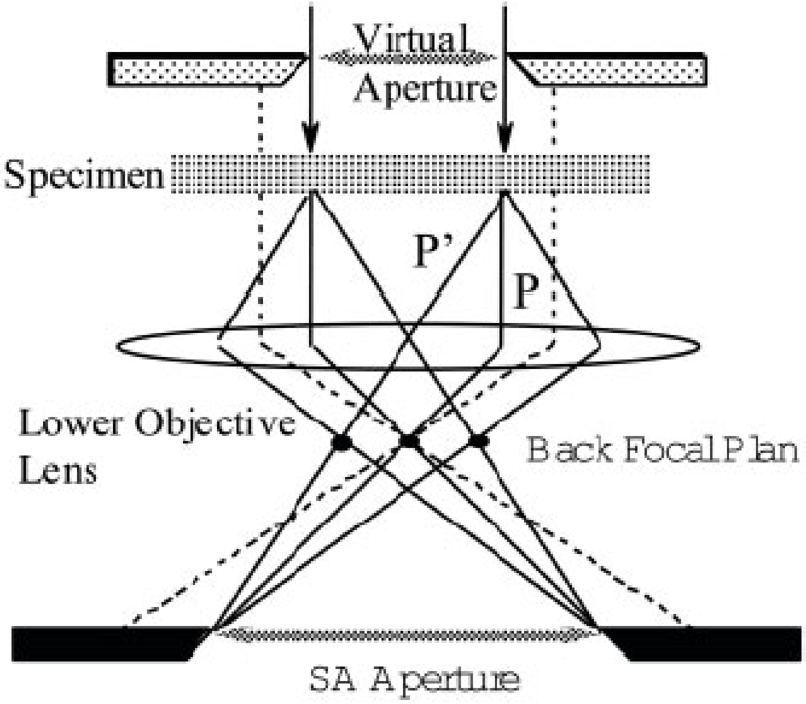


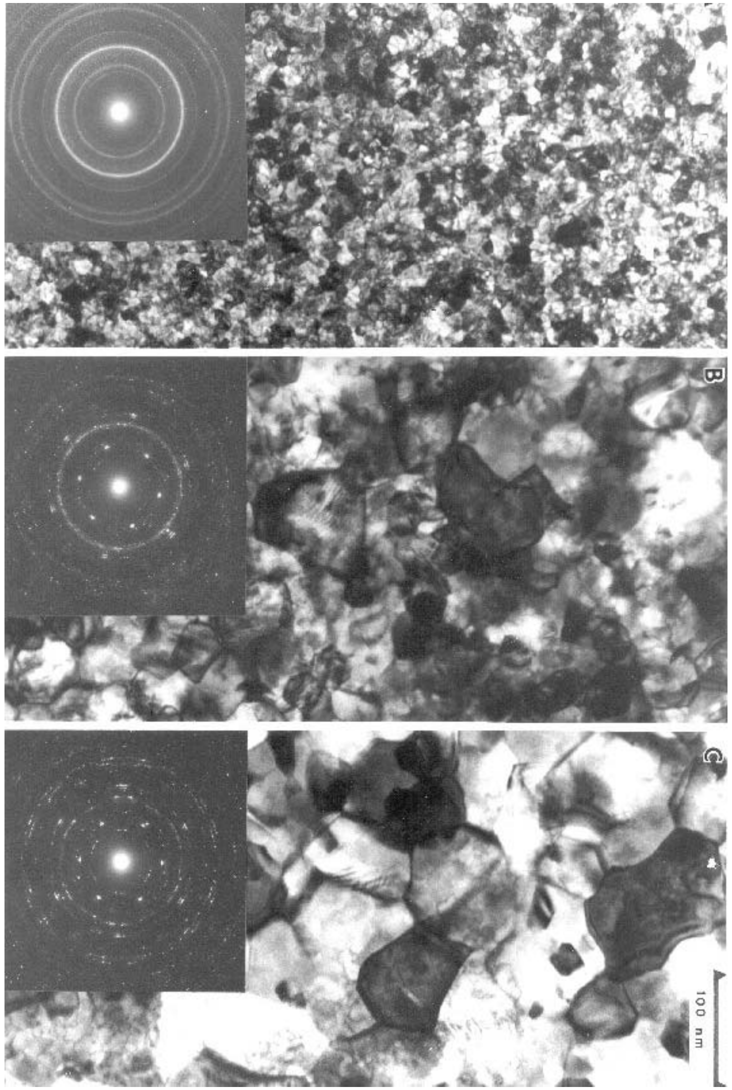
a) Selected Area Electron Diffraction **b) Nanoarea Electron Diffraction** **c) Convergent Beam Electron Diffraction**

Three modes of electron diffraction. Both a) selected area electron diffraction (SAED) and b) nanoarea electron diffraction (NED) use parallel illumination. SAED limits the sample volume contributing to electron diffraction by using an aperture in the image plane of the image forming lens (objective). NED achieves a very small probe by imaging the condenser aperture on the sample using a third condenser lens. Convergent beam electron diffraction (CBED) uses a focused probe.

Nano Characterization- Diffraction (TEM)

- ☐ Selected area diffraction





PtSi according to annealing time

Nano Characterization- Spectroscopy

❑ Spectroscopy

Branch of analysis devoted to identifying elements and compounds and elucidating atomic and molecular structure by measuring the radiant energy absorbed or emitted by a substance at characteristic wavelengths of the electromagnetic spectrum (including gamma ray, X ray, ultraviolet, visible light, infrared, microwave, and radio-frequency radiation) on excitation by an external energy source.”

❑The materials analysis acronym menagerie

Probe		Response
Electrons	Sample	Electrons
Radiation		Radiation
Atoms		Atoms
Ions		Ions

X-rays in, electrons out
- XPS: X-ray photoelectron spectroscopy
- UPS: Ultraviolet Photoemission spectroscopy

Electrons in, electrons out
- AES: Auger electron spectroscopy
- SAM: Scanning Auger Microscopy
- EELS: Electron Energy-loss spectroscopy

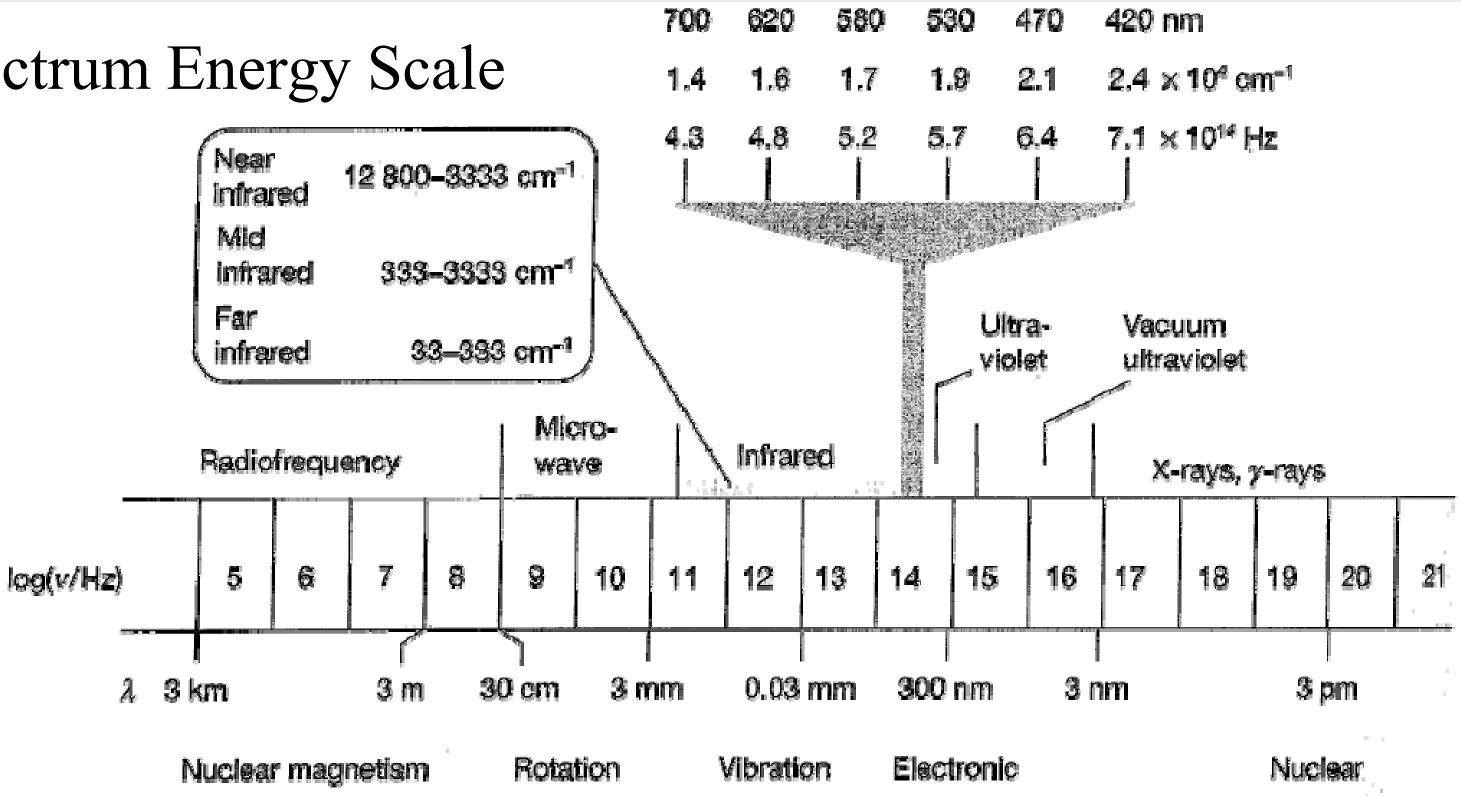
Electrons in, X-rays out
- WDX: Wavelength-dispersive X-ray Spectroscopy
- EDX: Energy-dispersive X-ray spectroscopy

X-rays in, electrons or X-rays out
- EXAFS: Extended X-ray absorption fine structure
- XANES: X-ray absorption near-edge structure

Ions in, ions out
- SIMS: Secondary Ion Mass Spectroscopy

Nano Characterization- Spectroscopy

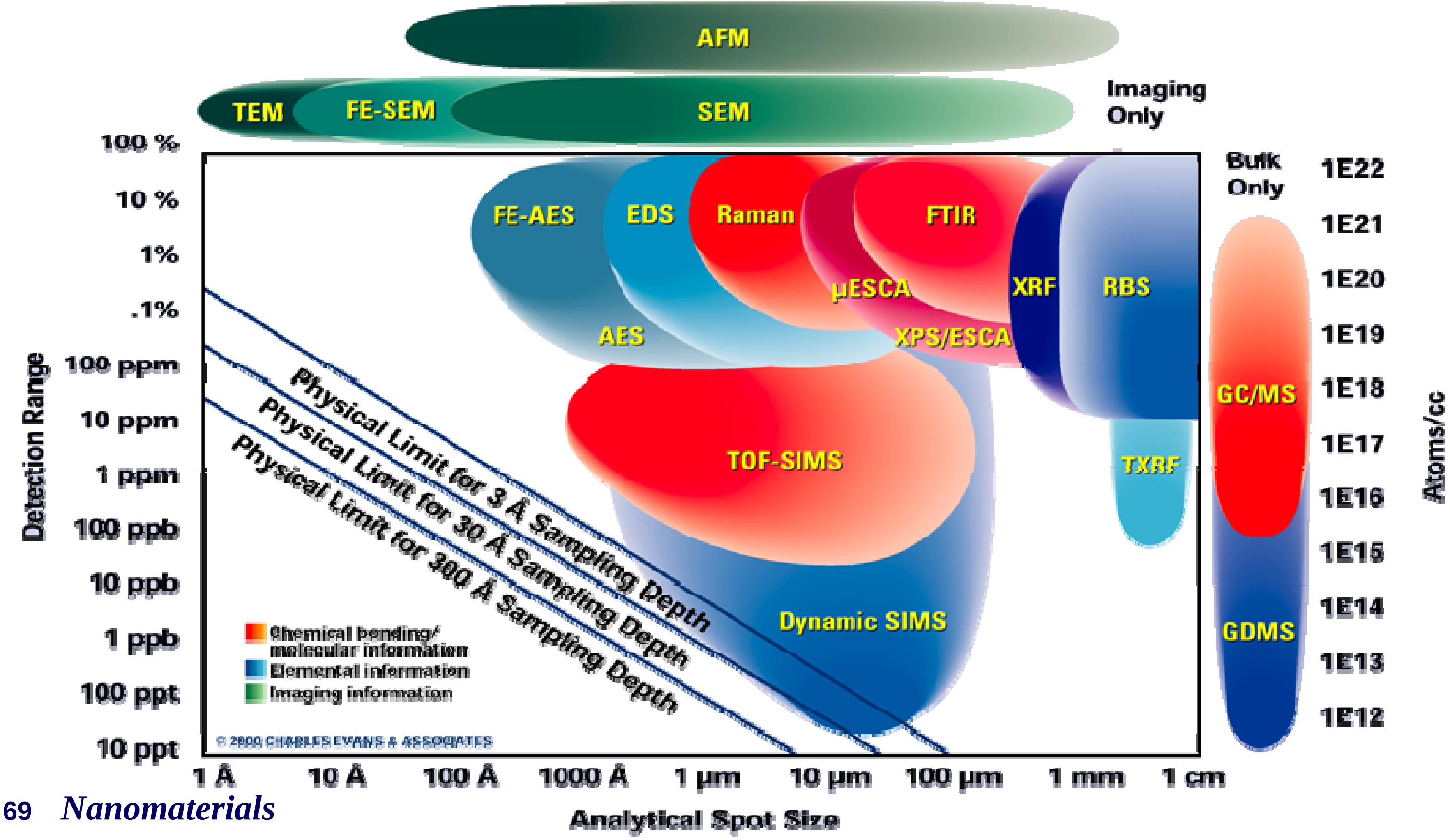
❑Spectrum Energy Scale



Unit	cm^{-1}	MHz	kJ	eV	kJ mol^{-1}
1 cm^{-1}	1	29 979.25	$1.986\ 45 \times 10^{-26}$	$1.239\ 84 \times 10^{-4}$	$1.196\ 27 \times 10^{-2}$
1 MHz	$3.335\ 64 \times 10^{-5}$	1	$6.626\ 08 \times 10^{-31}$	$4.135\ 67 \times 10^{-9}$	$3.990\ 31 \times 10^{-7}$
1 kJ	$5.034\ 11 \times 10^{25}$	$1.509\ 19 \times 10^{30}$	1	$6.241\ 51 \times 10^{21}$	$6.022\ 14 \times 10^{23}$
1 eV	8065.54	$2.417\ 99 \times 10^{8}$	$1.602\ 18 \times 10^{-22}$	1	96.485
1 kJ mol^{-1}	83.5935	$2.506\ 07 \times 10^{6}$	$1.660\ 54 \times 10^{-24}$	$1.036\ 43 \times 10^{-2}$	1

Nano Characterization- Spectroscopy

❑Analytical resolution vs. Detection limit



Nano Characterization- Spectroscopy (optical)

☐ Optical Spectroscopy

- Optical spectroscopy has been widely used for the characterization of nanomaterials.

- The Techniques can be categorized into absorption/emission spectroscopy and vibrational spectroscopy.

- The absorption & Emission spectroscopy can determine the electronic structure of atoms, molecules, or crystals, through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground states (emission).

- The vibrational spectroscopy provides information on chemical bonds in sample through the interactions of photons with species in a samples via vibrational excitation or de-excitation.

Nano Characterization- Spectroscopy (optical)

❑ Absorption Spectroscopy

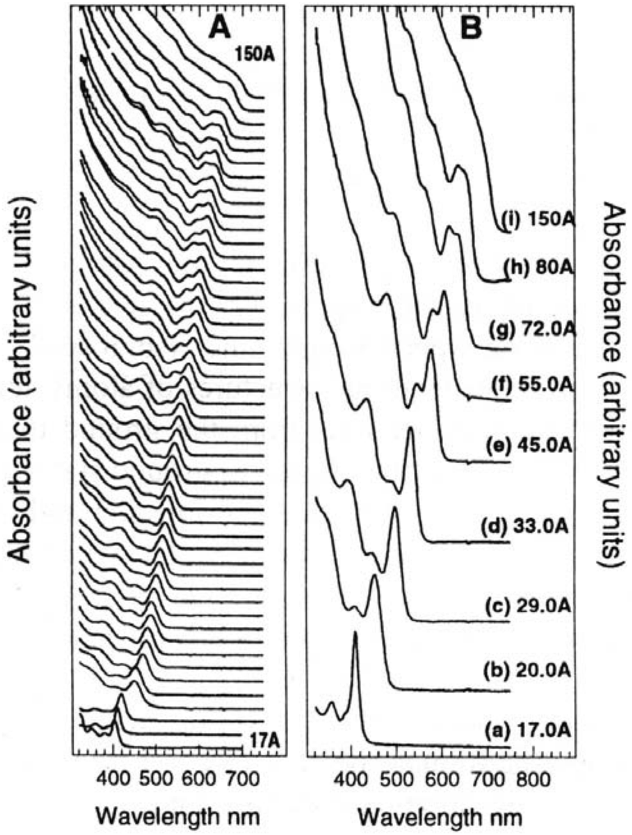


Fig. 8.10. Optical absorption spectra of CdSe nanocrystals with varying diameters. (A) This is seen spectroscopically as a blue shift in the absorption edge and a larger separation between electronic transitions for a homogeneous size series of CdSe nanocrystal dispersion, collected at room temperature. (B) Observation of discrete electronic transitions in optical absorption. [C.B. Murray, C.R. Kagan, and M.G. Bawendi, *Ann. Rev. Mater. Sci.* **30**, 545 (2000).]

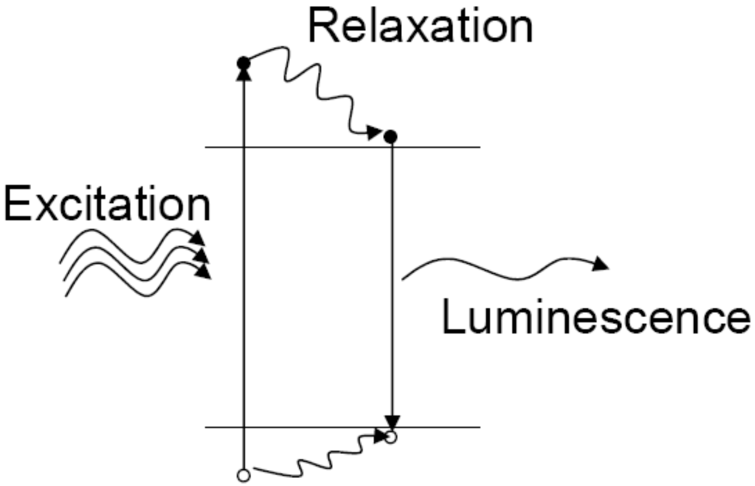
Nano Characterization- Spectroscopy (optical)

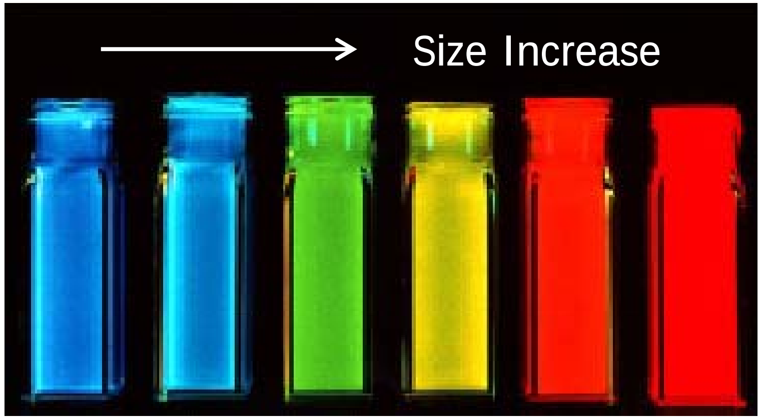
- ❑FTIR (Fourier Transform Infrared) spectroscopy
  - ❑ Lattice dynamics (phonons)
  - ❑ Optical transitions (band structure)
  - ❑ Absorption
- ❑X-ray Spectroscopy
  - ❑ Core electrons: chemical analysis
  - ❑ Local structural information (EXAFS)
- ❑Photoluminescence (PL) or Fluorescence
  - ❑ Band gap
  - ❑ Electronic states (impurities, etc)
- ❑Raman scattering
  - ❑ Electronic excitations (single particle excitations, plasmons)
  - ❑ Lattice dynamics (phonons)
  - ❑ Magnetic excitations (magnons)

Nano Characterization- Spectroscopy (PL)

☐ Photoluminescence – Emission spectroscopy

- Luminescence refers to light emission by a material through processes other than blackbody radiation.
- Photoluminescence is that due to excitation by photon, or light. The peak position related to the energy "bandgap" of the material, which may also be size dependent in nanostructures.

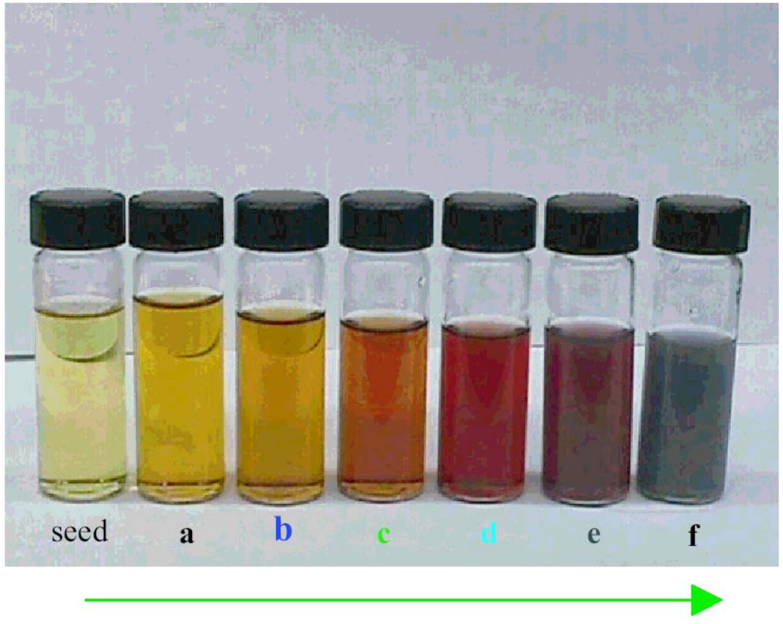


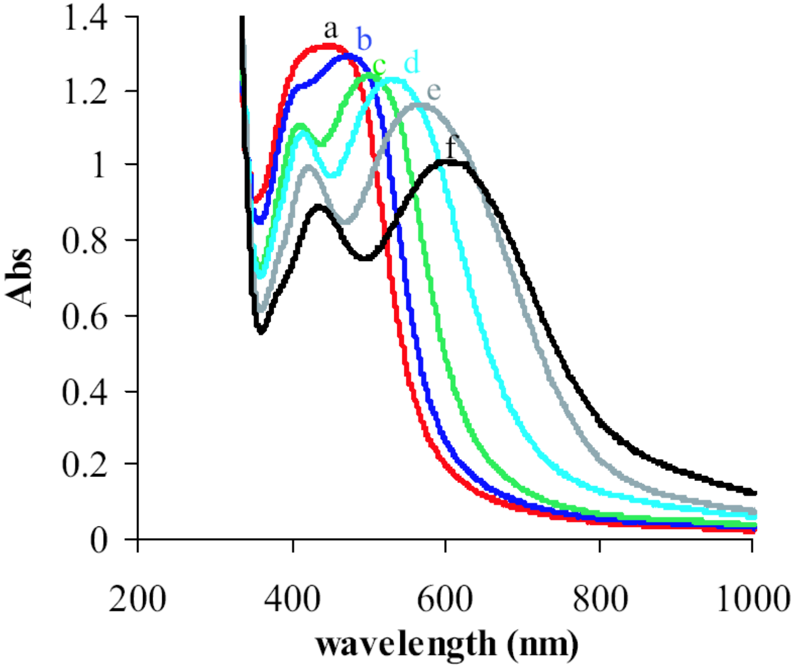


Size dependent Photoluminescence of CdSe Nanoparticles

Nano Characterization- Spectroscopy (Absorption)

❑ Absorption spectroscopy





Aqueous solution of silver nanoparticles show a beautiful variation in visible color depending on the aspect ratio of the suspended nanoparticles: far left in the photograph, silver nanoparticles 4nm in diameter that are used as seeds in subsequent reactions: a-f) silver nanorods of aspect ratio 1~10.

Nano Characterization- Spectroscopy (Absorption)

❑ Absorption/Photoluminescence spectroscopy

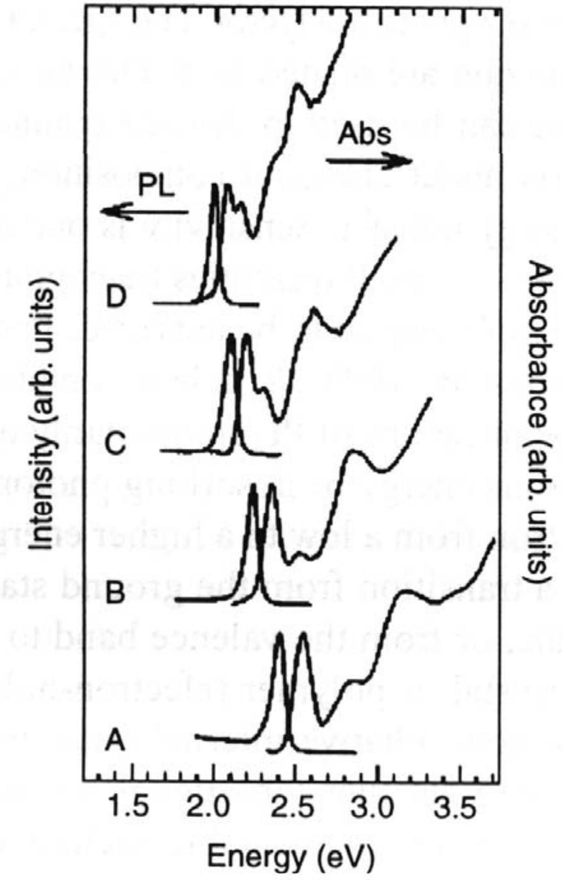
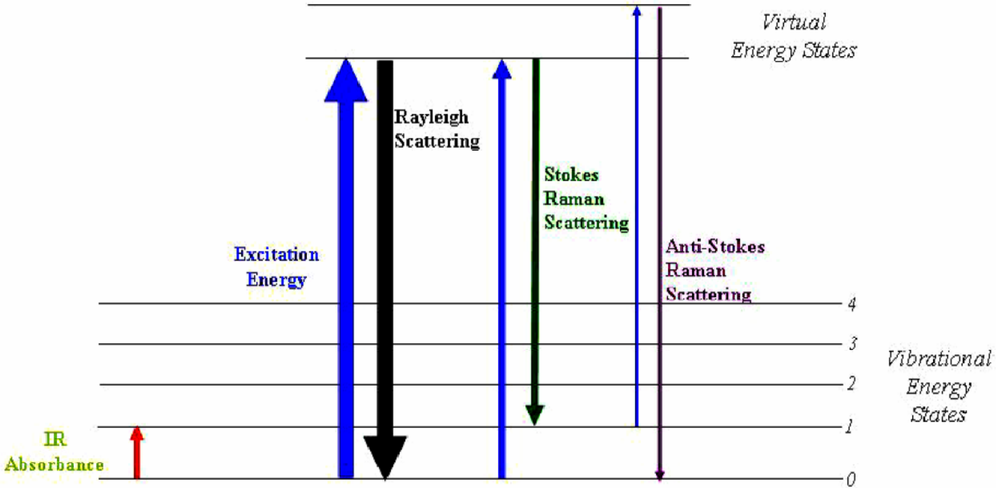


Fig. 8.11. 10-K optical absorption and photoluminescence spectra of optically thin and clear, close-packed nanocrystals of CdSe of (A) 30.3, (B) 39.4, (C) 48.0, and (D) 62.1 Å in diameter. [C.R. Kagan, C.B. Murray, and M.G. Bawendi, *Phys. Rev.* **B54**, 8633 (1996).]

Nano Characterization- Spectroscopy (Raman)

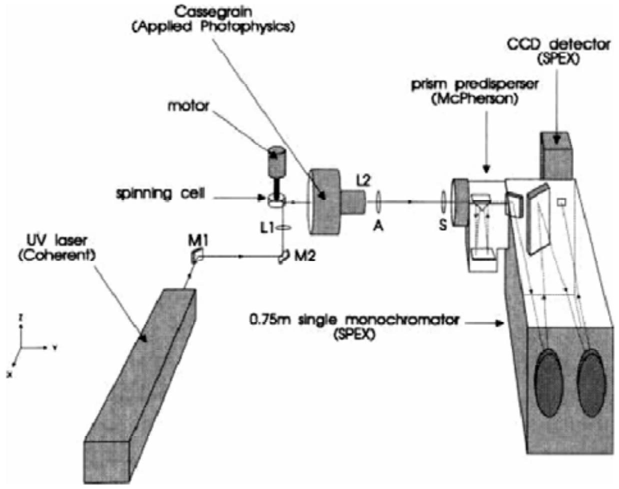
❑ Raman Scattering concept and Technique

Infrared active vibrational modes aris from a change in the electric dipole moment μ of the molecule, while Raman-active vibrational modes involve a change in the polarizability $P = \mu_{ind}/E$, where the electric vector E of the incident light induces the dipol moment μ_{ind} in the sample.



❑ Raman spectrometer

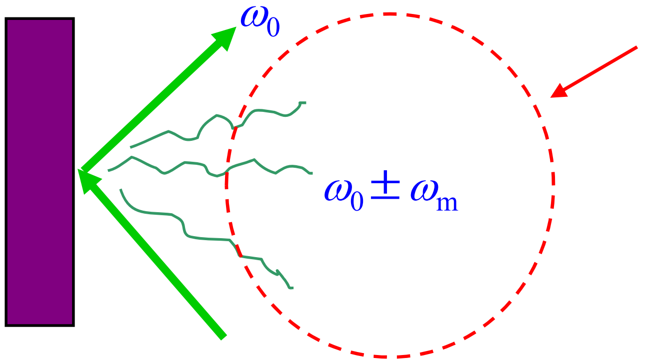
M. P. Russell, S. Vohník, and G. J. Thomas, Jr., Biophys. J. 1995 April; 68(4): 1607–1612.



Nano Characterization- Spectroscopy (Raman)

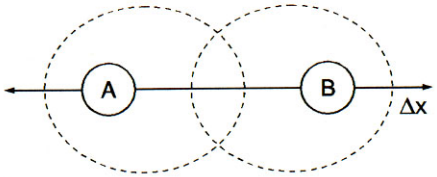
❑Origin of Raman spectroscopy

Inelastic Light Scattering : Raman scattering arises from a change in the polarizability of molecules or the susceptibility of crystals by the excited quasi-particles



response of interest

Light is inelastically scattered when there is spatial and temporal fluctuation, or modulation in the polarizability



: two-atom molecule with polarazability α

$P_D(\omega) = \alpha_0 E(\omega)$: dipole moment induced by an applied field E(ω)

$P_D(\omega) = (\alpha_0 + \alpha_1 \cos\Omega t)\, E_0 \cos\omega t$: DM when the molecule is vibrating with Ω

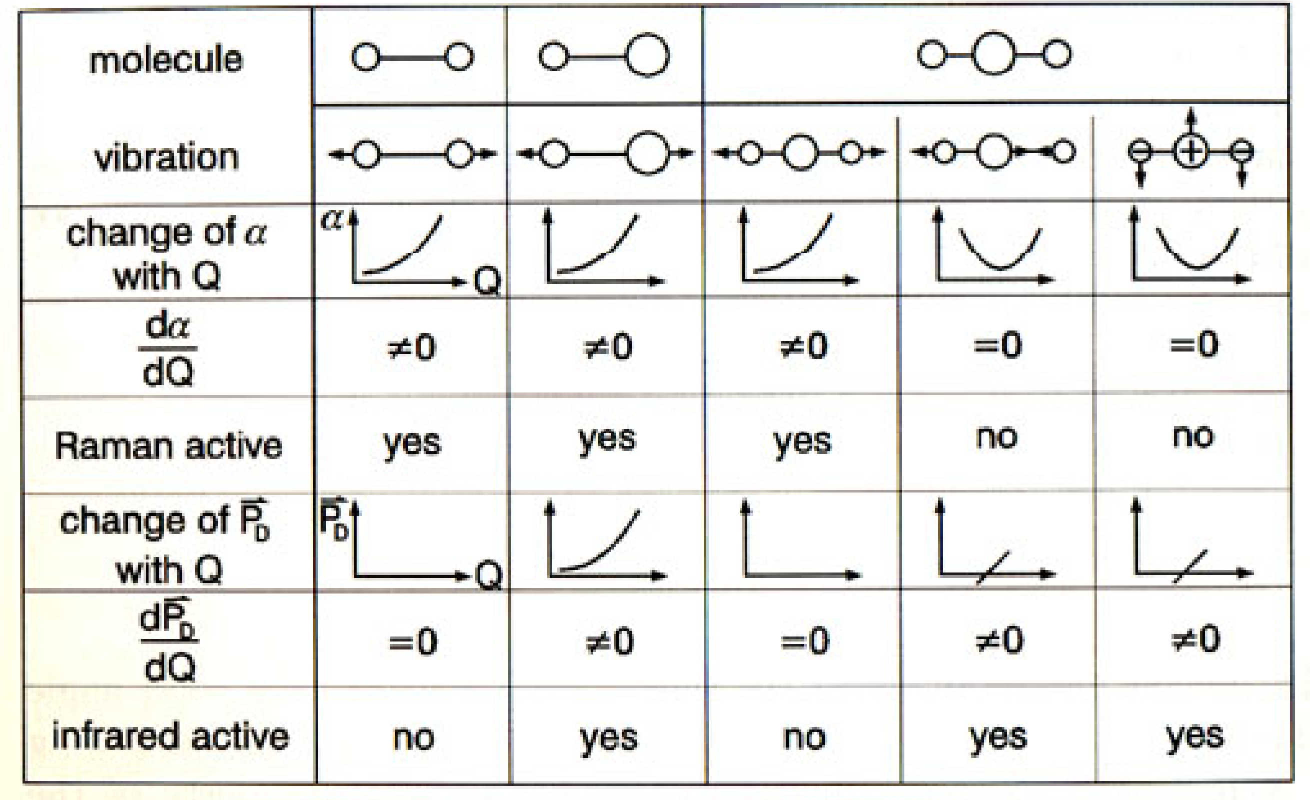
$$P_D(\omega) = \alpha_0 E_0 \cos\omega t + (\alpha_1 E_0/2)[\cos(\omega + \Omega)\, t + \cos(\omega - \Omega) t]$$

light oscillates not only with ω but also with $\omega \pm \Omega$ $\omega >> \Omega,\ \alpha_0 >> \alpha_1$

Nano Characterization- Spectroscopy (Raman)

❑Fundamentals of Raman scattering

❑ Raman activity



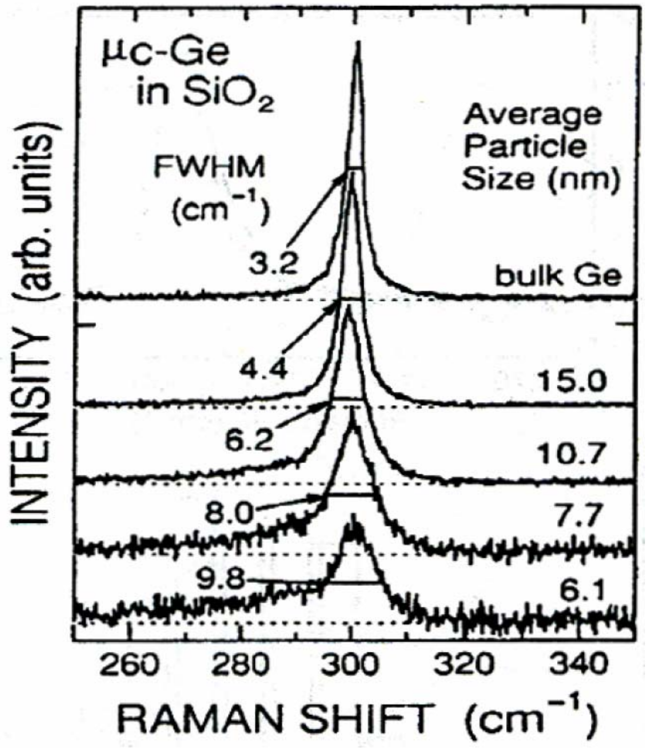
molecule					
vibration					
change of α with Q					
$\frac{d\alpha}{dQ}$	$\neq 0$	$\neq 0$	$\neq 0$	$=0$	$=0$
Raman active	yes	yes	yes	no	no
change of $\vec{P}_D$ with Q					
$\frac{d\vec{P}_D}{dQ}$	$=0$	$\neq 0$	$=0$	$\neq 0$	$\neq 0$
infrared active	no	yes	no	yes	yes

Change in the polarizability!

Nano Characterization- Spectroscopy (Raman)

❑ RAMAN SCATTERING FROM n-Ge

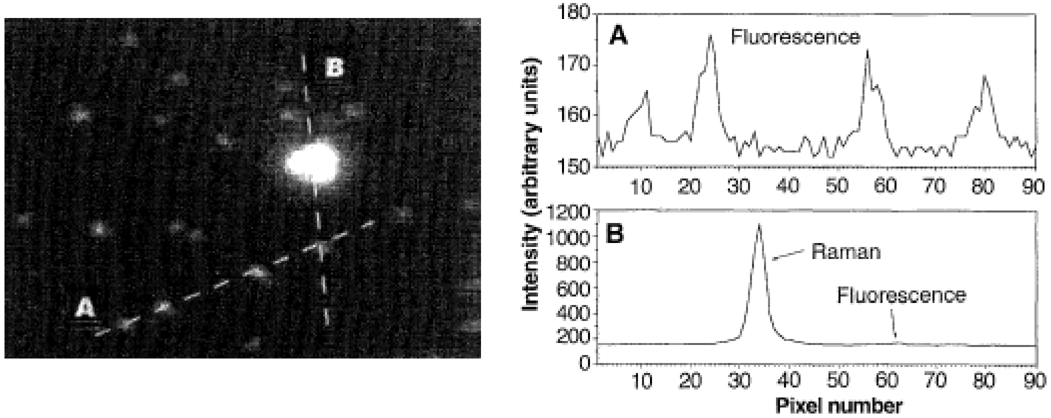
Dependence of the Raman spectra of germanium microcrytals (μC-Ge) embedded in SiO_2 thin films on the crystallyte size. The average particle size and the full width at half-maximum height (FWHM) of the Raman line of each sample are indicated. [From M.Fuji, S Hayashi, Jpn. J. Appl. Phys. 30, 657 (1991).]



Nano Characterization- Spectroscopy (SERS)

❑ Surface Enhanced Raman Scattering (SERS)

Plasmon resonance has been used in surface enhanced Raman spectroscopy (SERS) for many decades. Because the Raman signal is proportional to $I \propto E^4$, giant enhancement of the Raman signal (up to ~10^{12} - 10^{14} times) has been reported [Nie, S.; Emory, S.R. ***Science*** **275**, 1102 (1997)]. Experimentally reported values of enhancement are even higher than theoretical predictions.



Observation of hot spots with enhancement up to ~10^{12}-10^{14}

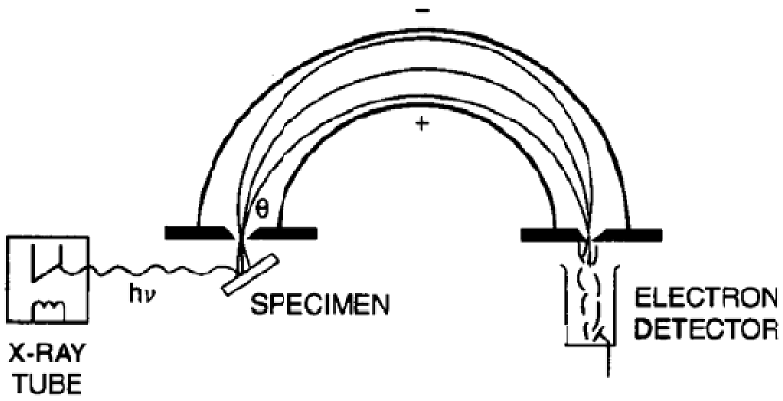
[Nie, S.; Emory, S.R. ***Science*** **275**, 1102 (1997)].

It has been demonstrated that only a few spots, so called “hot spots”, provide giant enhancement of the Raman signal. *Understanding the nature of the hot spots remains a challenge.*

Nano Characterization- Spectroscopy (XPS)

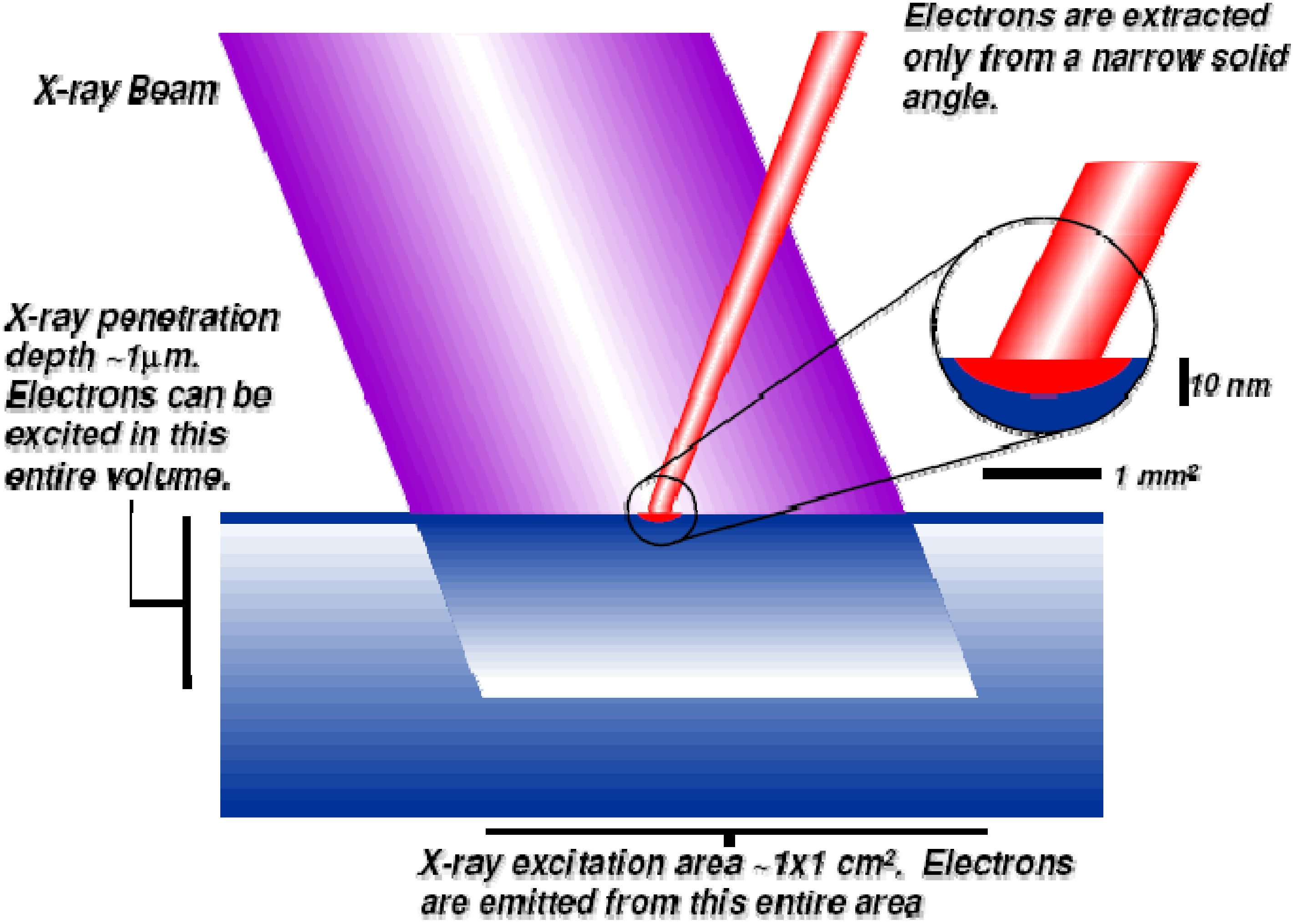
❑ X-ray Photoelectron Spectroscopy

The energy states of atoms or molecular ions in the valence band region have characteristic ionization energies that reflect perturbations by the surrounding lattice environment. Related spectroscopic techniques such as inverse photoelectron spectroscopy (IPS), Bremsstrahlung isochromat spectroscopy (BIS), electron energy-loss spectroscopy (EELS), and Auger electronic spectroscopy provide similar information as contained in an X-ray photoelectron spectrum (XPS).



XPS instrument diagram showing X-ray incident on the specimen, leading to photoelectron generation, with kinetic energies (K.E.) given by the equation K.E. = $h\nu_{ph} - E_{ion}$.

Nano Characterization- Spectroscopy (XPS)



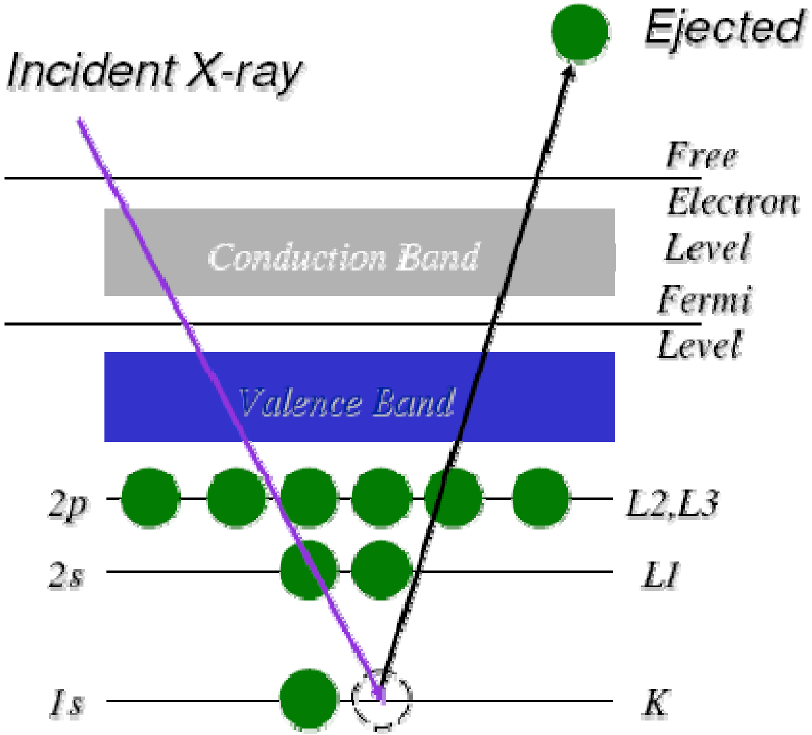
Electrons are extracted only from a narrow solid angle.

X-ray penetration depth ~1µm. Electrons can be excited in this entire volume.

X-ray excitation area ~1x1 cm². Electrons are emitted from this entire area

Nano Characterization- Spectroscopy (XPS)

❑The photoelectric process



- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy:

  $$KE=h\nu-BE-\Phi$$

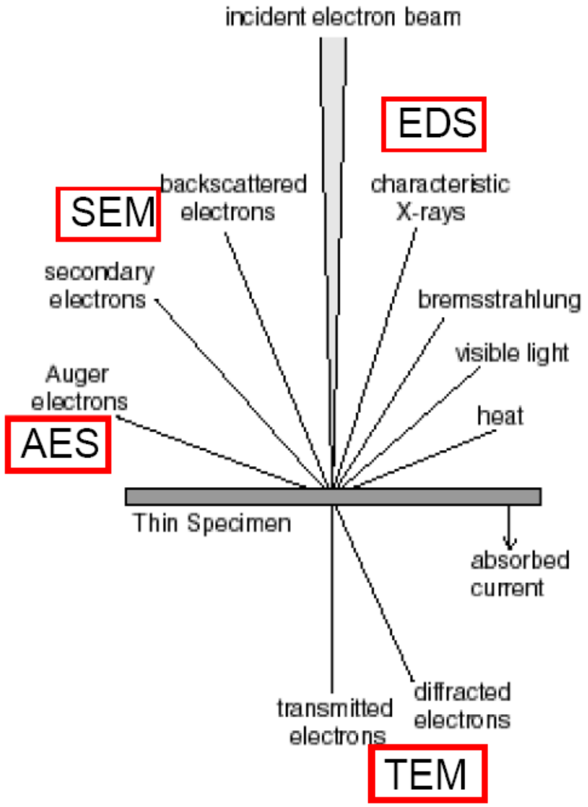
- Following this process, the atom will release energy by the emission of an Auger Electron.

Nano Characterization-Electron Spectroscopy

❑ Electron – Specimen Interactions

Electron bombardment of a specimen induces inelastic & elastic scattering w. specimen atoms

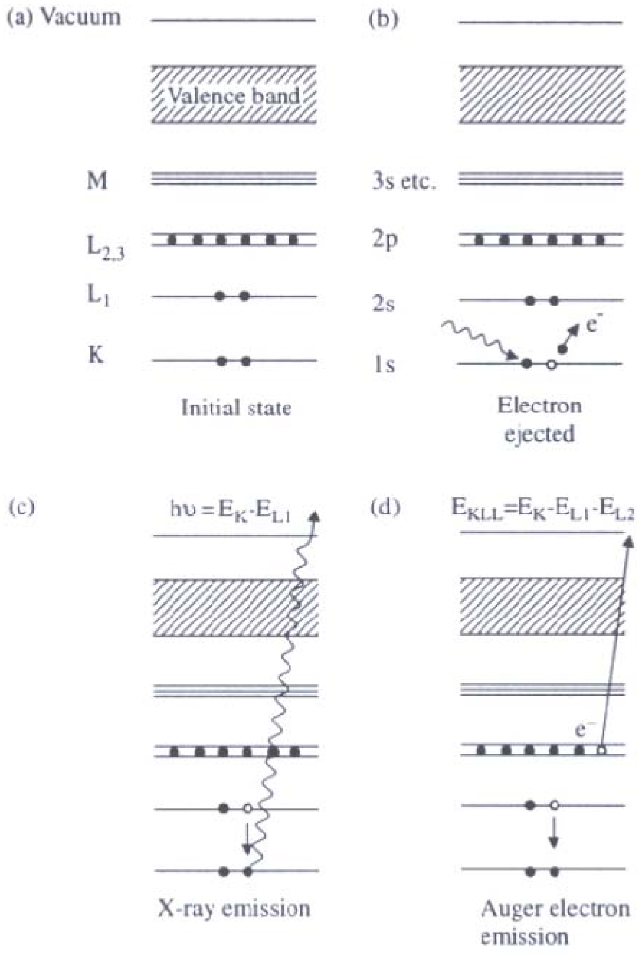
- elastic scattering : without energy loss
- Inelastic scattering : with significant energy loss
  - phonon excitation (heating)
  - cathodoluminescence (visible light fluorescence)
  - continuum radiation (or “braking” or “deceleration” or “bremsstrahlung” radiation)
  - characteristic X-ray radiation
  - plasmon production (secondary electrons)
  - Auger electron production (ejection of outer shell electrons)



Nano Characterization-Electron Spectroscopy

☐ Electron Spectroscopy

- It is mainly used to identify the chemical compositions of the Sample.
- Depending on the source of excitation & the identity being detected, there are a variety of spectroscopic techniques available, including AES, XPS, EDX, etc

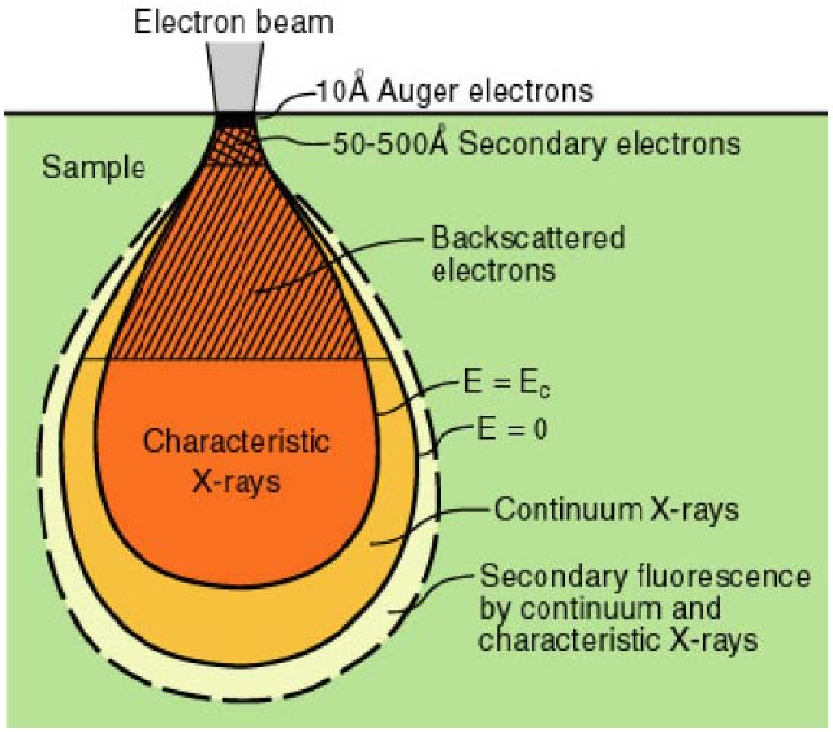


Nano Characterization-Electron Spectroscopy

☐ Electron – Specimen Interactions

How deep the produced effects (Auger electrons, secondary electrons, backscattered electrons, characteristic X-ray, etc.) of electron bombardment on specimens can be effectively detected, considering absorption by specimen itself.

- EDS – characteristic X-rays
- Auger Electron Spectroscopy (AES) – Auger electrons



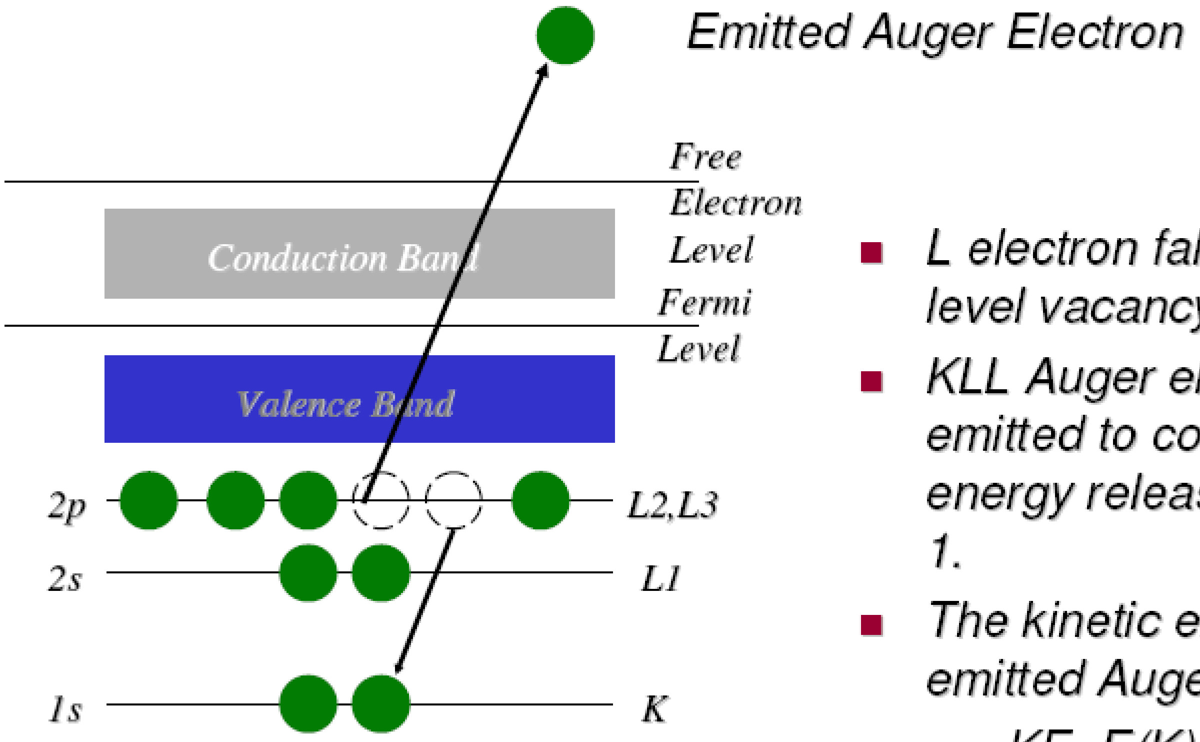
Nano Characterization-Electron Spectroscopy

- ☐ Auger Electron Spectroscopy
  - ☐ Chemical information near the surface
- ☐ Photoelectron Spectroscopy (XPS, UPS)
  - ☐ Chemical analysis
  - ☐ Valence band structure
- ☐ Electron energy-loss spectroscopy
  - ☐ Chemical analysis
  - ☐ Conduction band structure
- ☐ Secondary Ion Mass Spectroscopy
  - ☐ Composition Analysis

Nano Characterization-Electron Spectroscopy (AES)

❑ AES (Auger Electron Spectroscopy)

- Auger relation of core hole



- L electron falls to fill core level vacancy (step 1).
- KLL Auger electron emitted to conserve energy released in step 1.
- The kinetic energy of the emitted Auger electron is:

  KE=E(K)-E(L2)-E(L3).

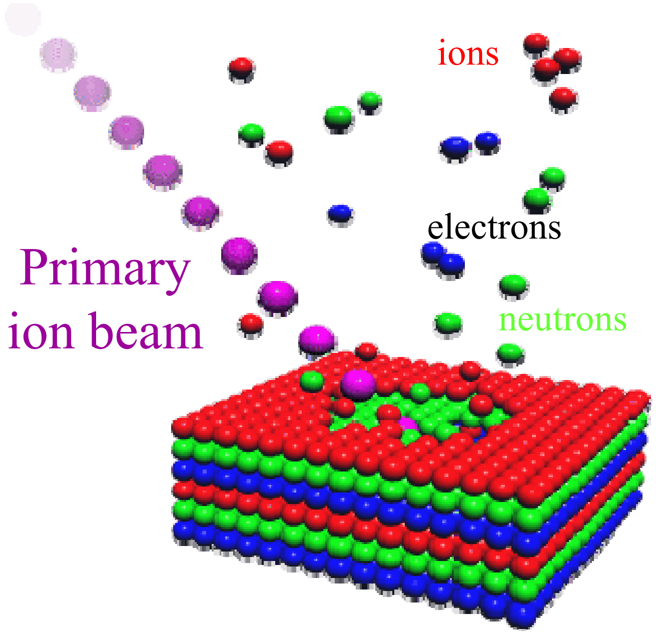
Nano Characterization-Electron Spectroscopy (SIMS)

❑ SIMS (Secondary Ion Mass Spectroscopy)

- Origin of SIMS

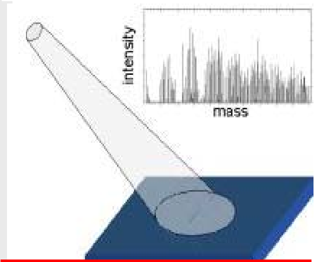
Bombardment of a sample surface with a primary ion beam followed by mass spectrometry of the emitted secondary ions constitutes secondary ion mass spectrometry

- Advantage
  - ❑ Ability to detect hydrogen
  - ❑ Ability to distinguish isotope
  - ❑ High sensitivity-ppm, ppb
  - ❑ Good depth resolution and high dynamic range
  - ❑ Rapid collection of mass spectra
  - ❑ Rapid element and molecular mapping capability
- Disadvantage
  - ❑ Destructive
  - ❑ Not quantitative for non-dilute system

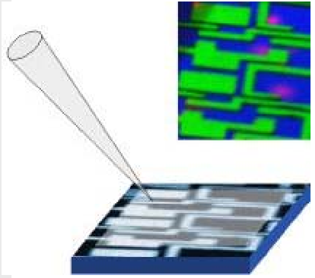


Nano Characterization-Electron Spectroscopy (SIMS)

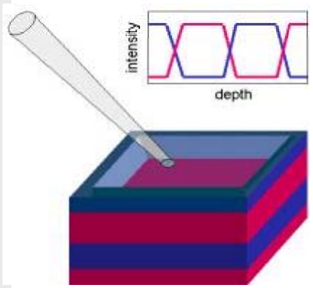
Surface Spectroscopy



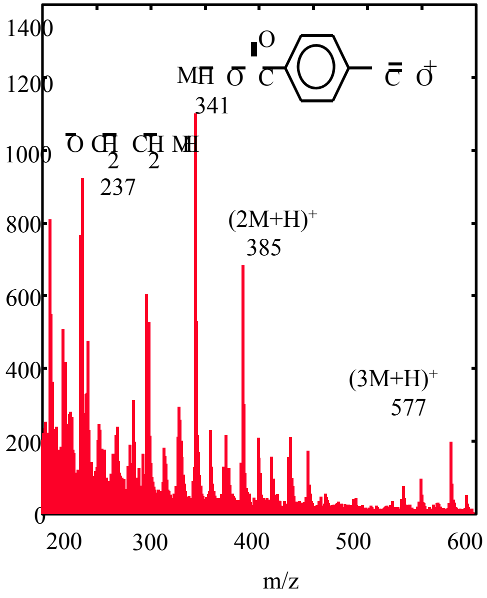
Surface Imaging



Depth Profiling



Mass Spectrum

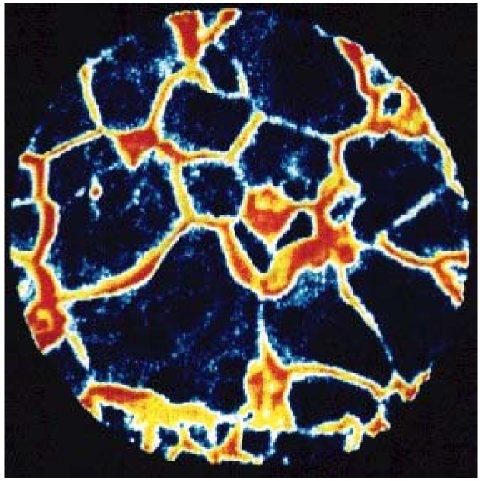


Surface Spectroscopy (static SIMS) : Mass resolution

Application of very low primary ion dose densities

=> quasi non-destructive surface analysis

Image



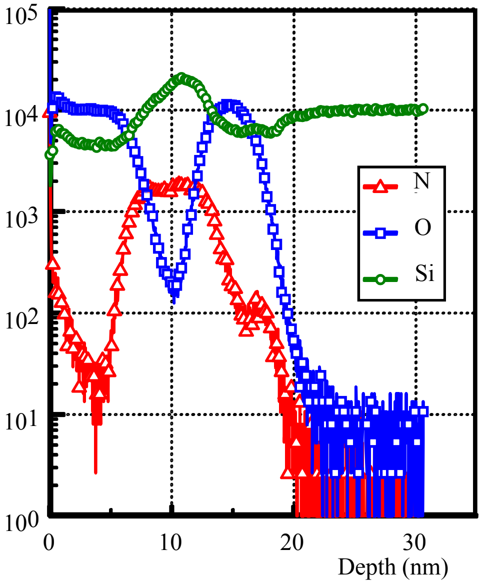
^{18}O mapping in NiO

Surface Imaging : lateral resolution

Rastering of a finely focused ion beam over the surface

=> mass resolved secondary ion images (chemical maps)

Depth profile



Depth Profiling (dynamic SIMS) : depth resolution

Application of high primary ion dose densities

=> successive removal of top surface layers

=>elemental in-depth distribution

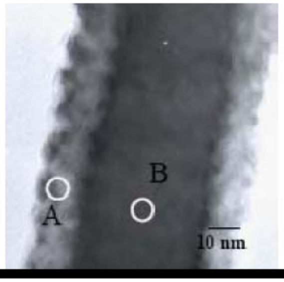
Nano Characterization-Electron Spectroscopy (EDS)

❑ Energy Dispersive Spectroscopy (EDS)

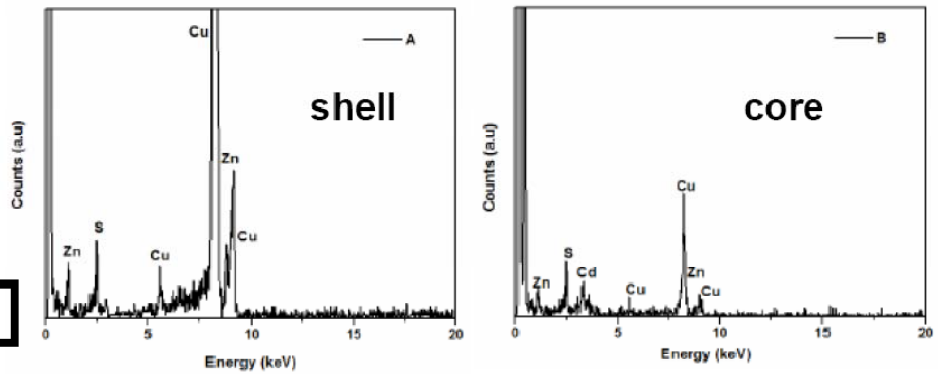
Probes samples with electron beam and results in emission of X-rays with energies characteristic of the elements present in the sample.

Composition of particles in nm (combine with TEM, <1 μm if with SEM) range can be examined due to the use of electron beam. Probe depth is about 1 μm. Detection limit of 0.1% for Z (atomic number) >11.

Maps (composition as a function of position) of a particle -> quantify chemical homogeneity of multicomponent particles.



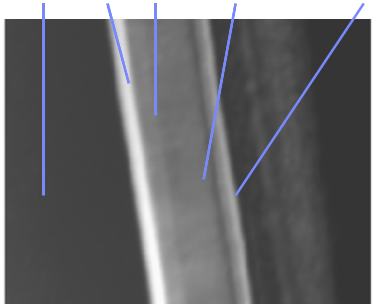
core-shell CdS-ZnS nanowire

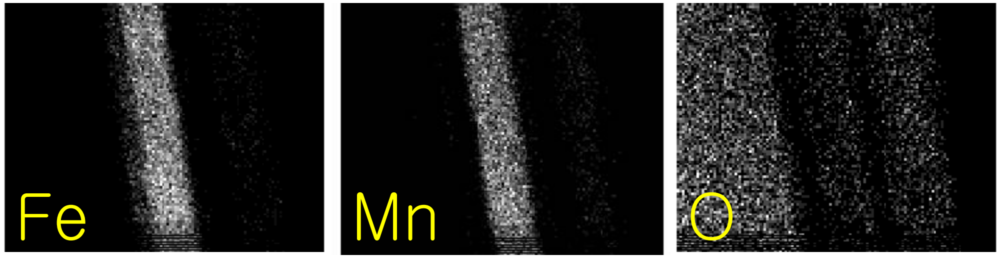


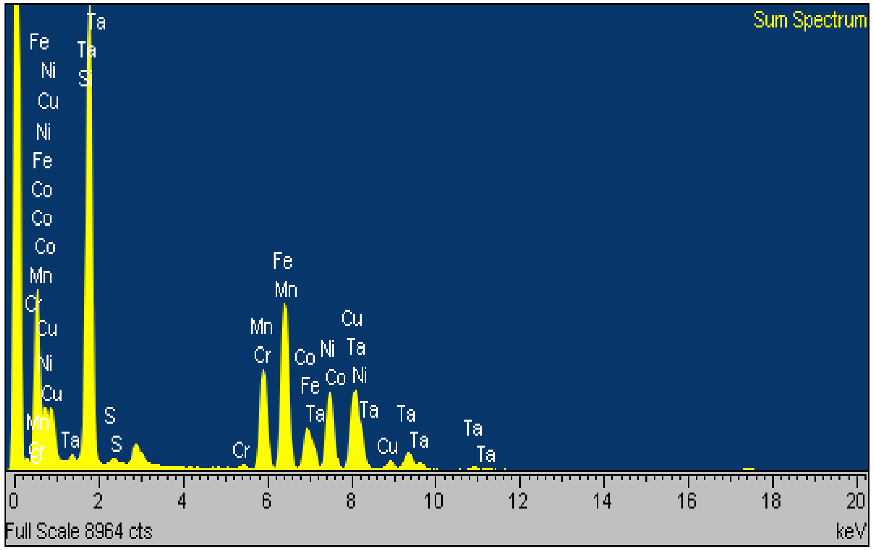
Hsu & Lu, Chem. Comm., **18**, 2102, 2004

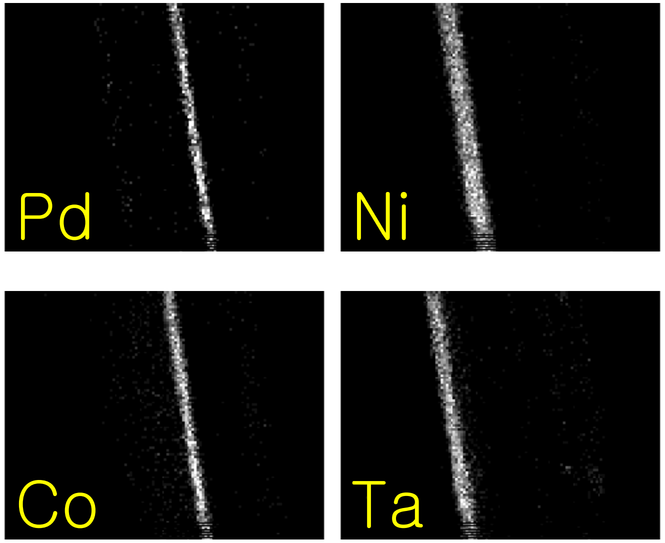
Nano Characterization-Electron Spectroscopy (EDS)

SiO2/Ta/Ni-Fe/Fe-Mn/Co/Pd









Nano Characterization-Electron Spectroscopy

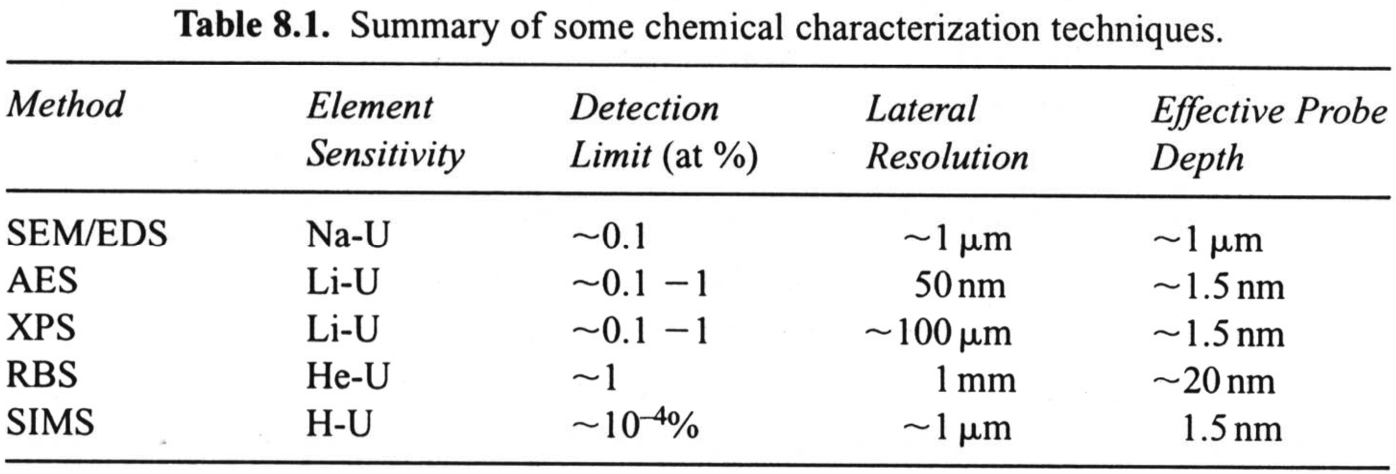


Table 8.1. Summary of some chemical characterization techniques.

Method	*Element Sensitivity*	*Detection Limit* (at %)	*Lateral Resolution*	*Effective Probe Depth*
SEM/EDS	Na-U	~0.1	~1 μm	~1 μm
AES	Li-U	~0.1 −1	50 nm	~1.5 nm
XPS	Li-U	~0.1 −1	~100 μm	~1.5 nm
RBS	He-U	~1	1 mm	~20 nm
SIMS	H-U	$\sim 10^{-4}\%$	~1 μm	1.5 nm