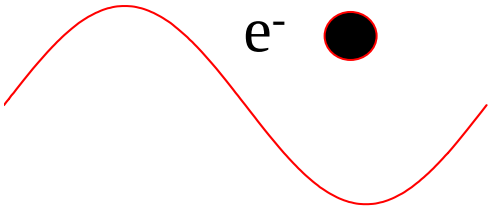
Natures of electrons



- **Wave Behaviours**
  - **images and diffraction patterns**
  - **wavelength can be tuned by energies**
- **Charged Particle Behaviours**
  - **strong electron-specimen interactions**
  - **chemical analysis is possible**

Electron microscopy and microanalysis: aims and means

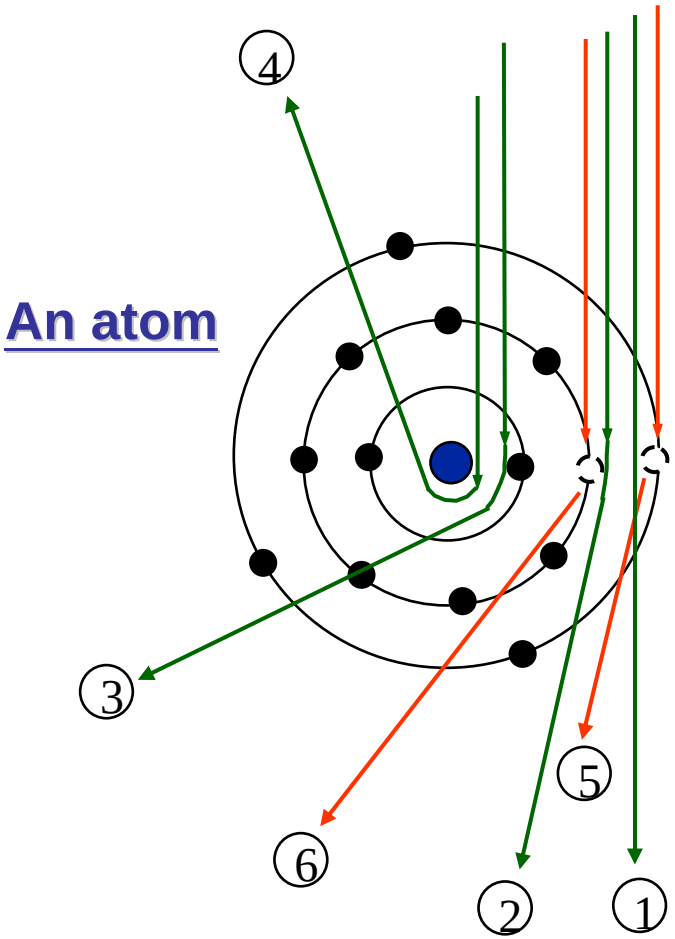
- **Microscopies: morphologies in small scales (micrometer or nanometer)**

  Optical microscopy, Electron microscopy, Ion microscopy, Scanning probe microscopy….., offer images only.

- **Microanalyses: composition and/or structures in small scales (micrometer or nanometer)**

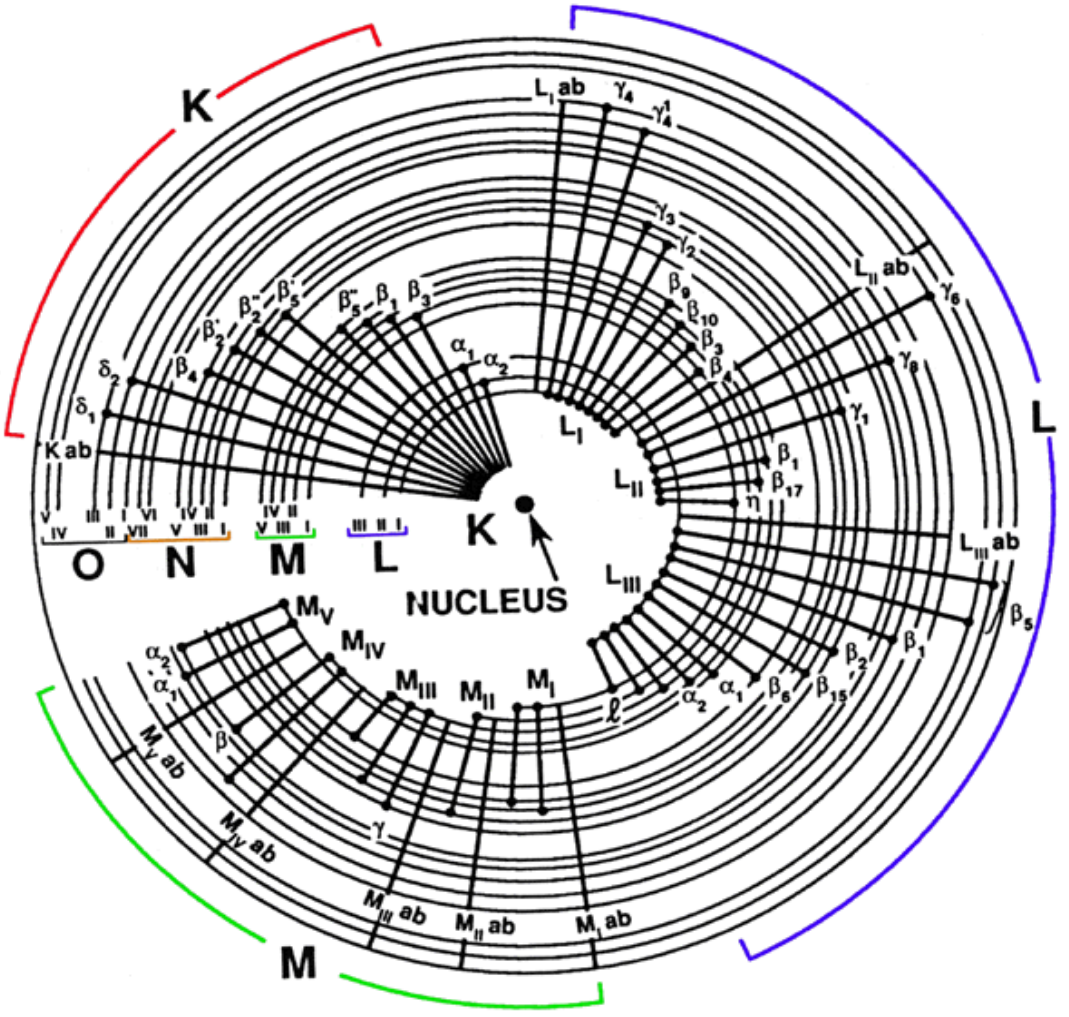
  Energy Dispersive Spectroscopy, Wave-length Dispersive Spectroscopy, Electron Energy Loss Spectroscopy, Auger Electron Spectroscopy, Convergent Beam Electron Diffraction, Select Area Diffraction….., offer spectra and/or diffraction patterns

Interaction of high energy (~kV) electrons with an atom



1. Unscattered
2. Low angle elastically scattered
3. High angle elastically scattered
4. Back scattered
5. Outer shell inelastically scattered
6. Inner shell inelastically scattered

Interaction of high energy (~kV) electrons with (solid) materials-I, cont.



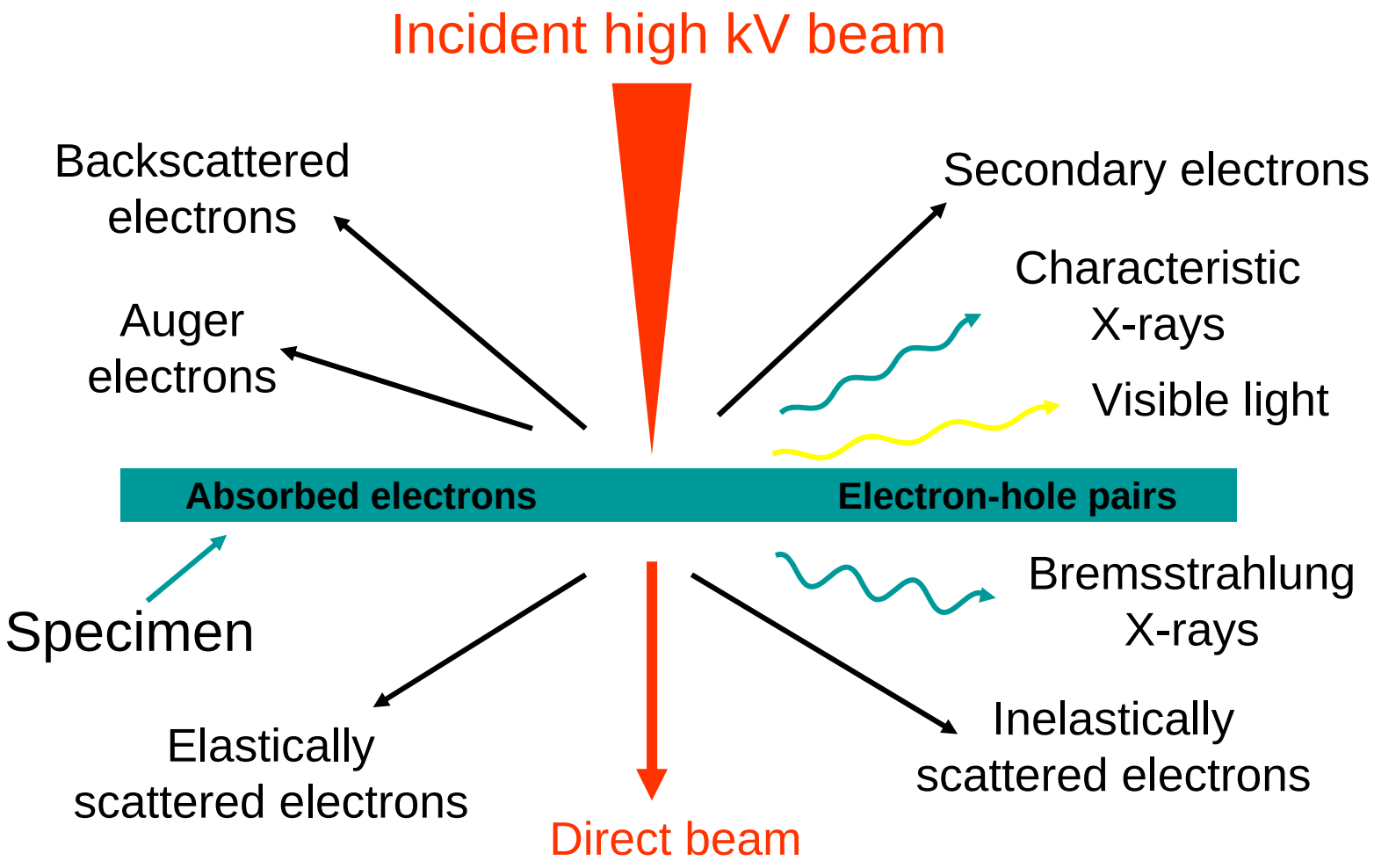
K lines

K α , L → K
K β , M → K

L lines

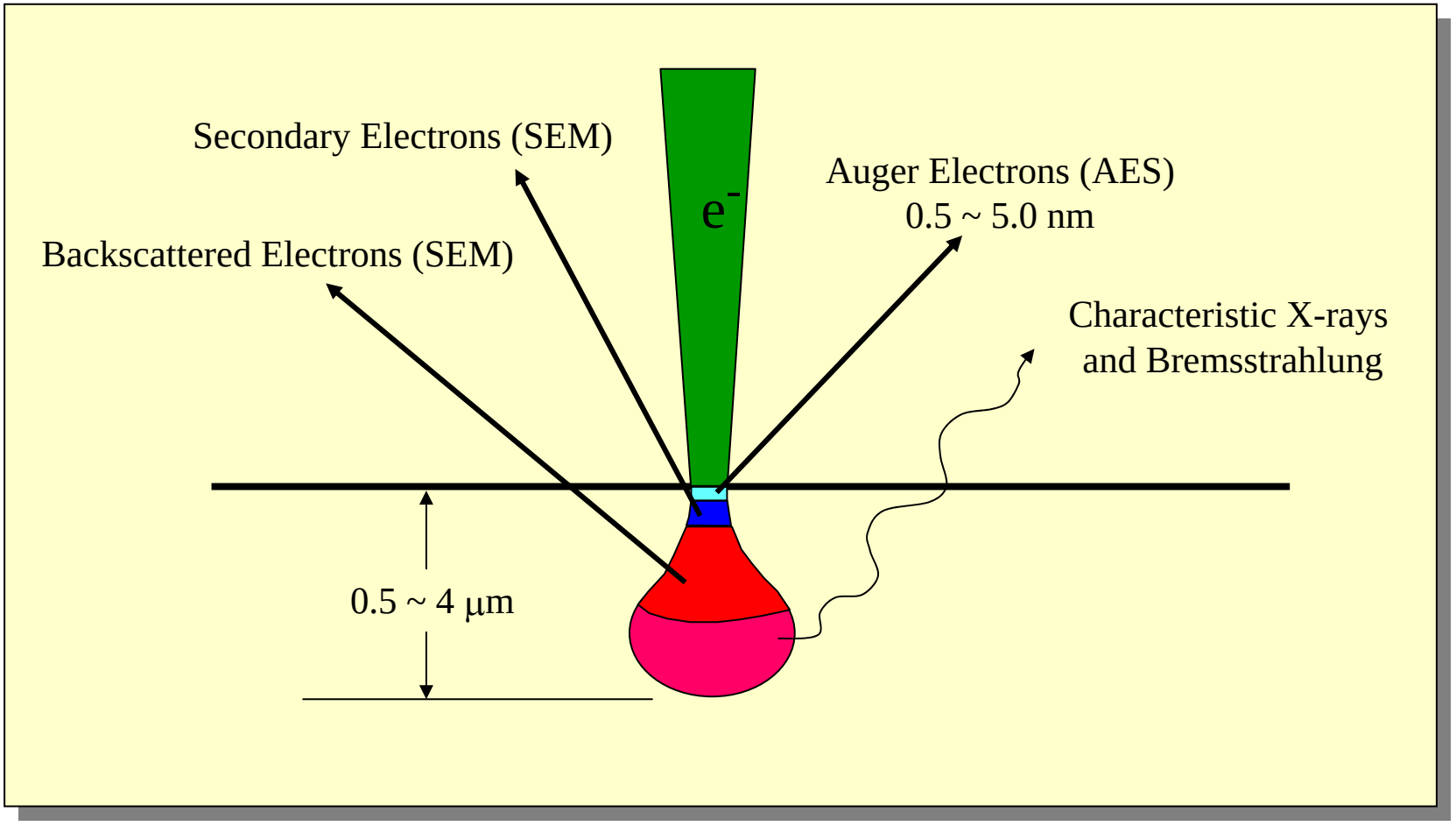
L α , M→L,
L β , N →L,
L γ , O →L

Interaction of electron beam with solid

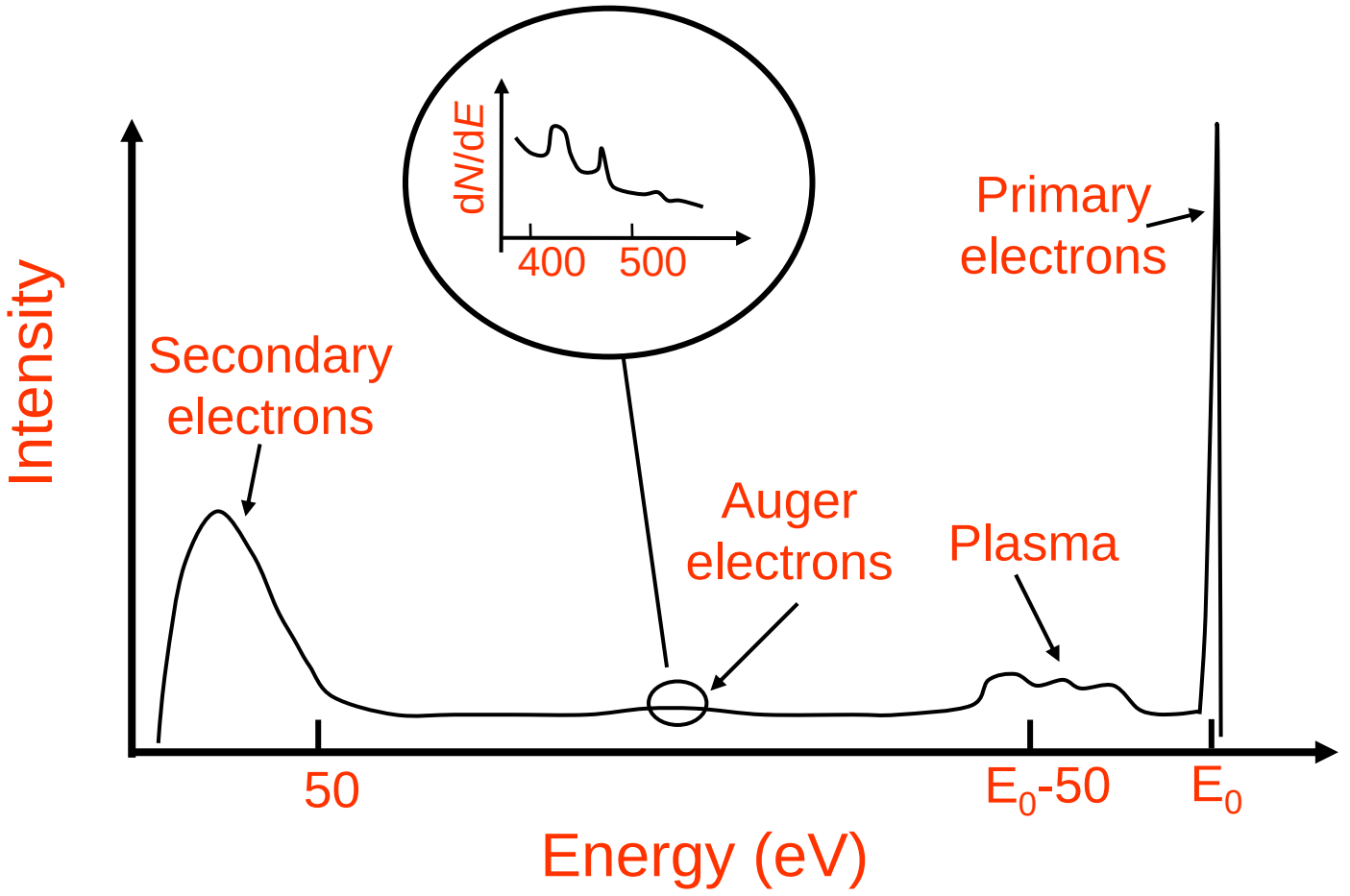


Interaction of high energy (~kV) electrons with (solid) materials-III

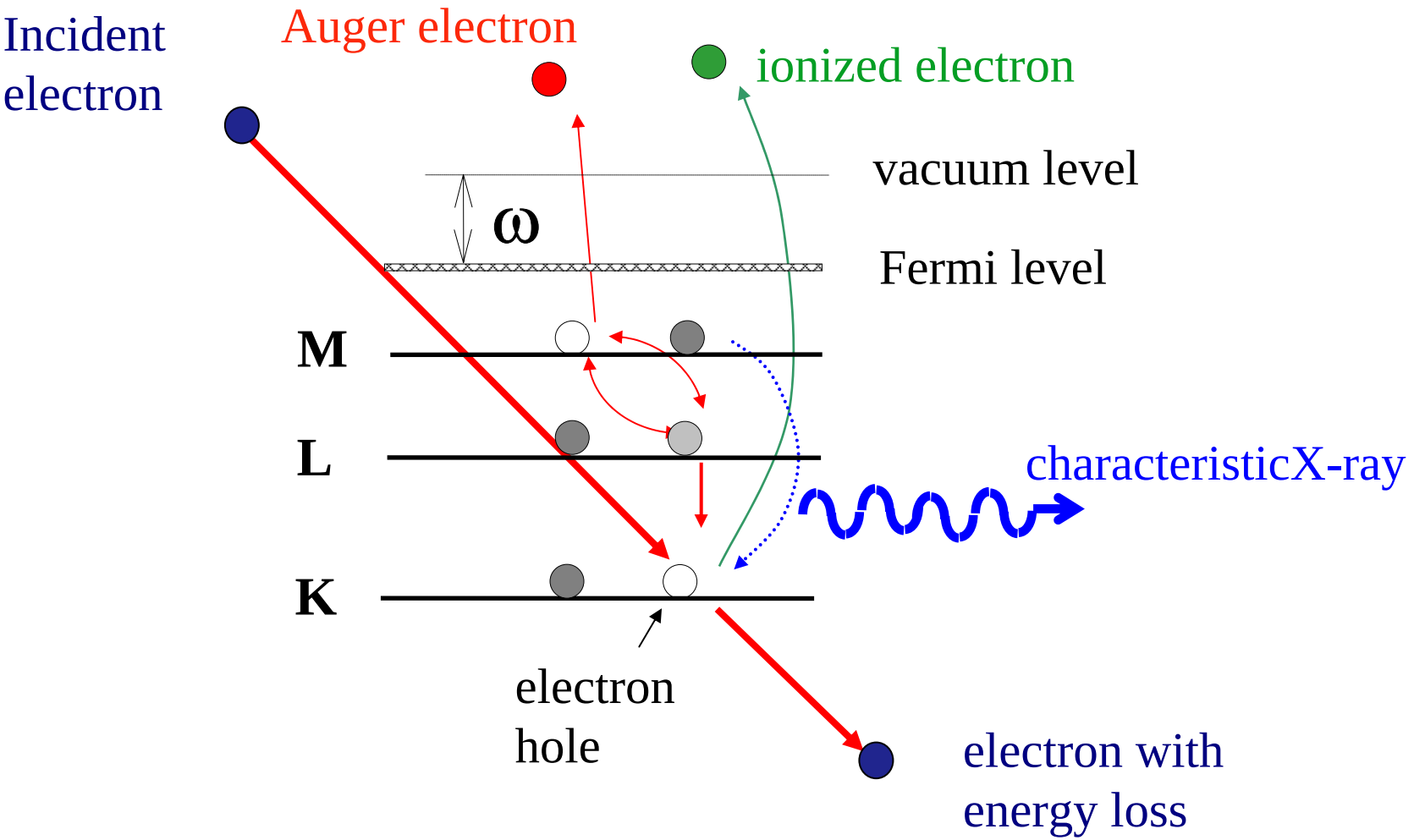
Interaction with a thick specimen (SEM)



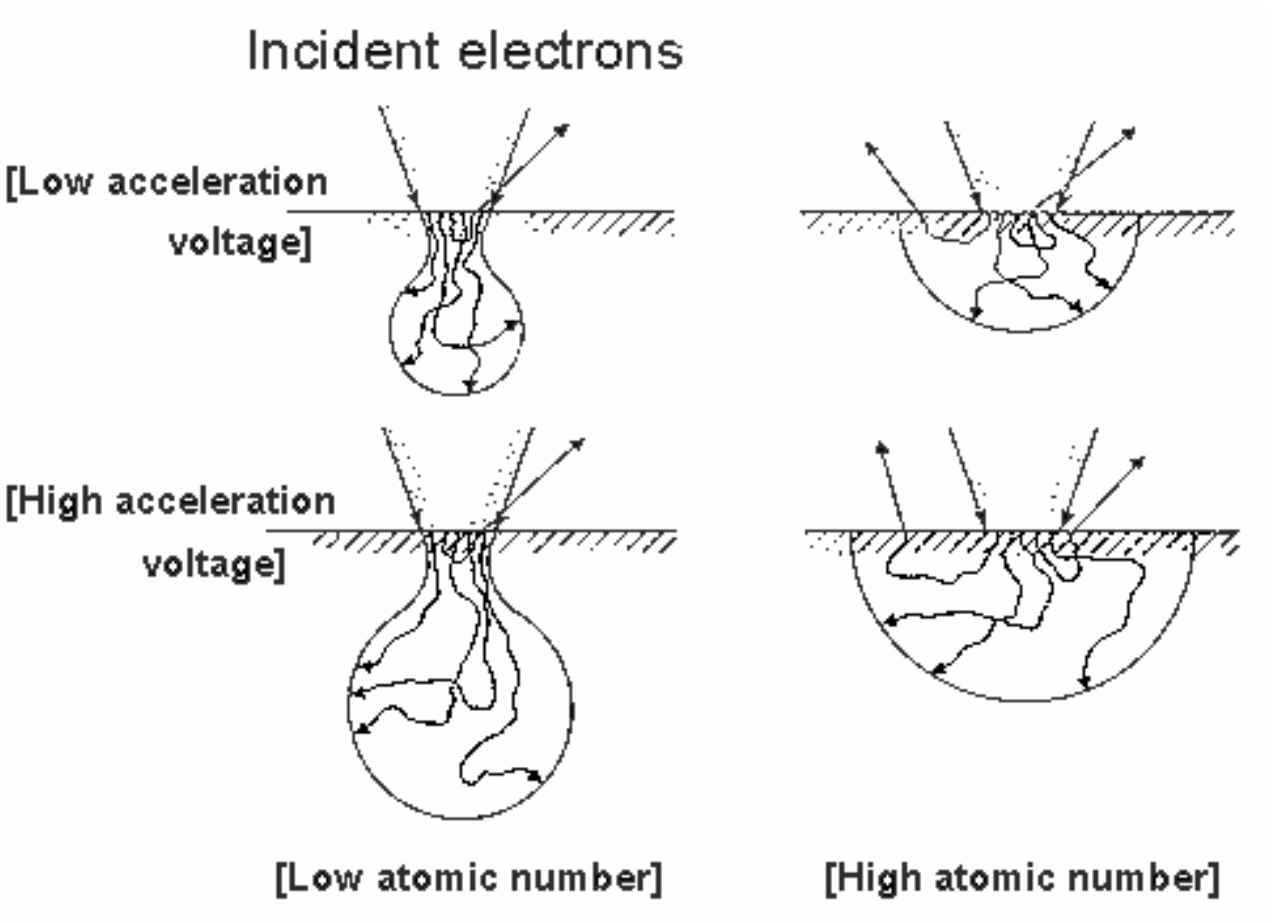
Energy distribution of detected electrons



Interaction of high energy (~kV) electrons with (solid) materials-I, cont.



Penetration power of e-beam



Electron Source

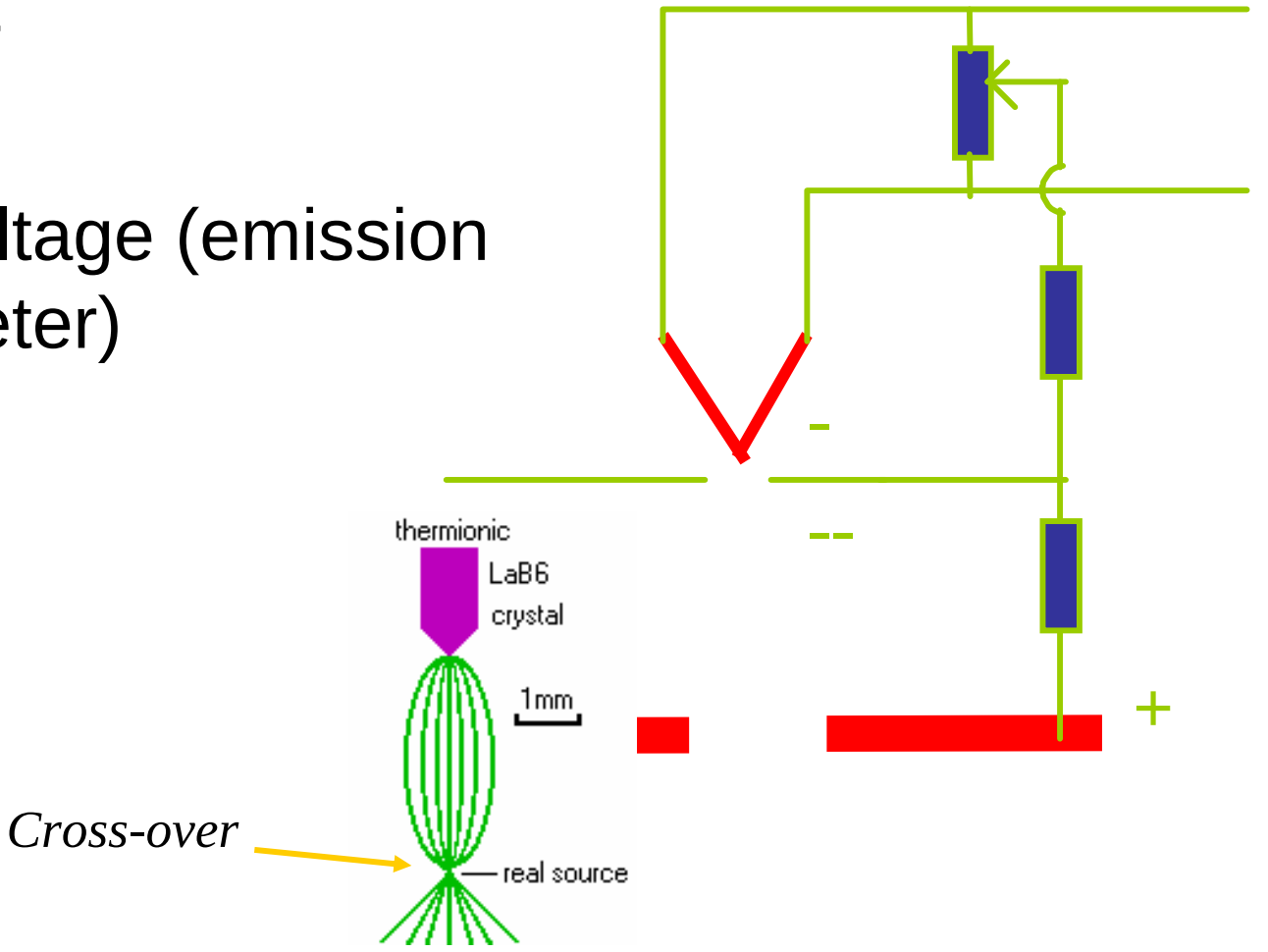
- Generation of electrons that can be accelerated by high tension to obtain the illuminating electron beam

Electron Source

- Thermionic Gun
  - triode or self-biasing gun
  - W, LaB_6, CeB_6
- Field Emission Gun
  - single crystal W
  - single atom tip

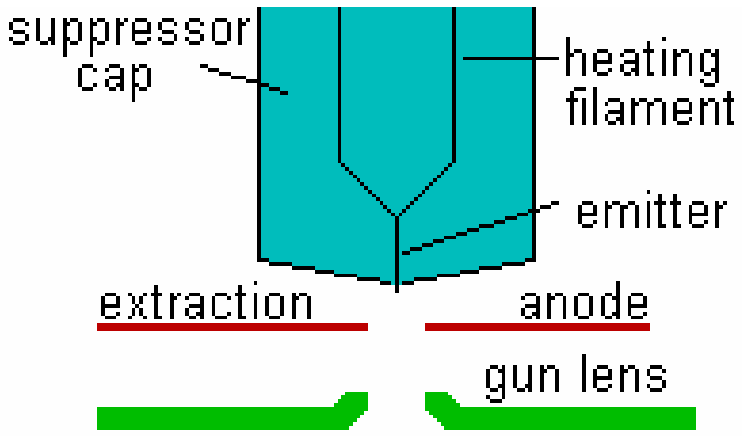
Electron Source
Thermionic Gun

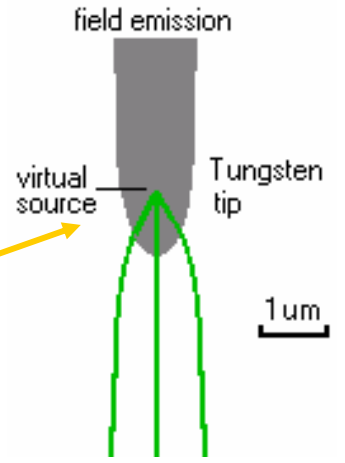
- Filament
- Wehnelt
  - bias voltage (emission parameter)
- Anode



Electron Source
Field Emission Gun (FEG)

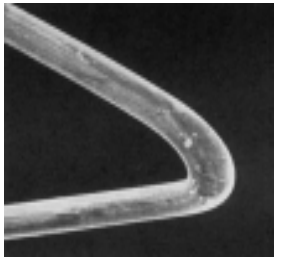
- Heating Filament
- Single Crystal Emitter
- Suppressor Cap
- Extraction Anode
- Electrostatic lens

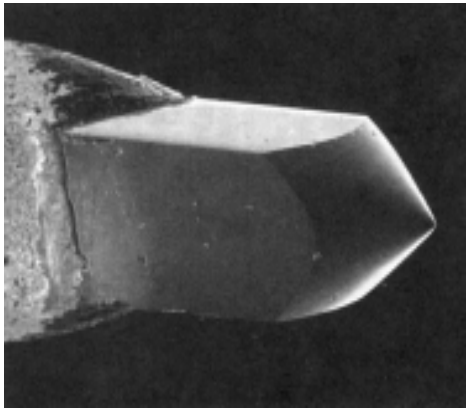




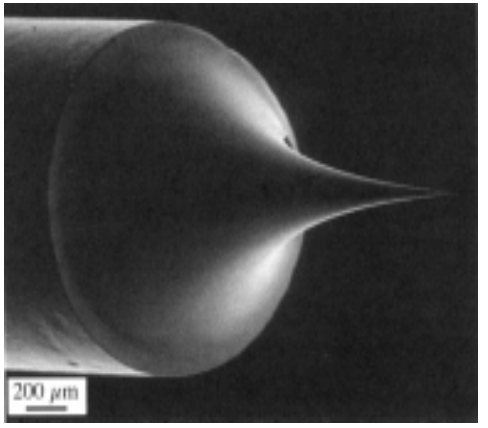
Electron seemingly originating from tip itself

W hairpin





LaB_6



W tip

Comparison of Electron Sources

	W	**LaB_6**	**FEG (Schottky)**
Maximum Current (nA)	1000	500	300
Normalised Brightness (-)	1	10-30	2500
Energy spread (eV)	3-4	1.5-3	0.6-1.2
Source spotsize	30-100 μm	5-50 μm	15-30 nm
Required Vacuum (Pa)	10^{-3}	10^{-5}	10^{-7}
Temperature (K)	2700	2000	1800
Life time (hr)	60-200	1000	>2000
Normalised Price (-)	1	10	100

Traditional Methods for Preparation of Single-Atom Tips

1. Tedious and unreliable.
2. Require very high electric fields, high temperatures, and high technical skills.
3. Require special equipments (FIM or FEM) to monitor the tip condition *in situ*.
4. Short lifetime for SAT --- not thermally or chemically stable.
5. No well-defined structure for SAT.

These problems seriously limit the applications of single-atom tips!

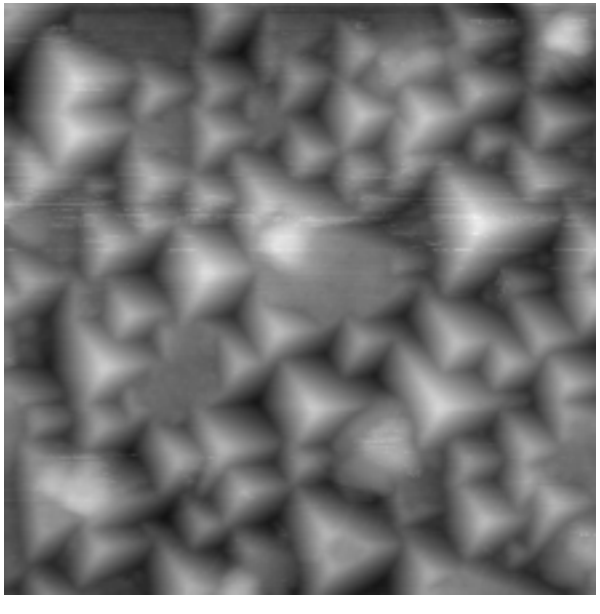
Adsorbate-Induced Faceting

1. One physical monolayer (1 PML) of Pd, Pt, Au, Ir, or Rh film grown on the clean W(111) surface can form three-sided pyramids with {211} facets upon annealing. (Madey et al.) Song, Madey, et al. *Surf. Sci. Lett.* **227**, L79 (1990); *Langmuir* **7**, 3019 (1991); Madey et al. *Surf. Rev. Lett.* **3**, 1315 (1996).

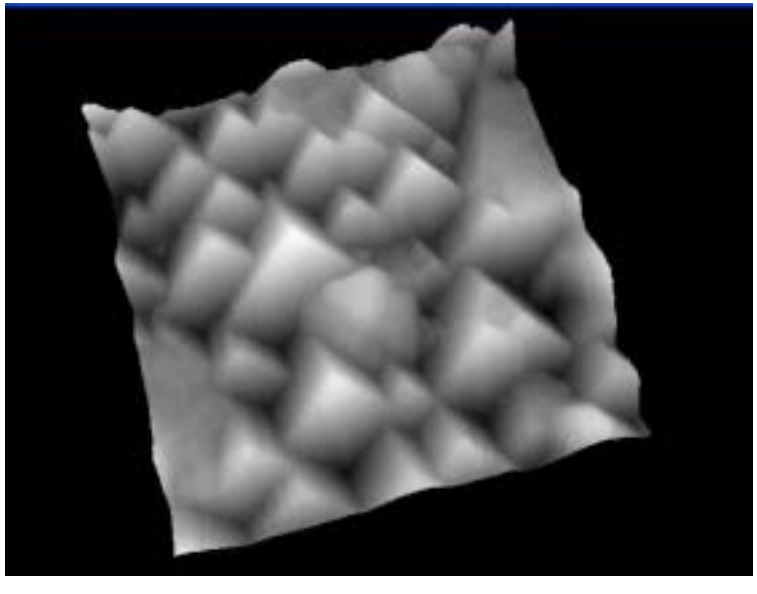
2. The thermodynamic driving force is due to the increase of the surface energy anisotropy as the metal films are adsorbed on the W(111) surface.

Pd/W(111) Nano-Pyramids

120 nm ⨯ 120 nm



80 nm ⨯ 80 nm

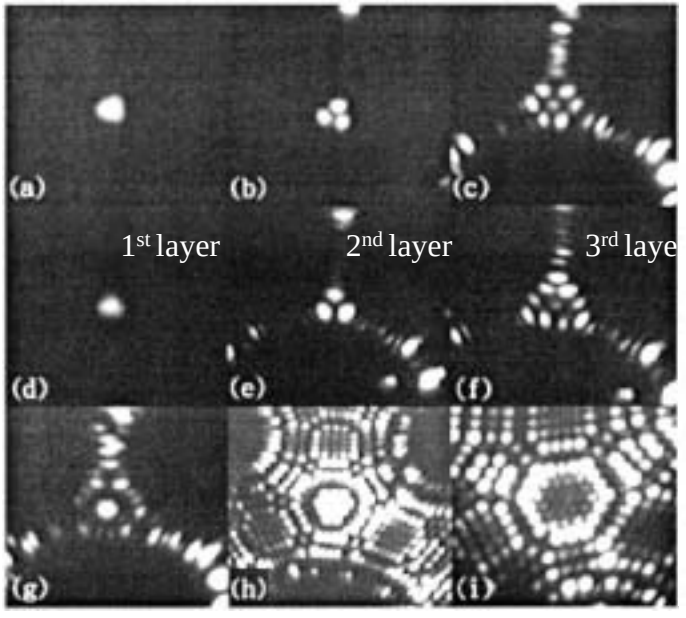


Noble Metal-Covered W(111) Single-Atom Tips

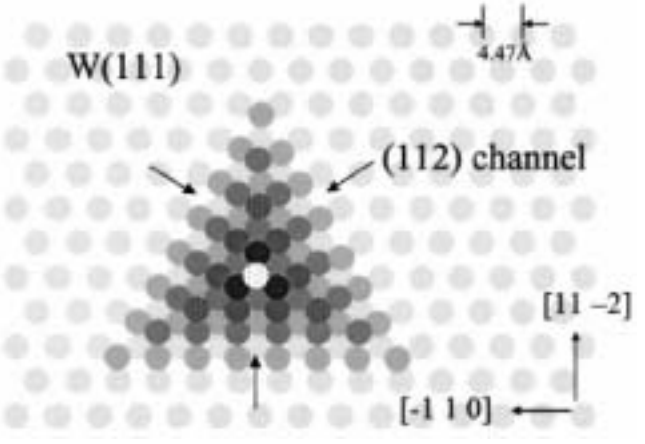
1. **Thermally and chemically stable.**
2. **The single-atom tip can be regenerated if damaged or contaminated.**
3. **A well-defined structure after each regeneration.**
4. **Long lifetime.**

Field Ion Microscopy (FIM)

Regeneration



Fu, Cheng, Nien, Tsong,
Phys. Rev. B 64, 113401 (2001).



New Method for Preparation of Single-Atom Tips

single crystal W <111> tip

Cover the tip with a nail polish

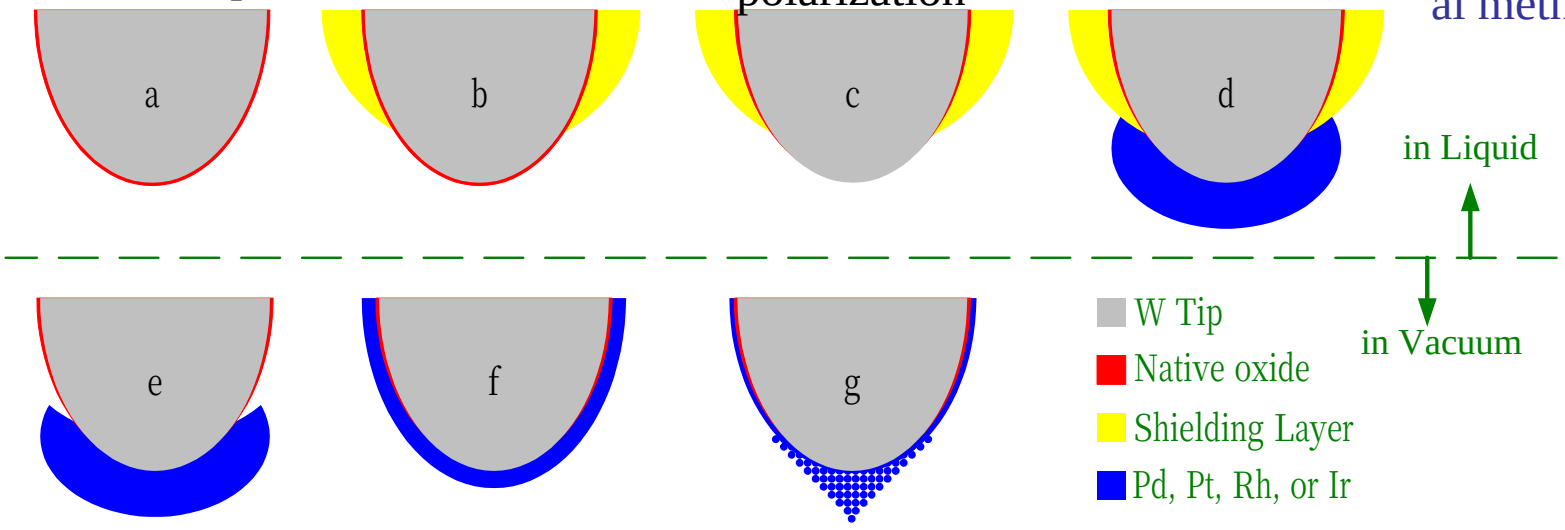
Clean W surface

Reduce the oxide with a cathodic polarization

Metal deposition

Electroplate a noble metal film on the tip

Electrochemical method



Remove the nail polish

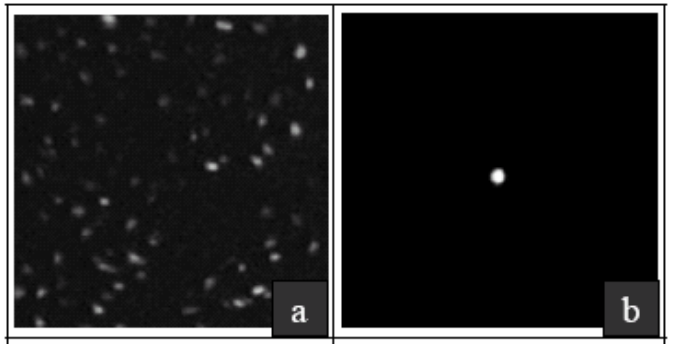
Anneal the tip

Build up of pyramidal single crystal tip

The plated tips can be stored in the ambient condition for many months.

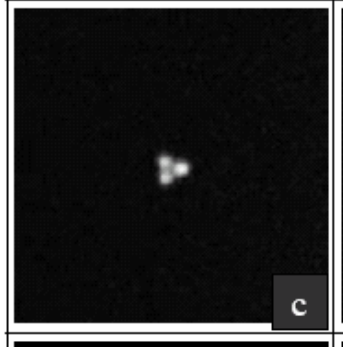
Pt-Covered W(111) Single-Atom Tip

Before annealing

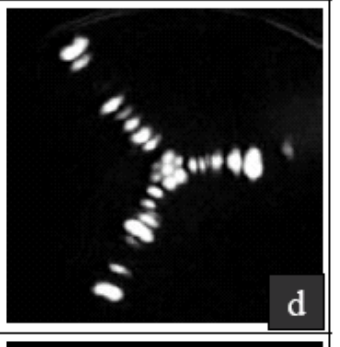


Annealing to 1100 K

Field evaporation

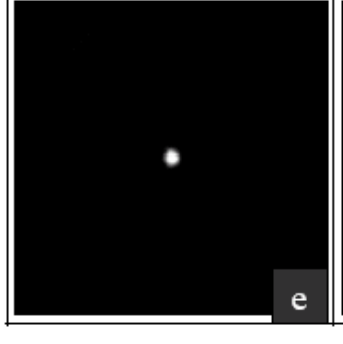


Field evaporation

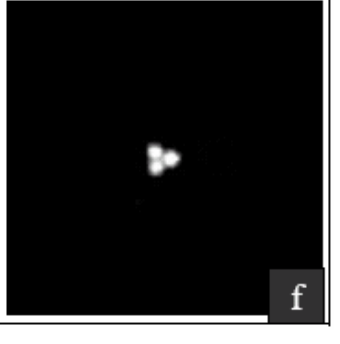


Regeneration

Annealing to 1100 K

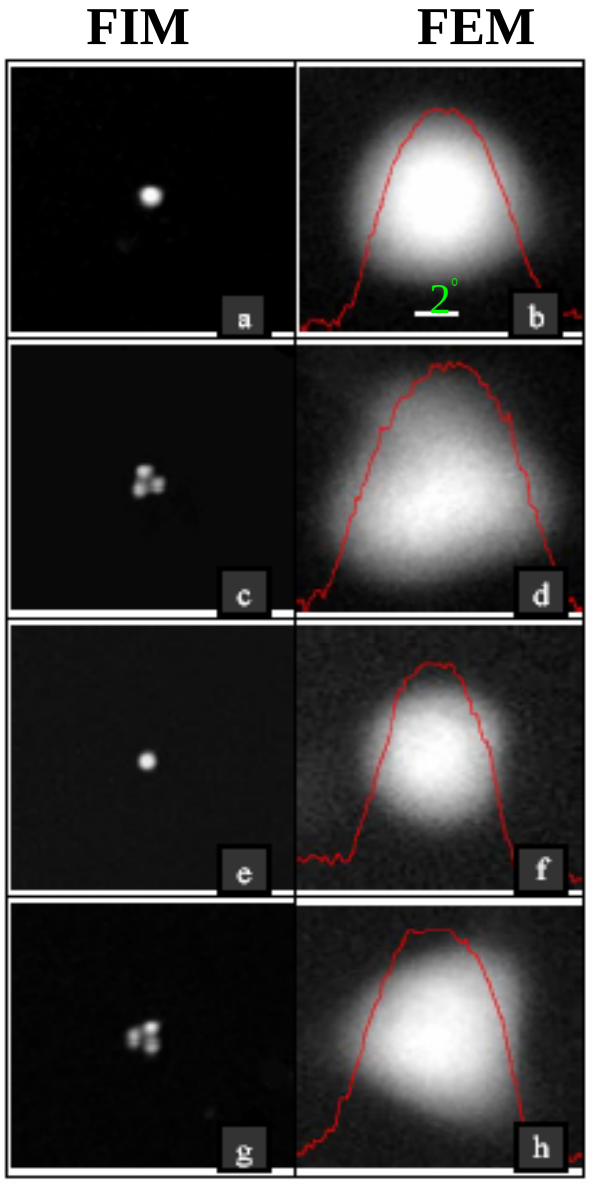


Field evaporation



Other pyramidal single-atom tips : Rh/W(111), Ir/W(111), Au/W(111).

Electron Field Emission Pattern



Pd/W(111)

-1100V

Small opening angle

Pd/W(111) SAT: 6.6°

Pt/W(111) SAT: 5.6°

-1300V

-1300V

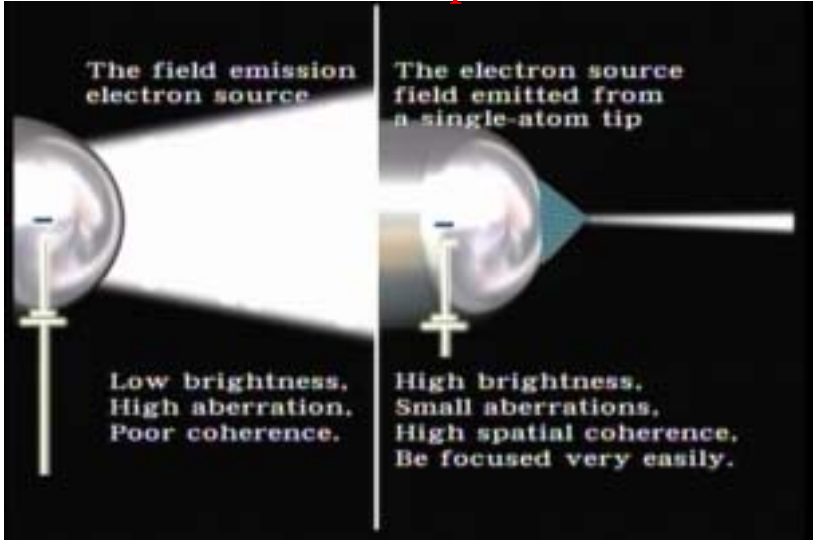
Pt/W(111)

-1500V

Noble Metal/W(111) Pyramidal Single-Atom Tips

Traditional

Ideal electron point source



Traditional

Ideal ion point source

Current Field Ion Sources: liquid-metal ion source (LMIS)

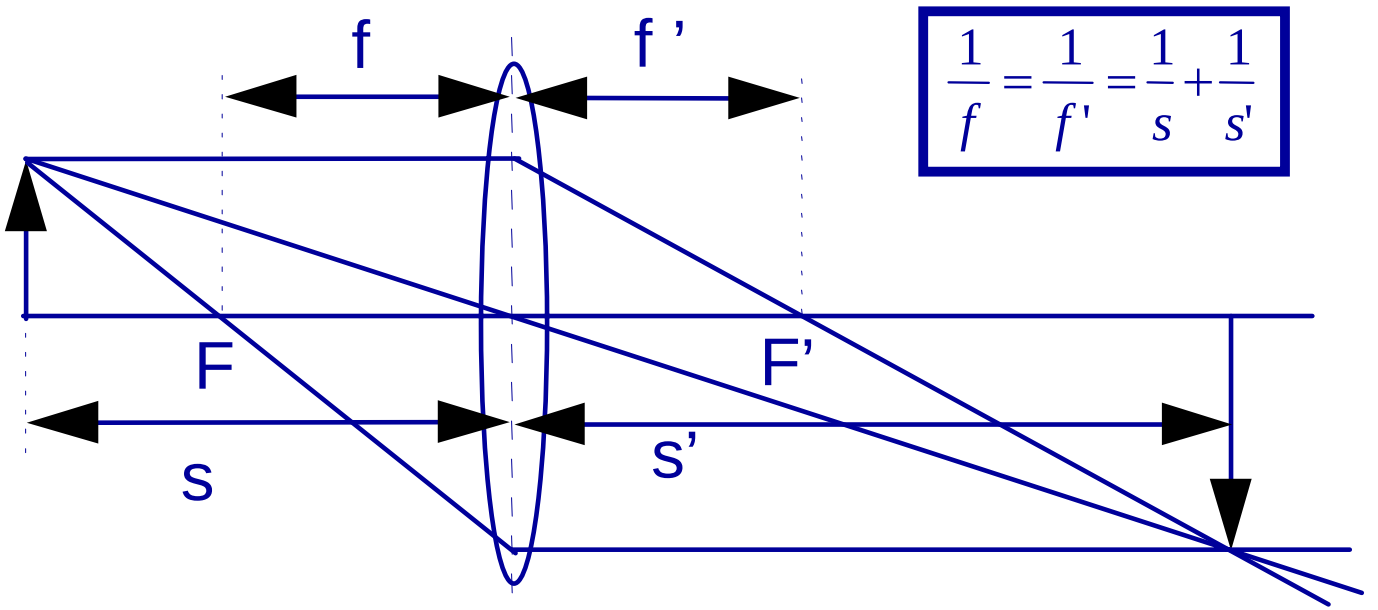
1. Ga^+ ion source: spatial resolution: 10-50 nm.
2. Implantation of Ga^+ ions into samples.
3. Large energy distribution: 5~50 eV, chromatic aberration.
4. Large opening angle: ~30°, spherical aberration.
5. Large virtual source size of LMIS: 50 nm.

New Type of Gas Field Ion Source Emitted from Single-Atom Tips

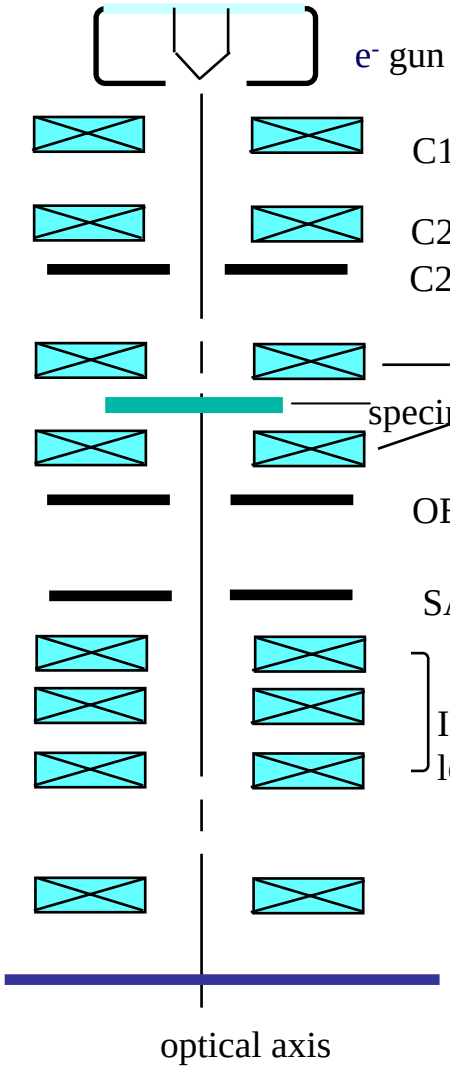
1. Small energy distribution: < 1 eV.
2. Small opening angle: ~1°.
3. Small source size: 0.3 nm.
4. In principle, a highly focused ion beam can be achieved.

Lenses

- Gaussian Law



Lens System of TEM



providing high energy e-

spot and beam control

stopping the undesired e- beams

transmitting and magnifying the first enlarged image or diffraction pattern to projector lens

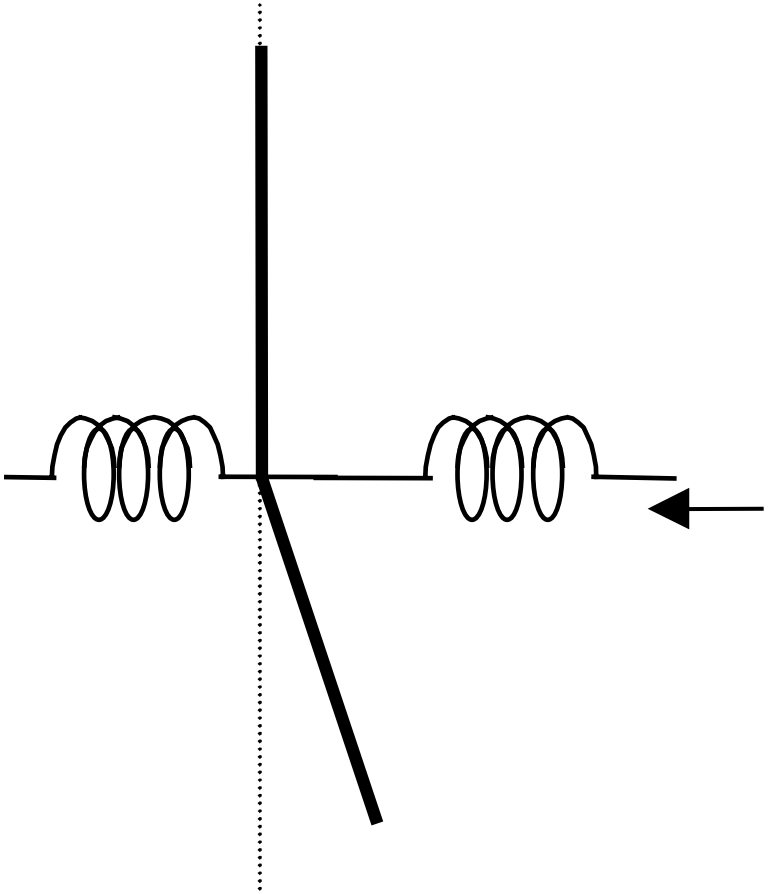
projecting the image or diffraction pattern to the screen

Deflection Coils

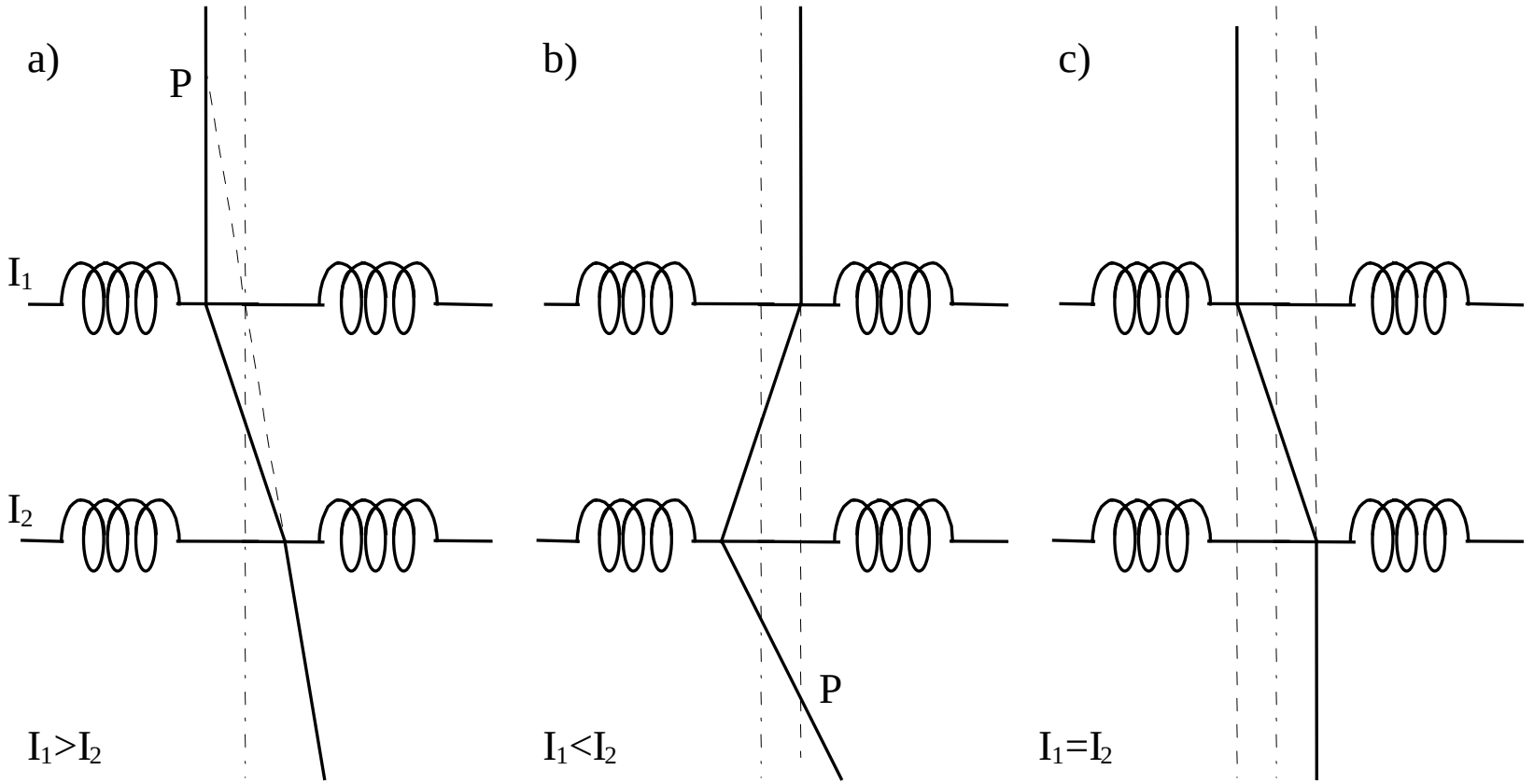
- Provide means to shift or to tilt the electron beam, to correct for mechanical misalignments of the optical system, and to obtain specific imaging effects

Deflection Coils

- Basic Principle
  - Gun coils
  - Beam coils
  - Image coils
  - Scanning coil
  - …….
  - ……



Deflection Coils



Electron Detectors

- TEM
  - phosphor screen, Film, CCD, Image Plate…
- SEM
  - SE detector, BE detector….
- STEM
  - BF detector, DF detector, ……

Attachments for photons or X-rays

WDS:

- Crystal Spectrometers
- detecting the wave-length of characteristic X-rays
- Gas proportional counter is used as the X-ray detector
- Single-Channel Analyzer (SCA)
- Long acquisition time (~ 30 min.)
- High energy resolution (~ 5 eV)

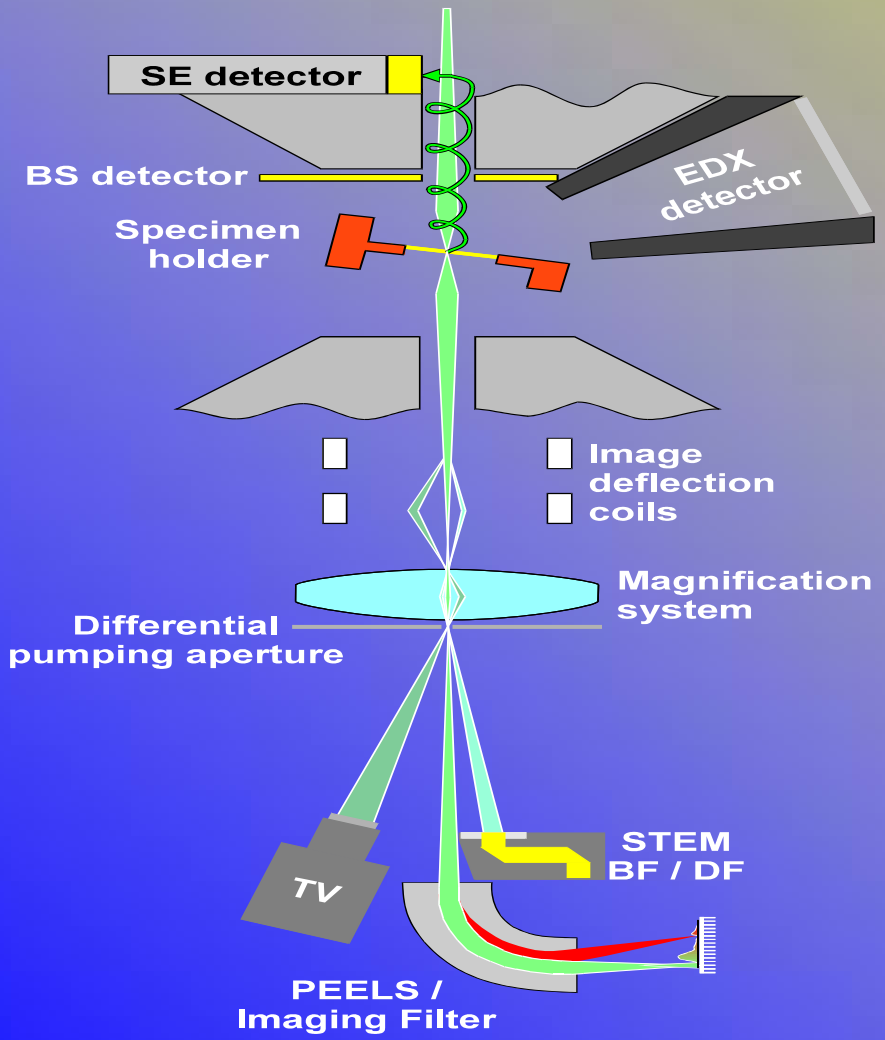
EDS:

- Solid State X-ray Detectors
- detecting the energy of characteristic X-rays
- Si(Li) detector is used as the X-ray detector
- Multi-Channel Analyzer (MCA)
- Short acquisition time (100 ~ 200 s)
- Low energy resolution (133 eV for Mo K_a)

•CL:

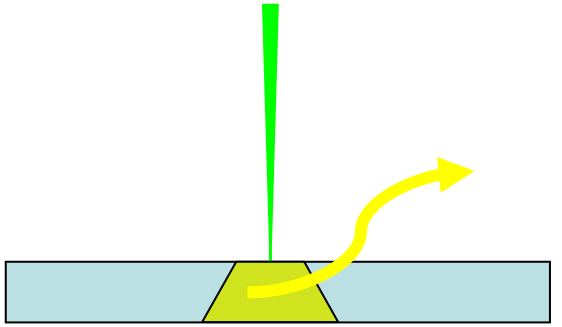
- detecting the photons

Signals and Detectors



- In TEM
  - Energy Filter
  - TV / CCD camera
  - Plate camera
- In STEM
  - BF / DF
  - HAADF
  - BS & SE (SEM)
- In STEM and TEM
  - EDX and PEELS

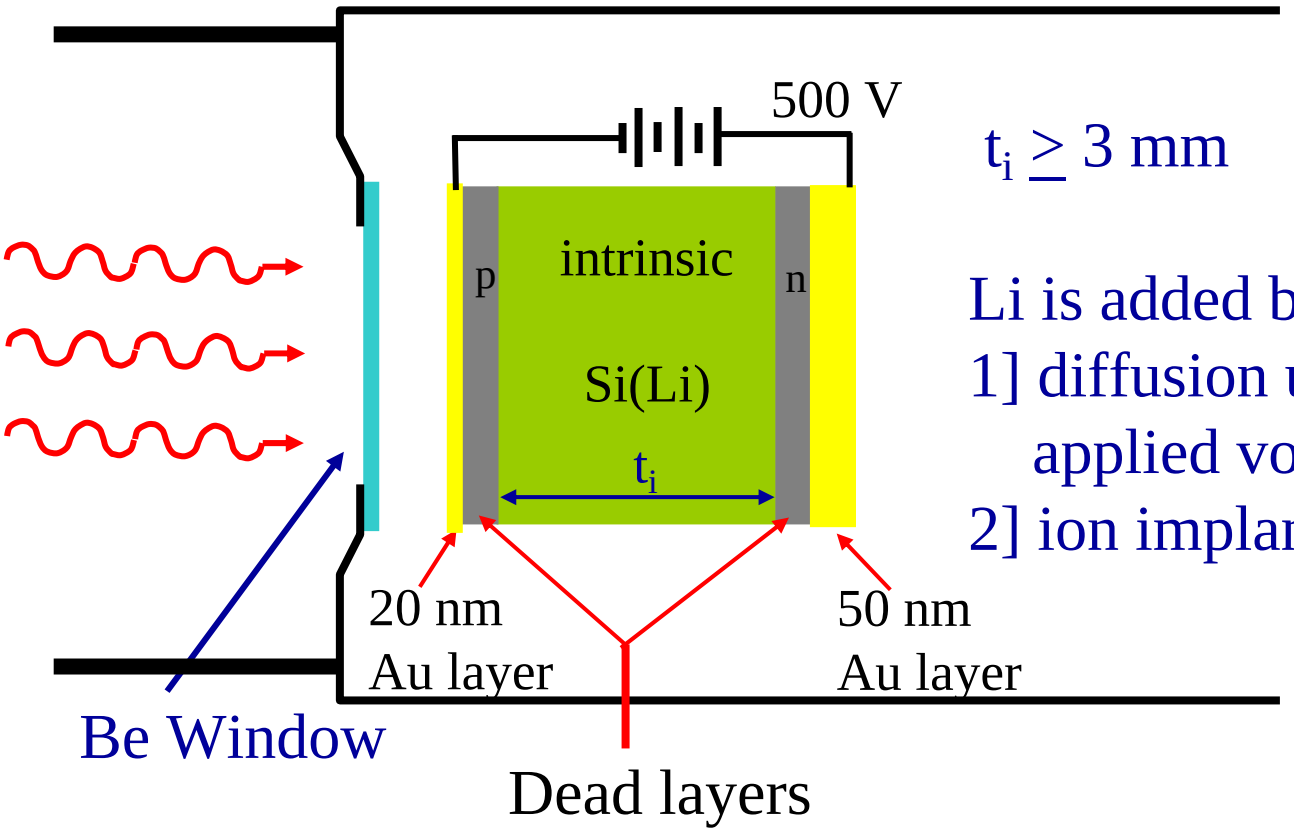
EDS



- Elements analysis
  - Qualitative, or quantitative [$Z \geq 5(B)$]
- Elemental mapping
- Spatial resolution (volume of X-ray generation) ≥ probe size

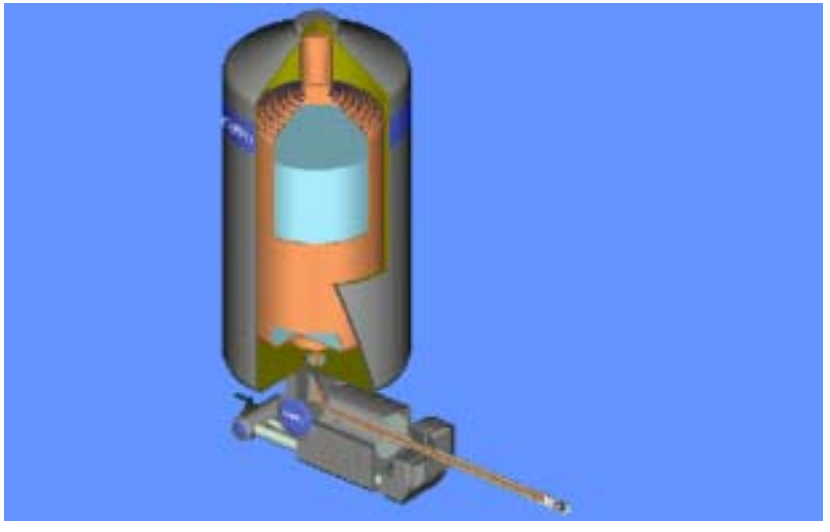
EDS system on TEM

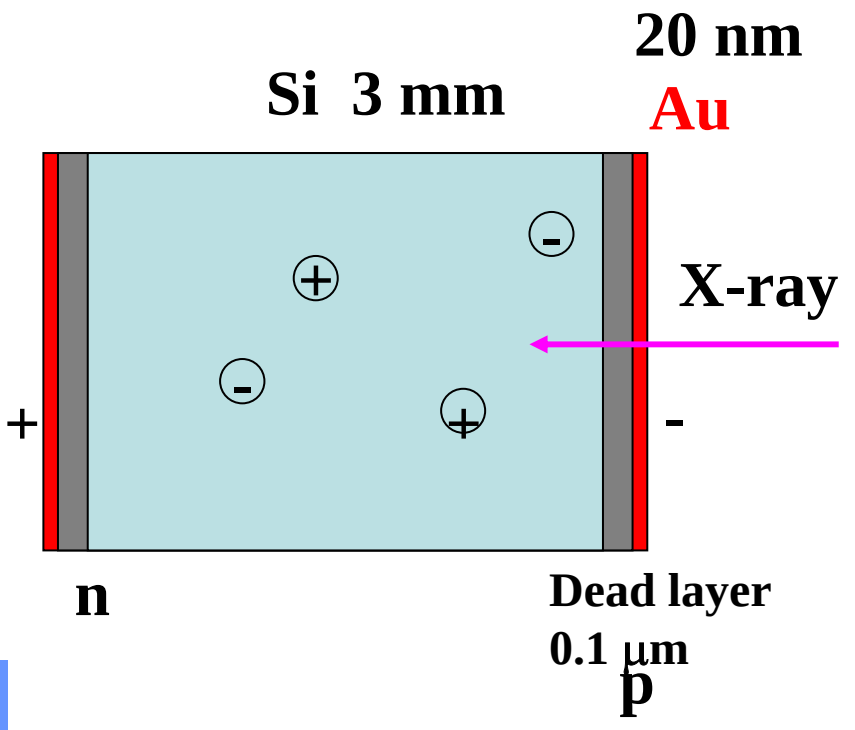
Reverse-biased p-i-n diode

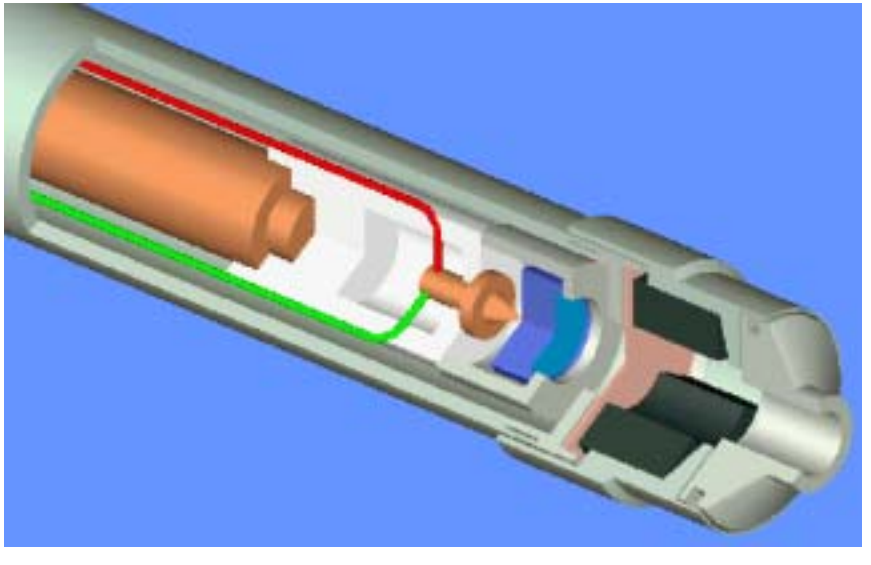


$t_i \geq 3$ mm

Li is added by
1] diffusion under an applied voltage
2] ion implantation/annealing



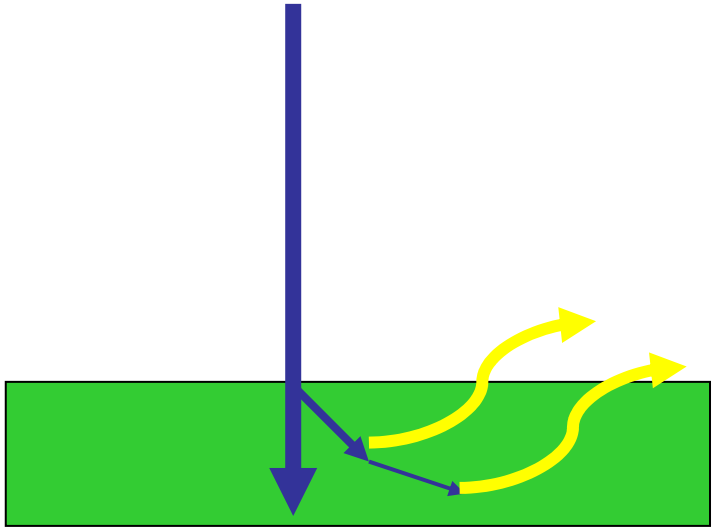




EDS Detector

Spatial Resolution

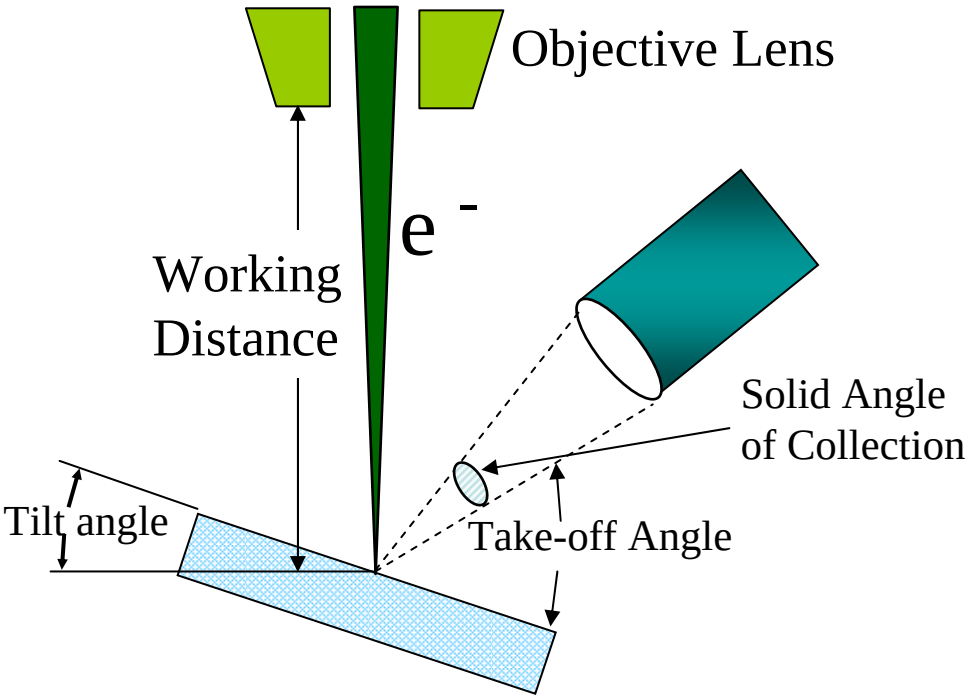
- Beam broadening size $b_{TEM} < b_{SEM}$
- Beam broadening size $b_{EELS} < b_{EDS}$



Factors on Spatial Resolution

- Probe size
- Interaction volume (SEM)
- Specimen thickness (TEM)
- Specimen drift
- Contamination

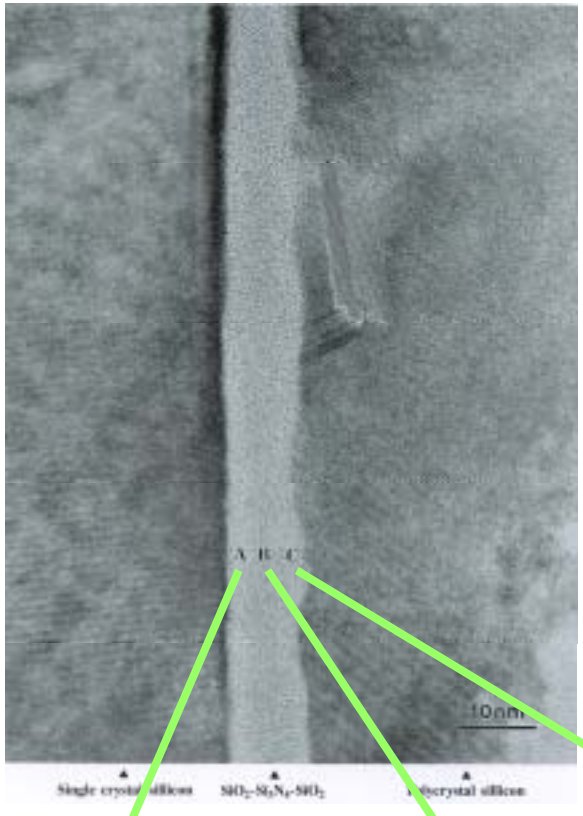
Parameters of EDS Collection

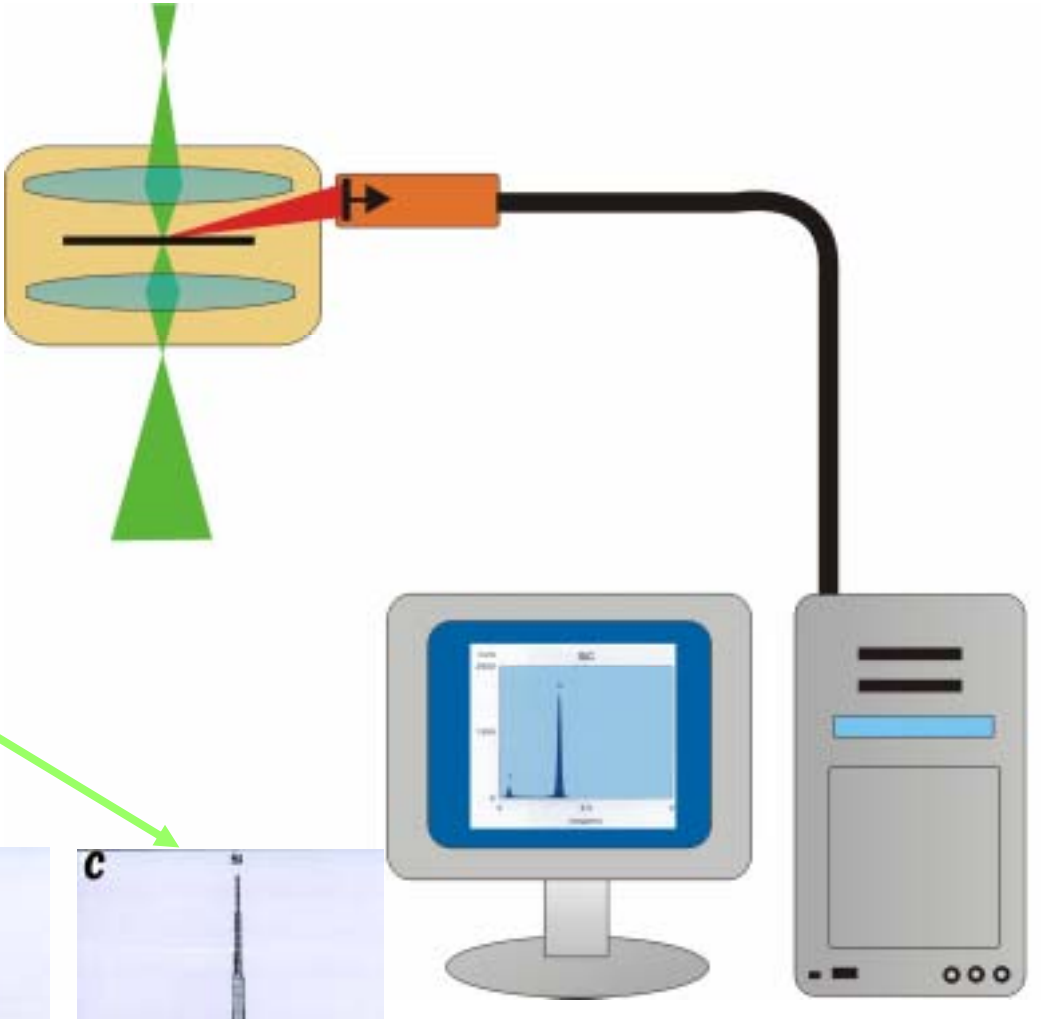


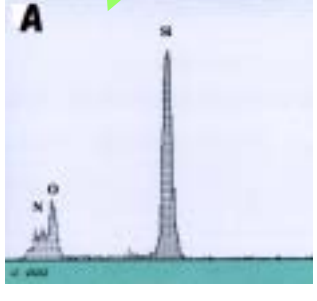
Strengths and Weaknesses of EDS

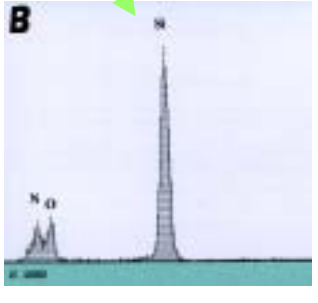
- **Strengths**
  - Quick, ‘first look’ analysis
  - Versatile & inexpensive
  - Quantitative for some samples (flat, polished, homogeneous)
- **Weaknesses**
  - Quantification
  - Size restrictions
  - May spoil subsequent analysis

EDS with spatial resolution

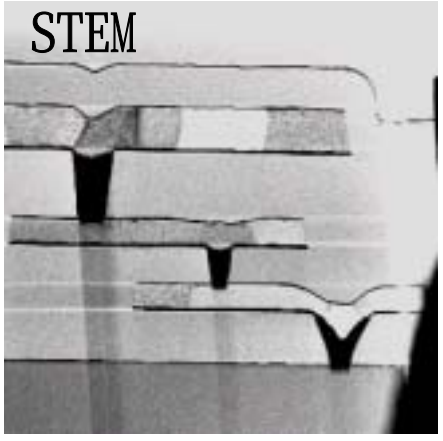


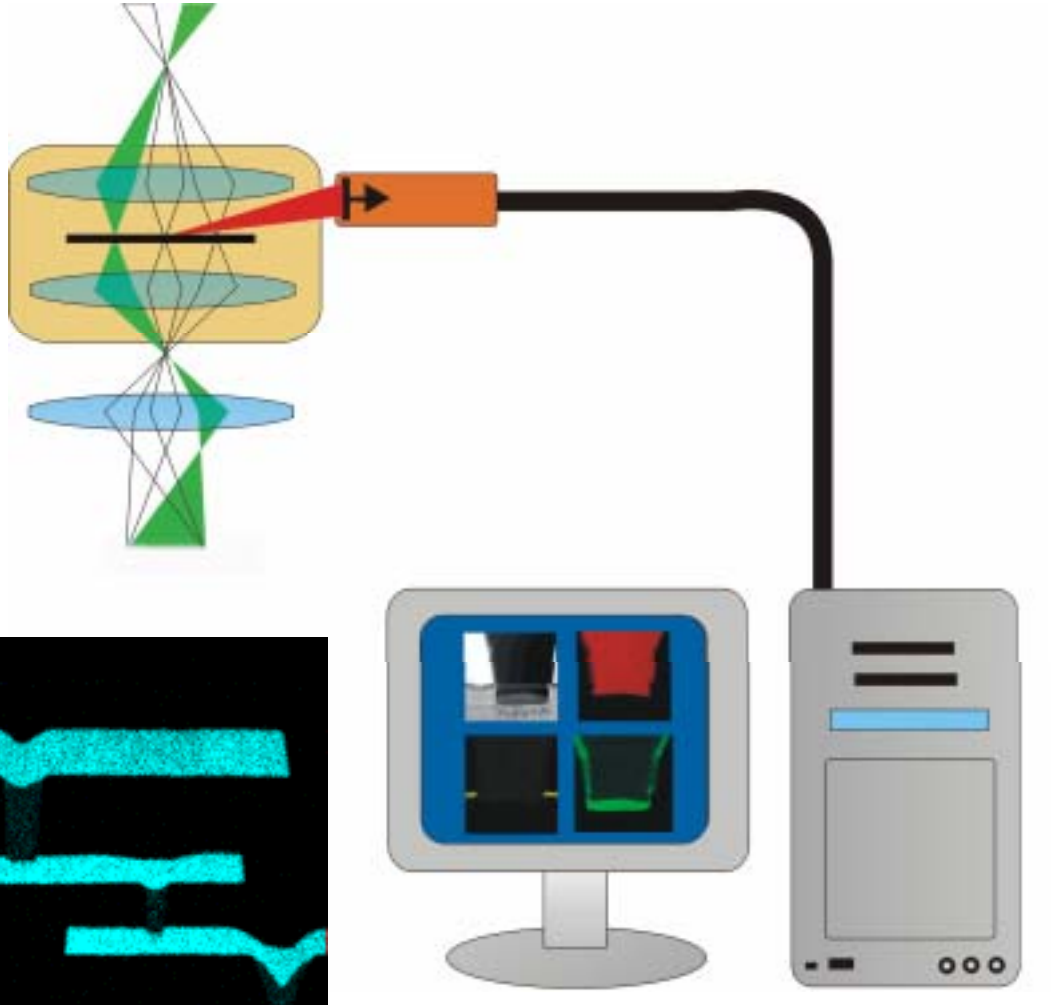


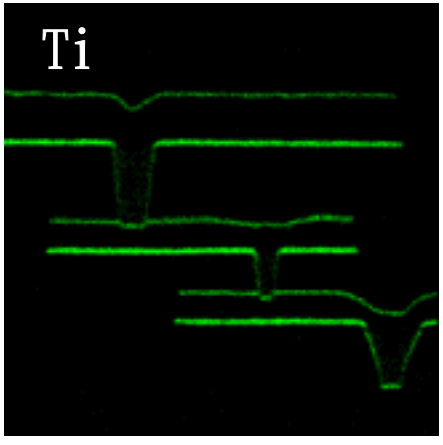




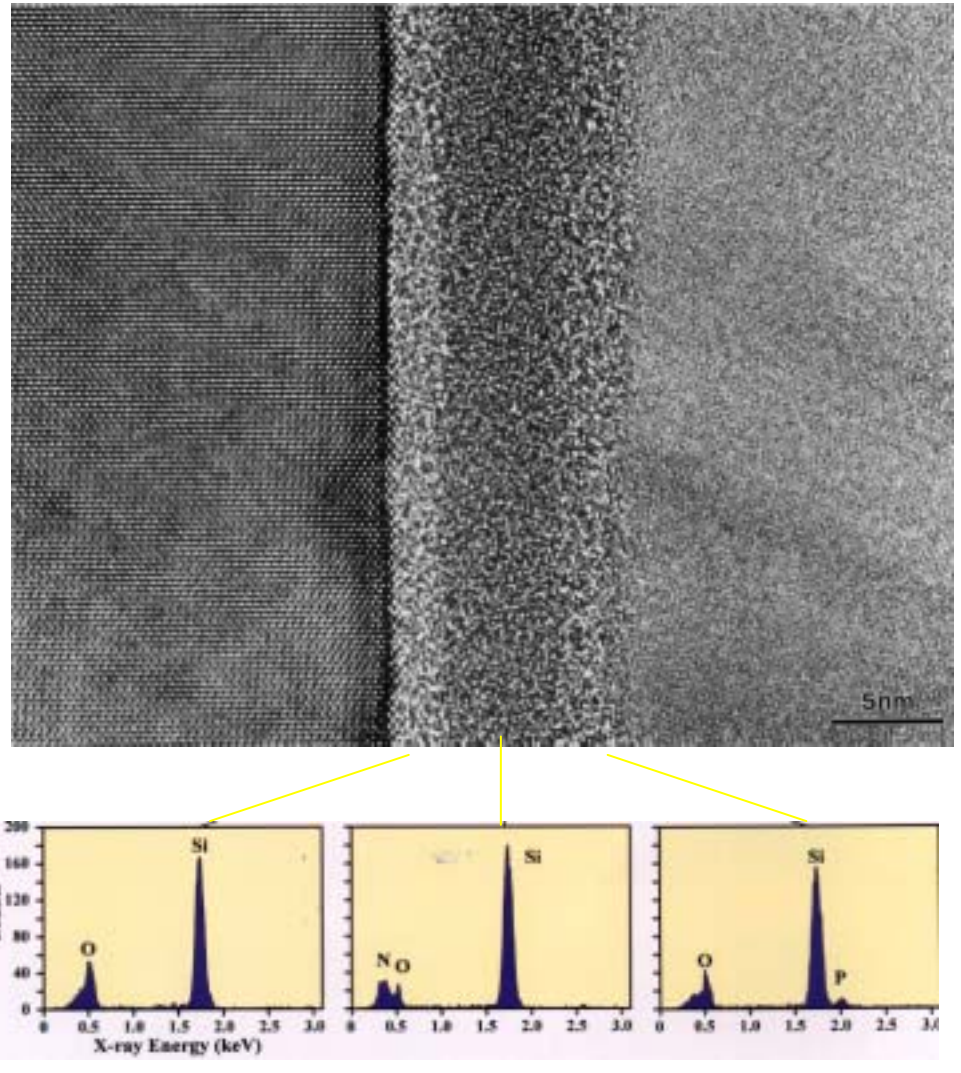
EDS mapping

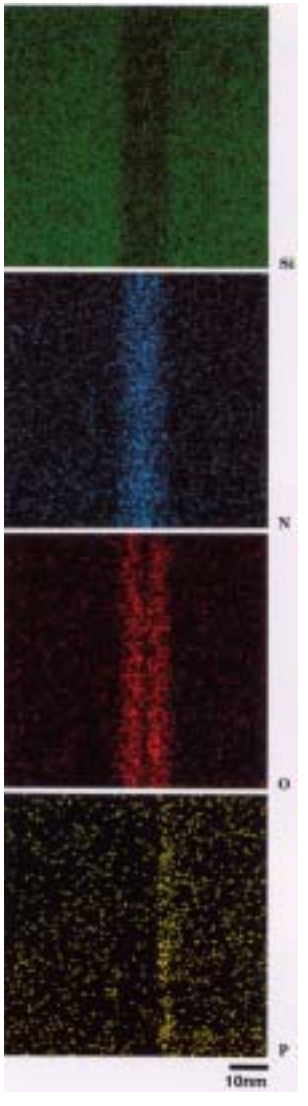




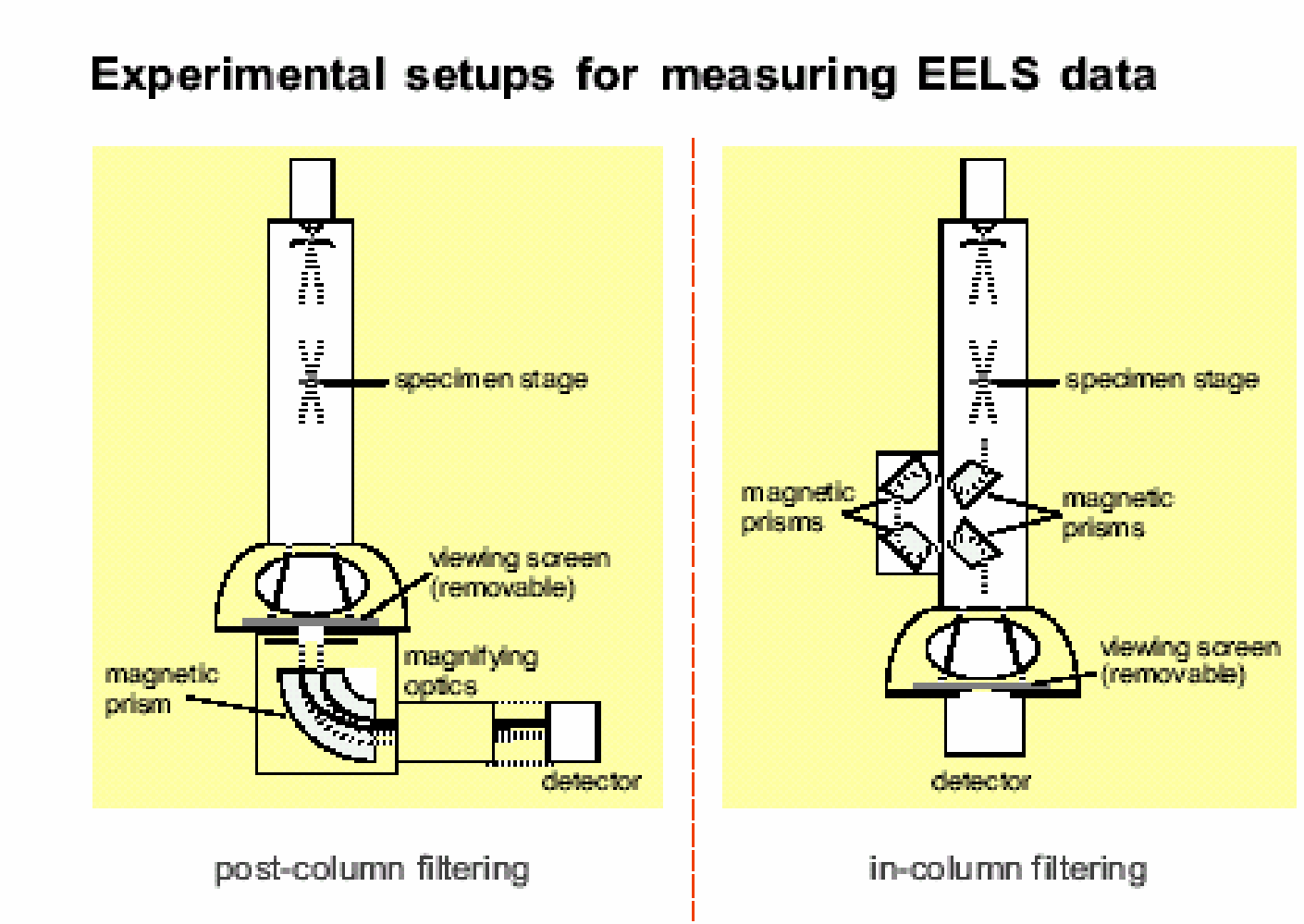


EDS Mapping (ONO)

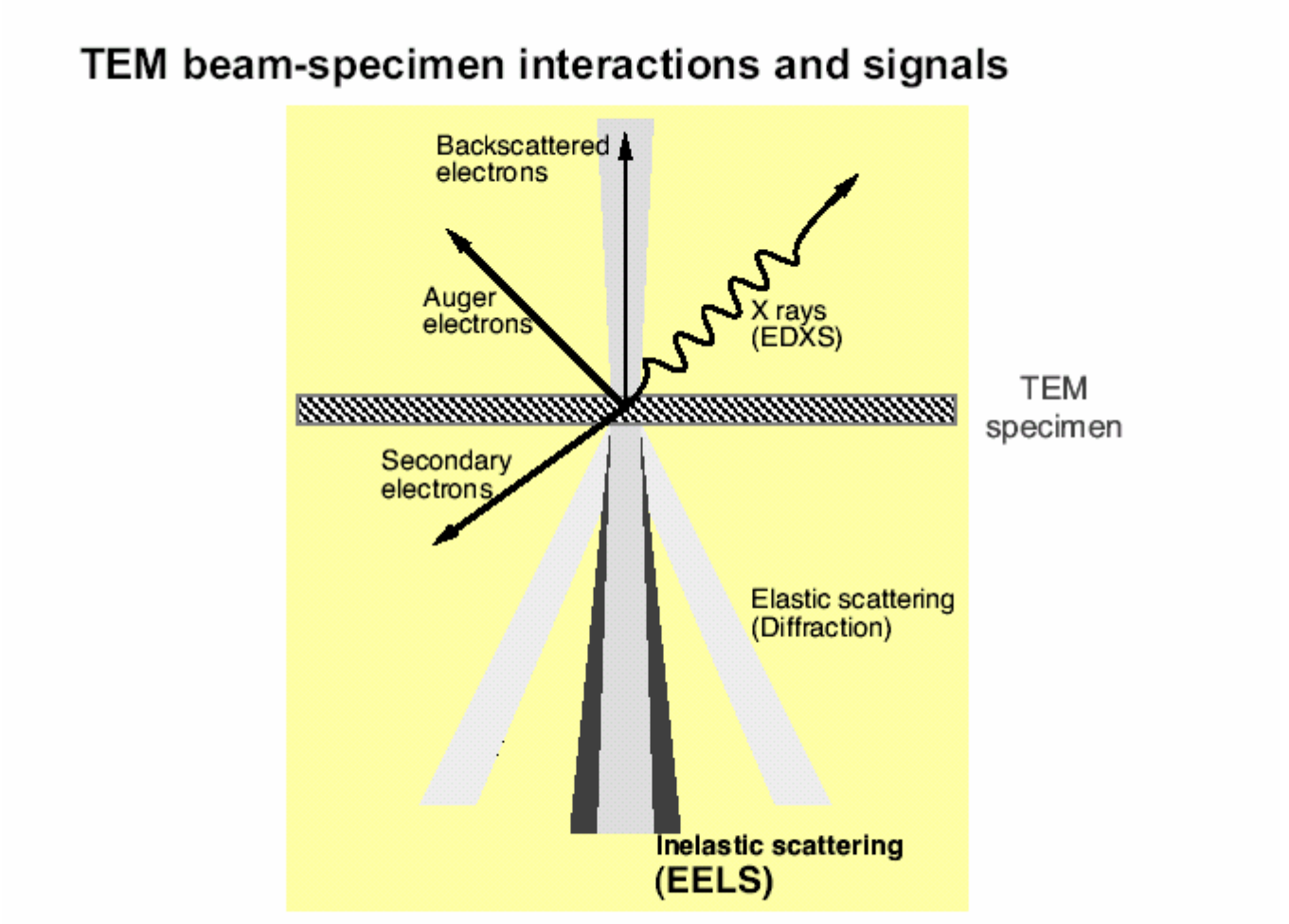




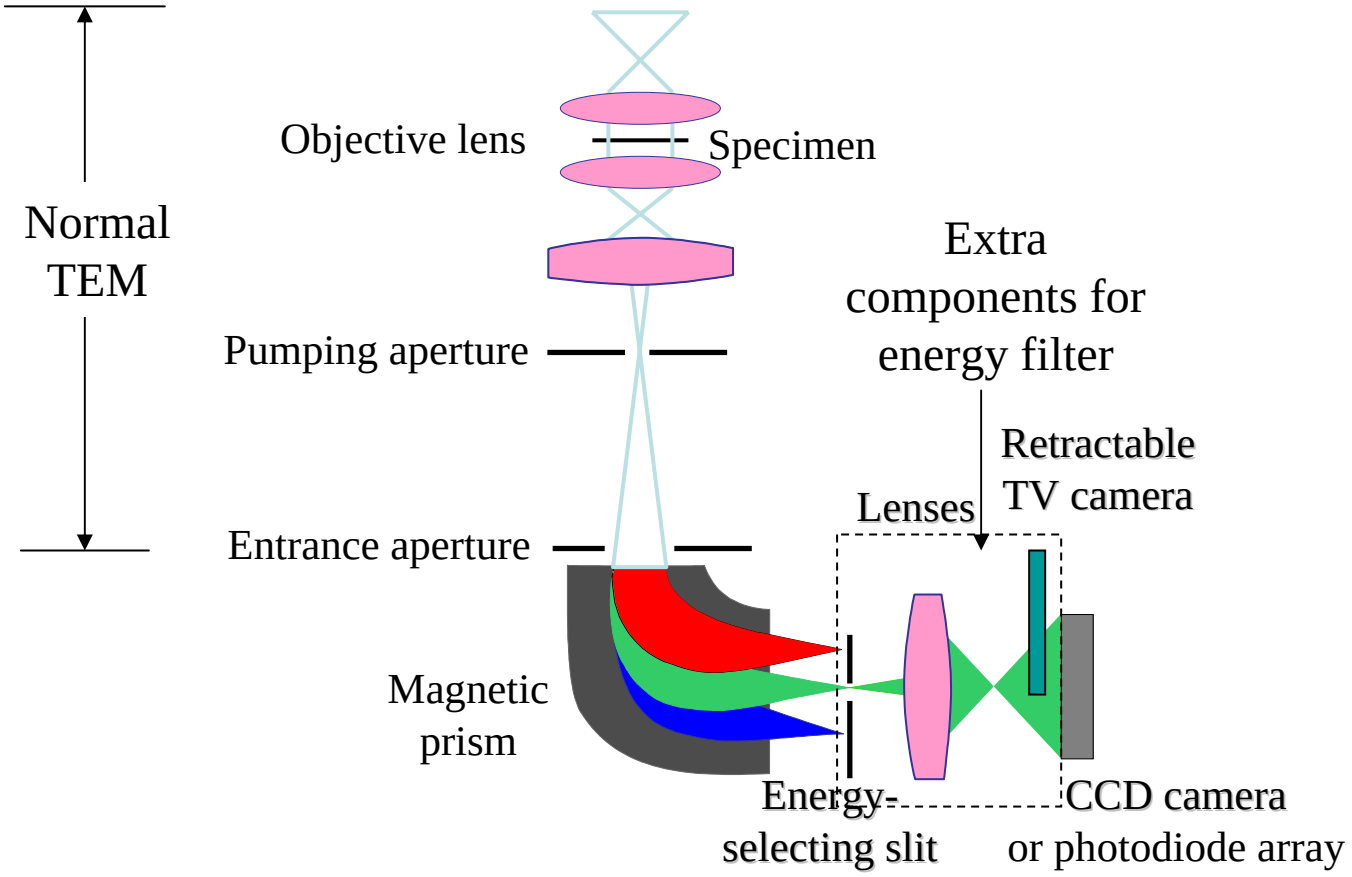
EELS configurations in TEM



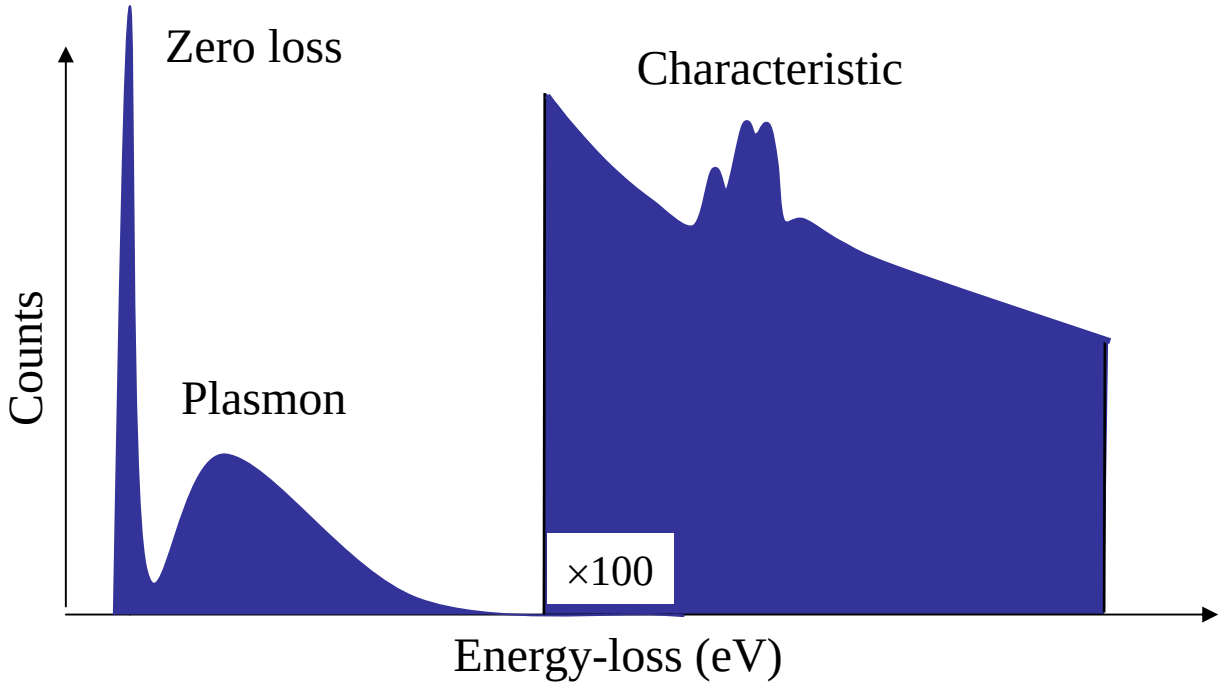
Signals for EELS



Post-column EELS

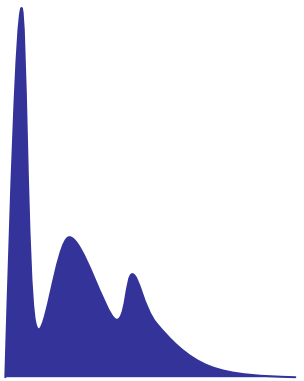


A typical EELS spectrum



Plasmon peak

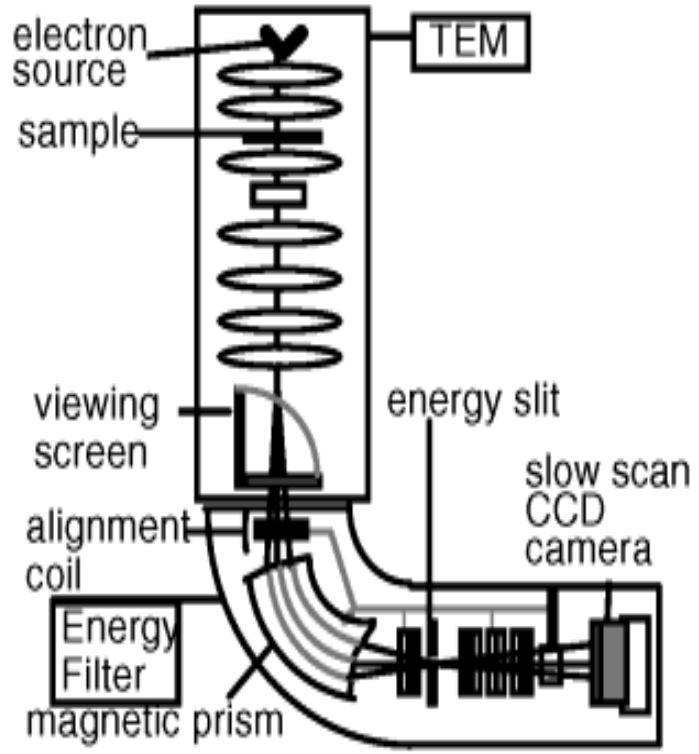
- Caused by the collective response to the incident beam by all the valence electrons
- If the sample is thicker, the plasmon peak is also higher and the second peak may appear
- The ratio of plasmon peak intensity to zero-loss peak intensity may estimate the sample thickness



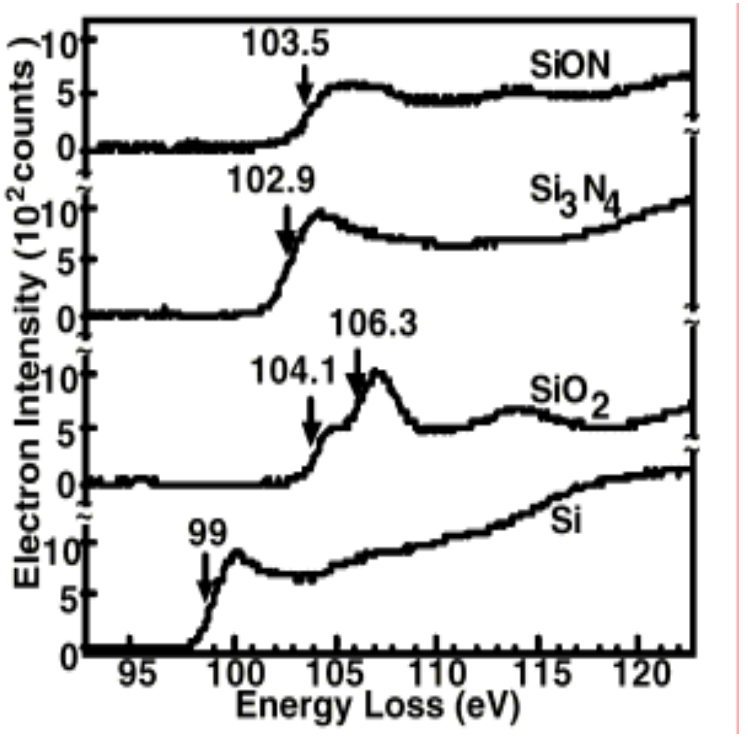
EELS vs. EDS

- More efficient signal collection
  - the first order phenomenon
  - most of the transmitted electrons enter the prism, comparing to 1% X-rays being detected
- Better signal to noise ratio
- Spectrum is electronic structure sensitive, e.g. O peaks in MnO and NiO are different in shape
- Slightly better spatial resolution
- Very high background and worse peak to background ratio, leading to the large error in quantification
- Complex peak structure makes identification difficult, it is worst when there is peak overlap
- Thin sample needed
- Operation and interpretation are more difficult

EELS for light elements



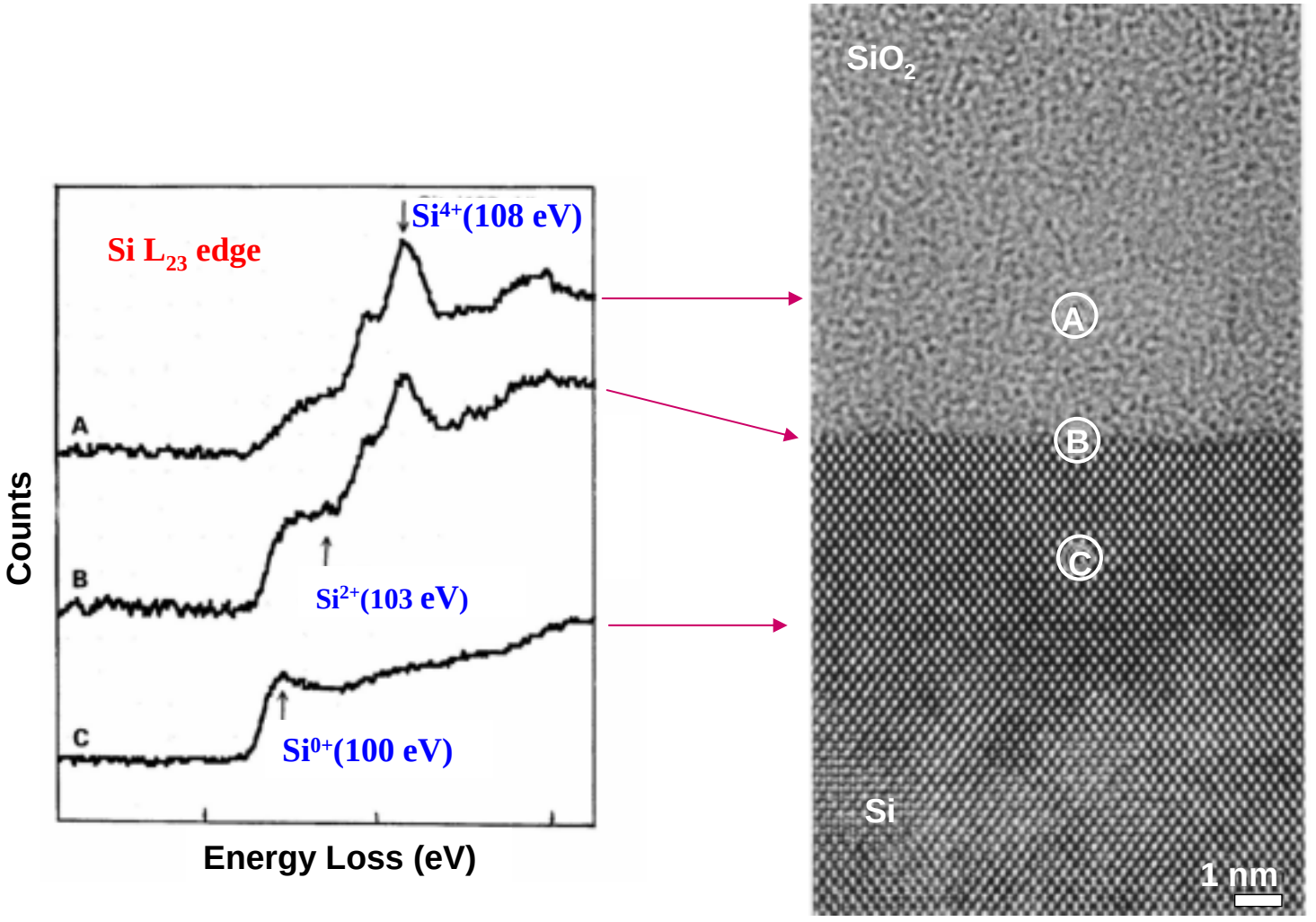
Schematic diagram of AEM-EELS



Chemical shift of core-loss edge energy in EELS spectra of some Si compounds

Y. Mitsui et al., IEDM'98

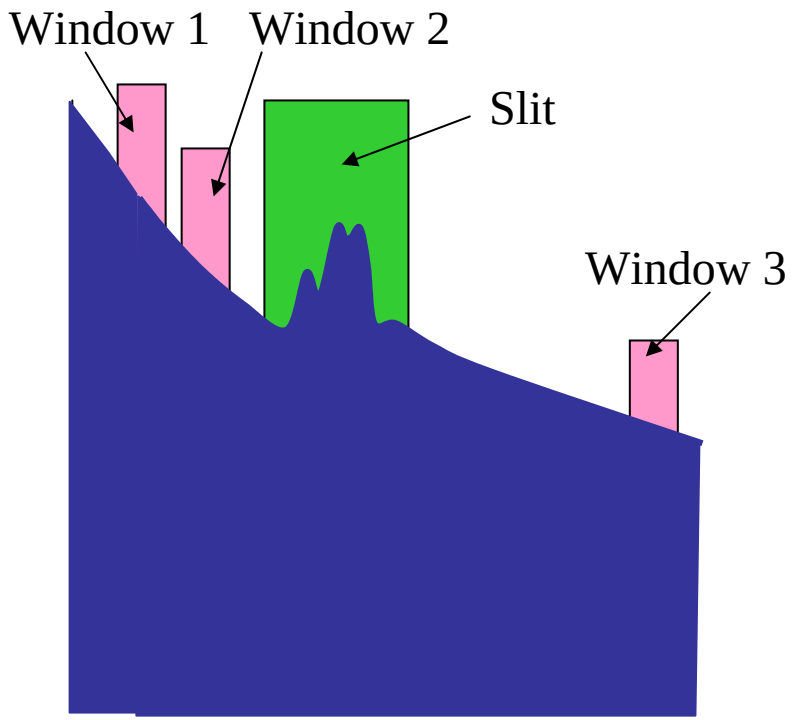
TEM and HREELS for the SiO2 / Si Interface



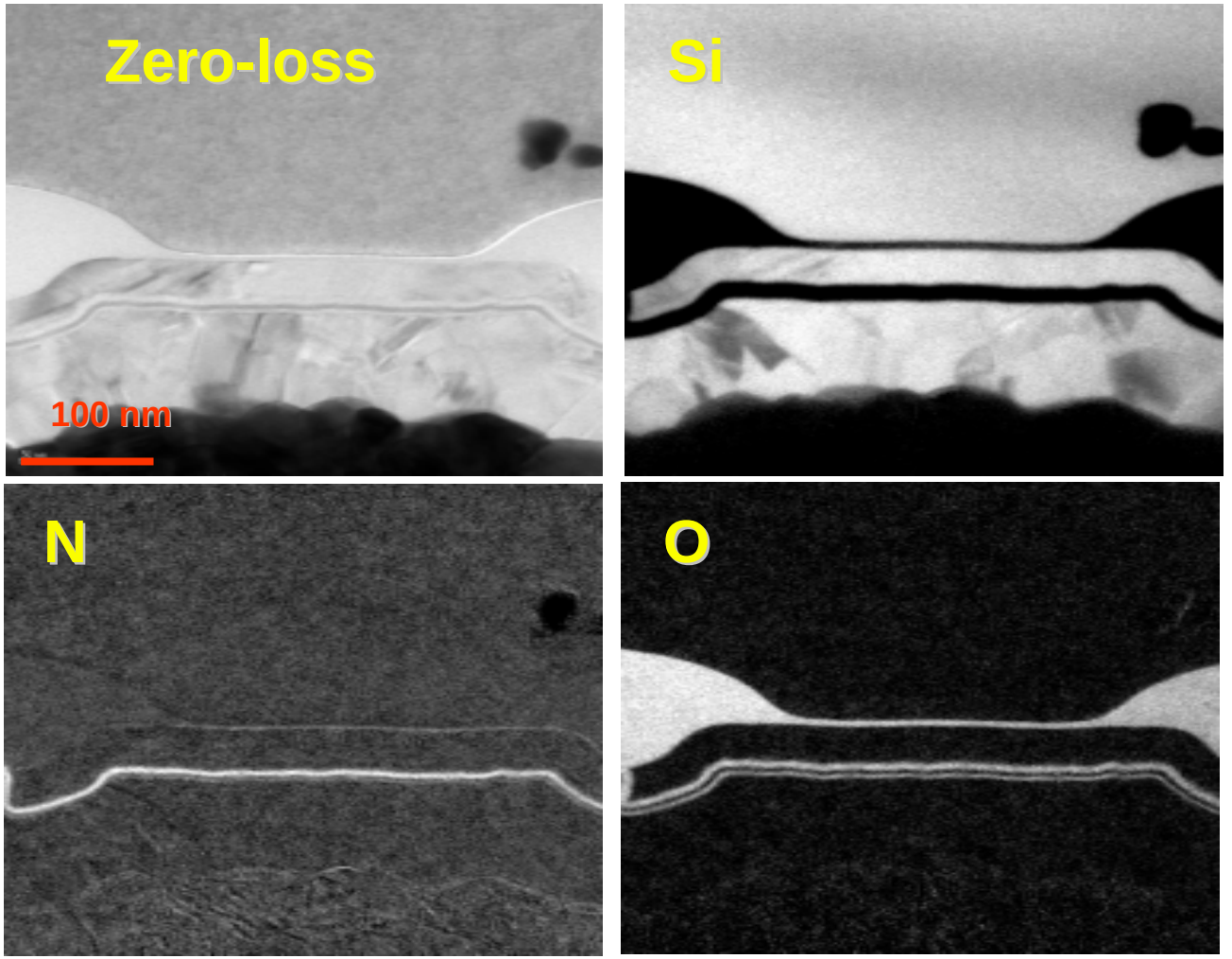
Energy filter

- An energy selective slit as small as 10eV is used
- Signal within the slit is collected and displayed, representing the element map
- For better mapping, background must be properly removed, normally by setting up windows before and after the slit

Energy filter

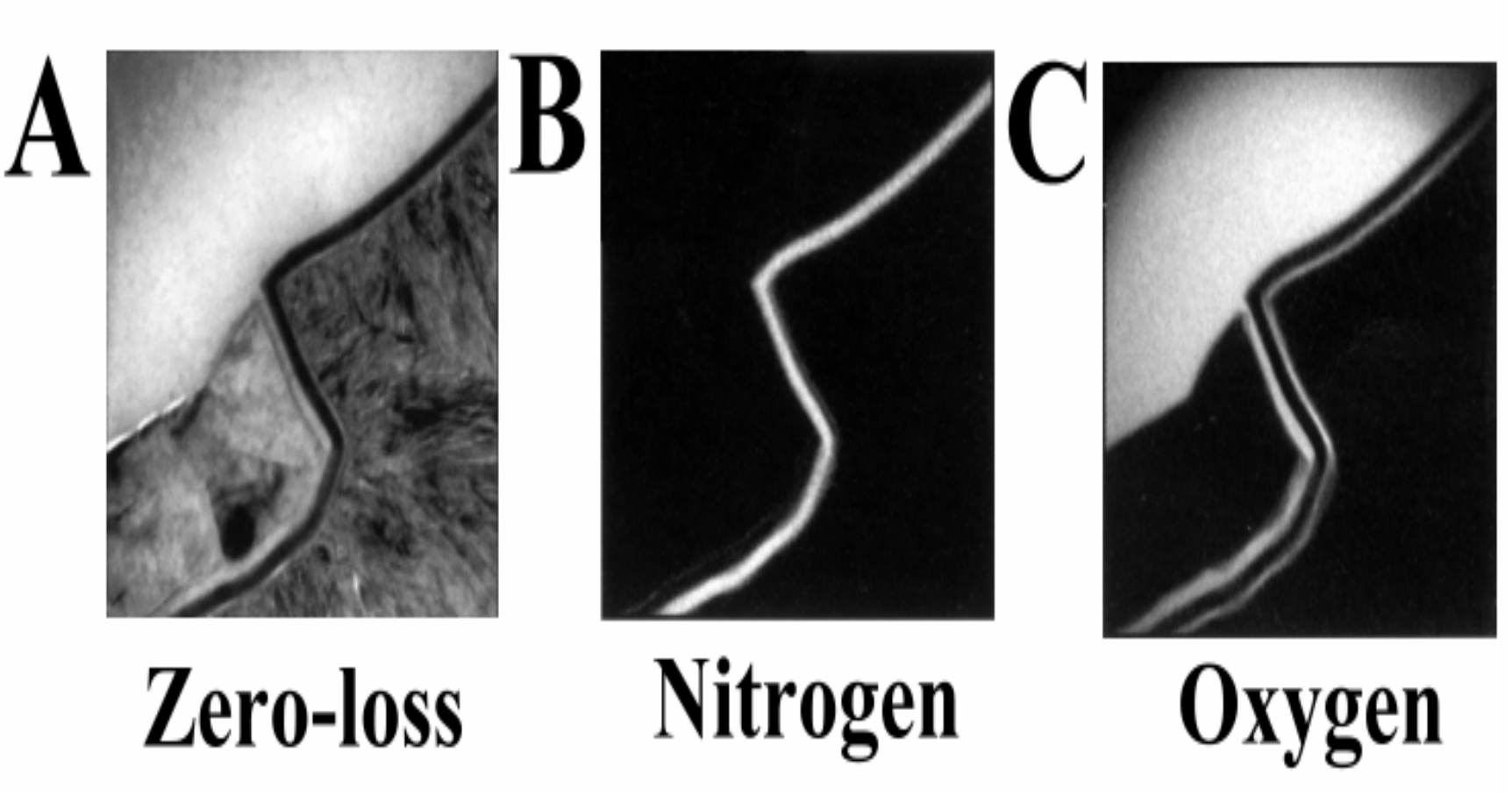


EFTEM mapping of a DRAM



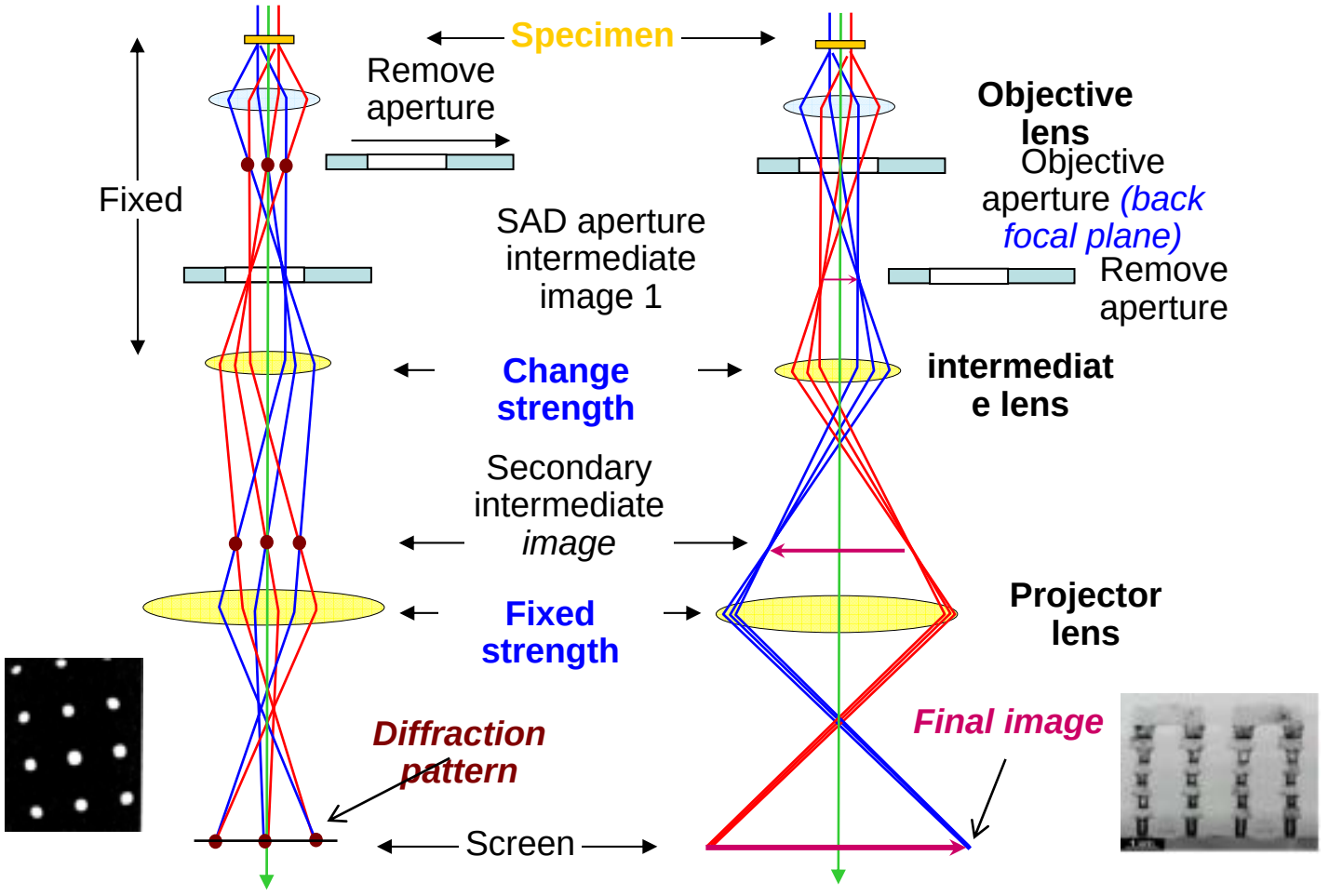
Tecnai F20 S-Twin

EFTEM mapping of the ONO layer in a DRAM



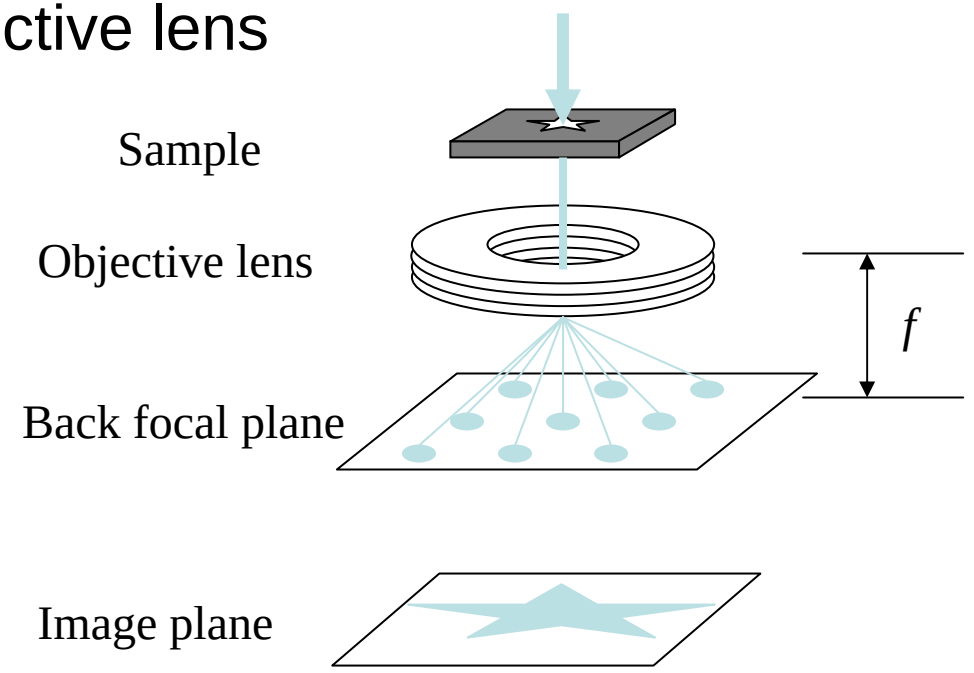
Diffraction mode

Image mode



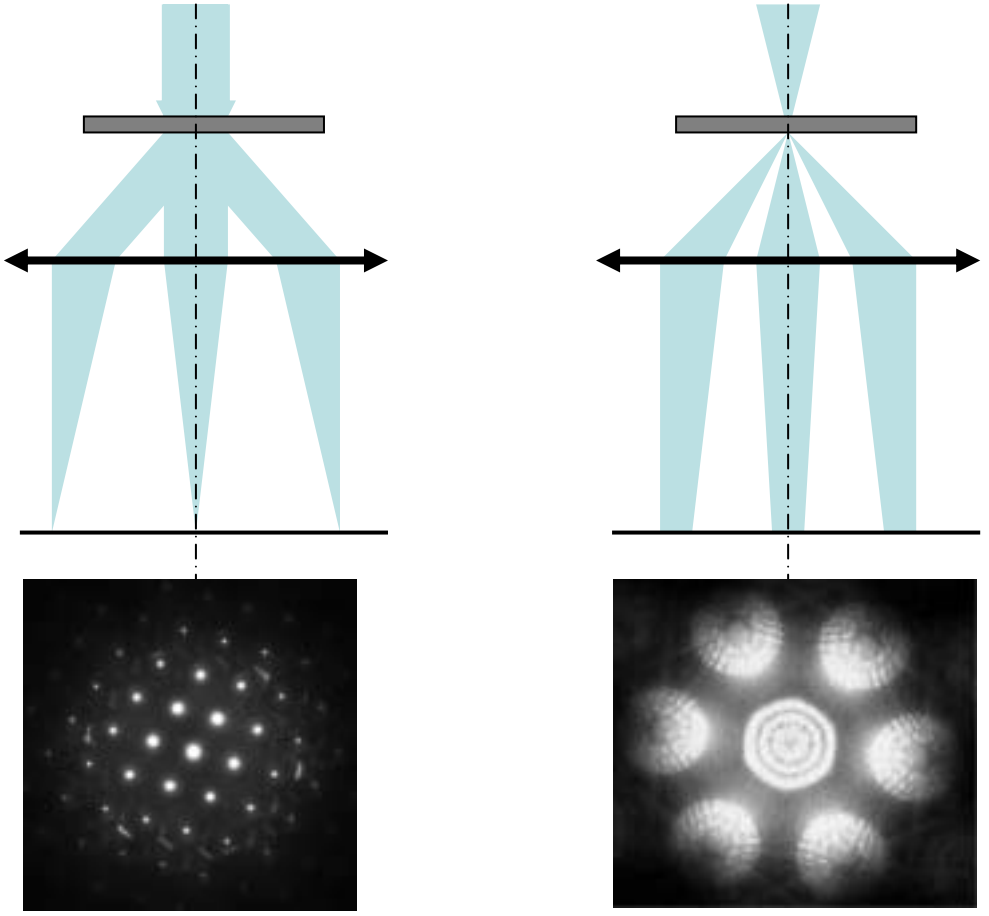
Electron diffraction

- Diffraction pattern locates at the back focal plane of the objective lens



Diffraction with parallel illumination and conical illumination

- Parallel beams are focused at the back focal plane
- Parallel illumination results sharp spots at the plane
- Conical illumination results discs at the plane



LACBED pattern along [111] of GaAs with buried InAs quantum dots

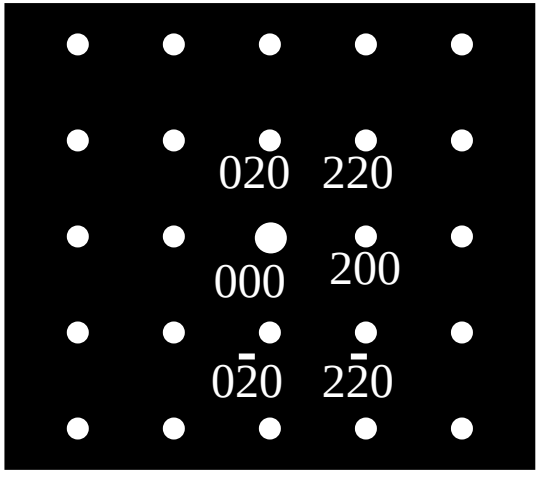
LACBED pattern along [111] of Ge

Spot pattern

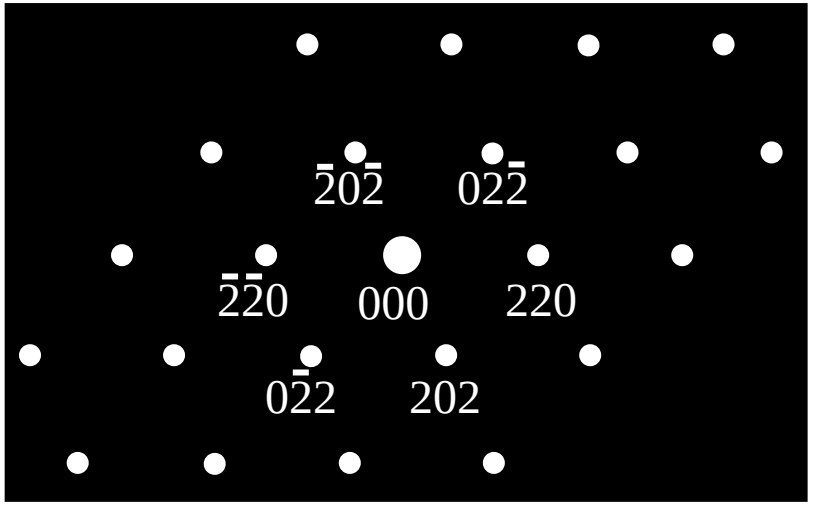
- Single crystal within the illumination area
- The regular arrangement of spots
- Spot brightness relates to the structure factor
- Spot position relates to the d-spacing

Standard spot pattern

- Example 1: f.c.c



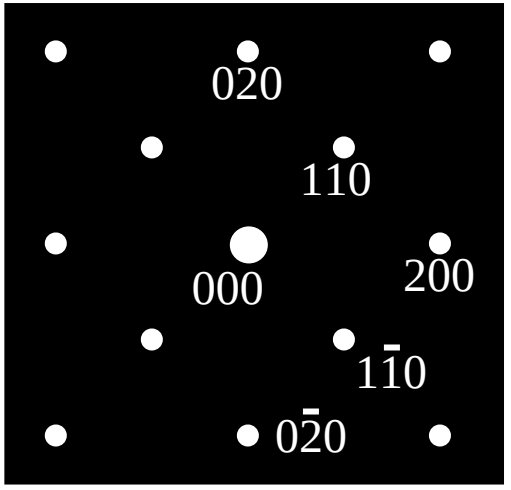
[001]



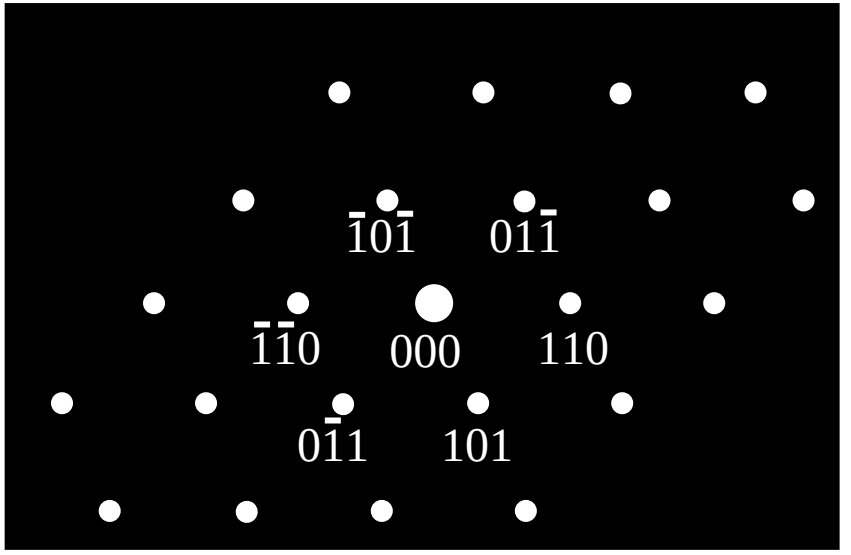
[$\bar{1}$11]

Standard spot pattern

- Example 2: b.c.c

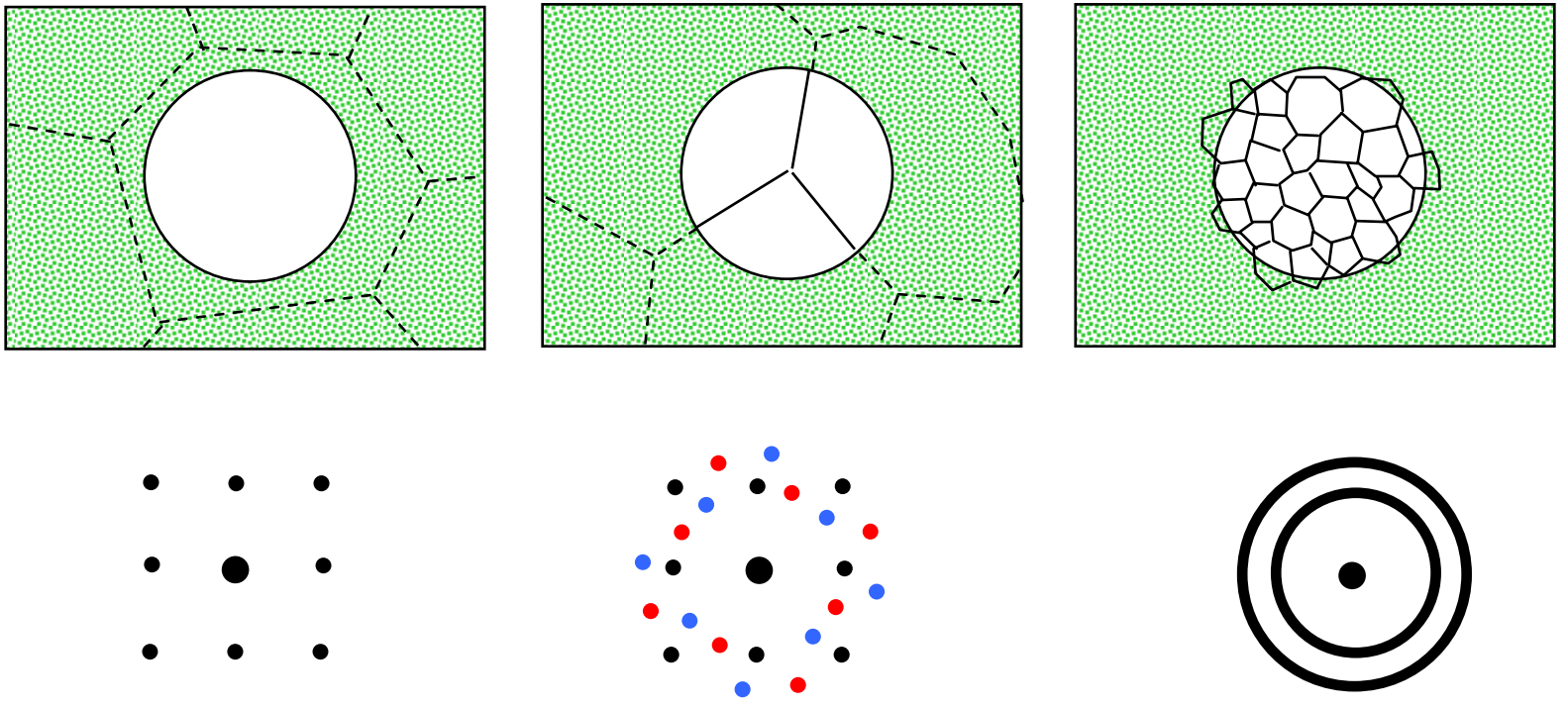


[001]



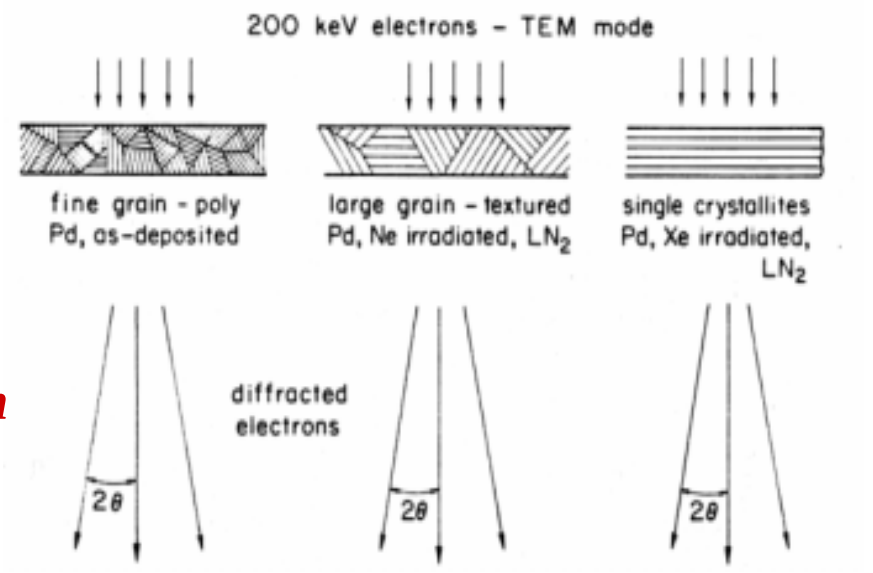
[$\bar{1}$11]

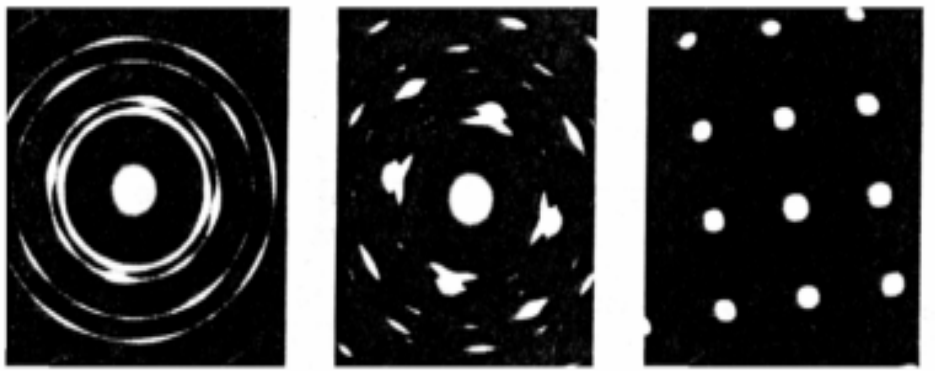
Electron Diffraction Pattern--Spot to Ring



(a) **(b)** **(c)**

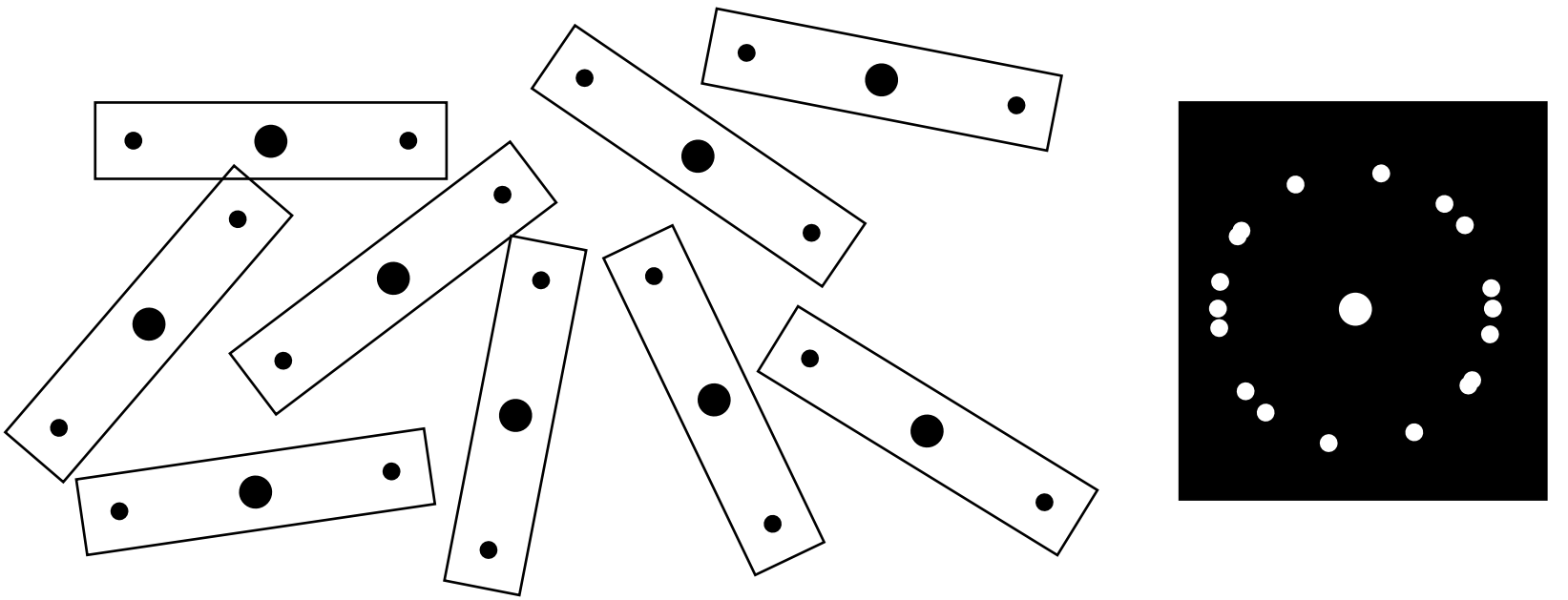
Electron Beam Diffraction of a Pd film





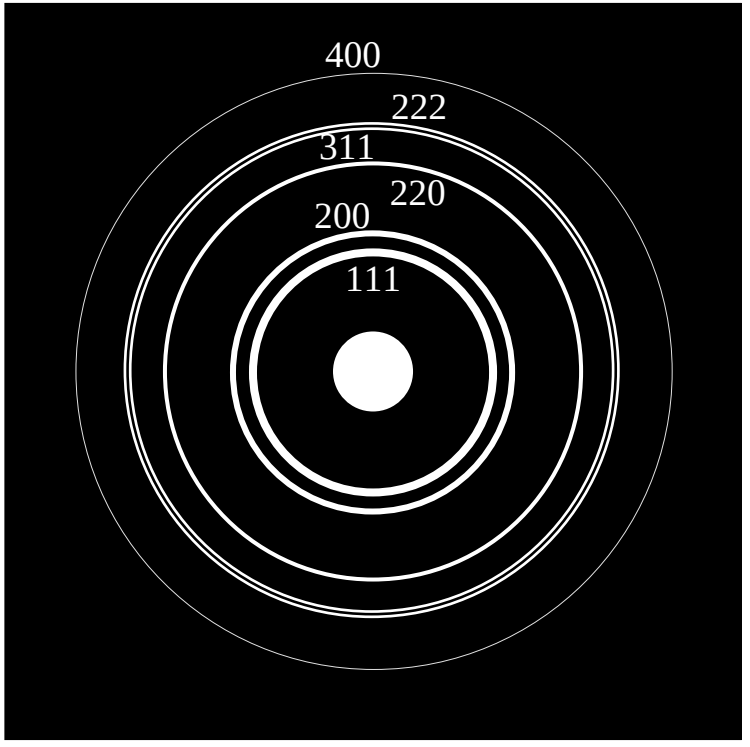
Ring pattern

- Many fine particles in the illumination area, each of them is a single crystal and orientated randomly



Ring pattern

- Typical polycrystalline Au diffraction pattern



Ring pattern: what can we obtain

- d-spacing

$$Rd_{hkl} = L\lambda$$

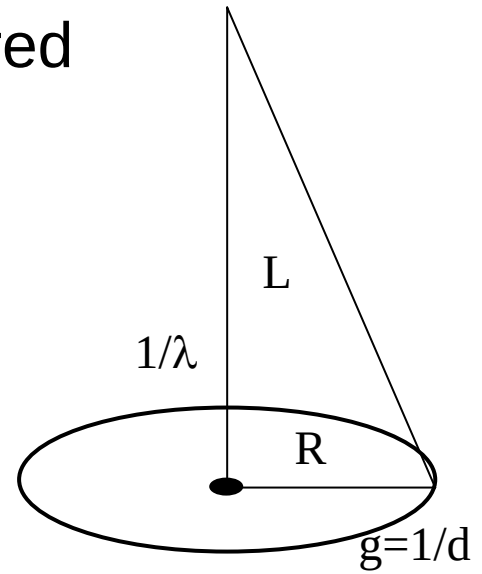
R: the measured ring radius

d_{hkl}: the d-spacing being measured

L: camera length

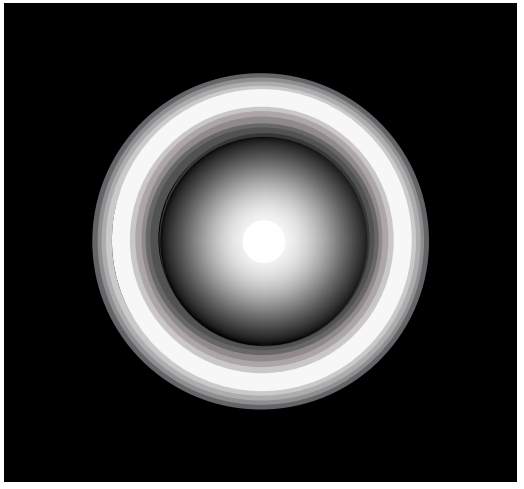
λ: wave length of electron beam

- Camera length calibration
- Crystalline / particle fineness



Amorphous materials

- Diffused ring pattern
- Reflecting the short range ordered structure
- Often seen at contamination layer or on carbon support film



AEM vs. Conventional TEM
(Differences in aimed signals)

- CTEM and HREM deal mainly with the **elastically scattered** electrons.
- AEM deals mainly with the **in-elastically scattered** electrons and their resulting X-rays (by EELS or EDS) for the composition determination. But **elastically scattered** electrons are also collected to obtain structural information (by STEM).

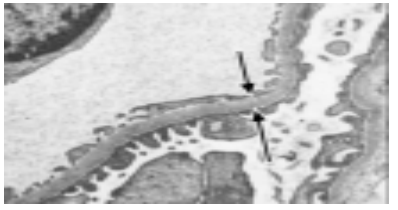
AEM vs. Conventional TEM

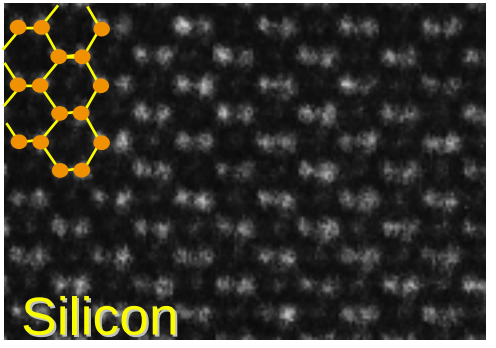
(Differences in Instrumentation)

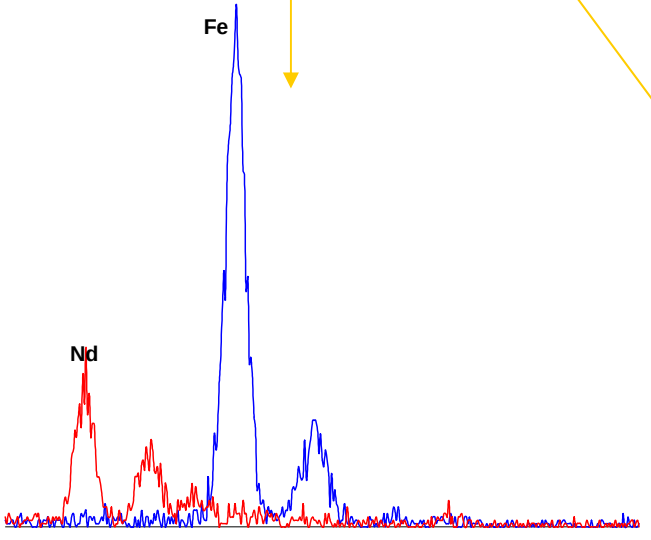
- Different illumination requirements: parallel illumination for CTEM (and HRTEM) but conical illumination for AEM
- Different designs for the objective lens to match the illumination system
- With analytical attachments: EDS for characteristic X-rays, EELS for in-elastic scattered electrons, and annular detectors for incoherent elastic electrons.
- Scanning function

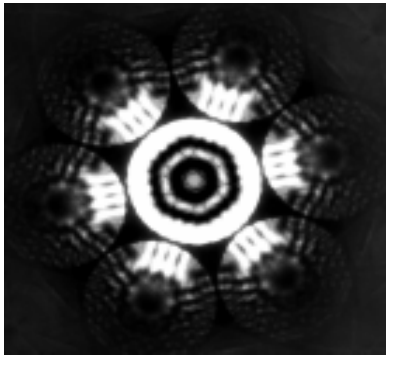
Types of Information from AEM

- Image
- Structure
- Chemistry









Examples of AEM Applications to the Characterization of Materials

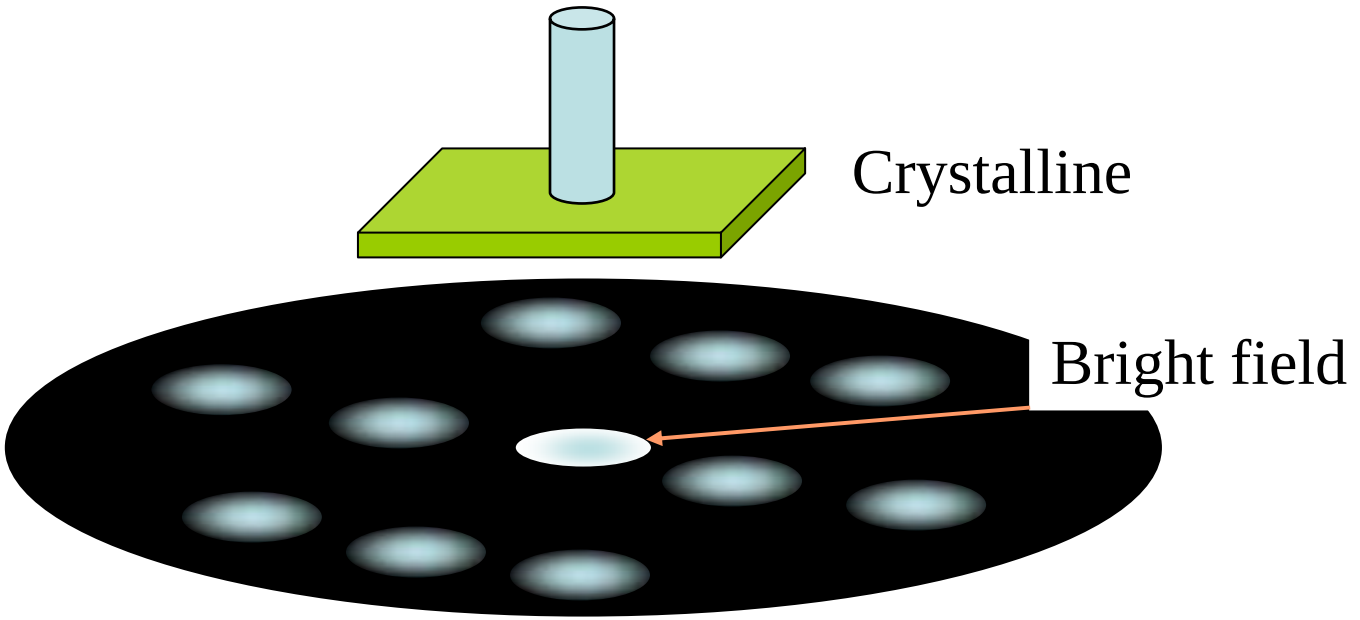
- Morphology (imaging): CTEM (BF,DF), HRETM, and STEM (BF,DF, and HAADF)
- Crystal Structure (diffraction): SAED, NBED, and CBED
- Chemistry: composition (EDS,EELS, and STEM HAADF), chemical state (EELS)

What is HREM?

- It is NOT defined by its direct resolution (1nm or 0.3nm?)
- It is NOT defined by directly seeing atomic structure (in most cases it does not directly show crystal structure!)
- It displays many-beam (2D) interference fringes
- It is phase contrast image

Many-beam

- Referred to the scattering effect
- Comparing to diffraction contrast, ‘one-beam’ technique



HREM image formation

- Scattering is a strong interaction
  - excellent statistics and useful signal
  - no simple relationship between an image and the specimen structure
- Imaging system is imperfect:
  - Generally no direct correspondence between image & structure
- Image interpretation is absolutely needed

High Resolution Electron Microscope (HREM):

Approaching atomic resolution.

Requirements:

(Ultra) high resolution pole piece

Electronic stability

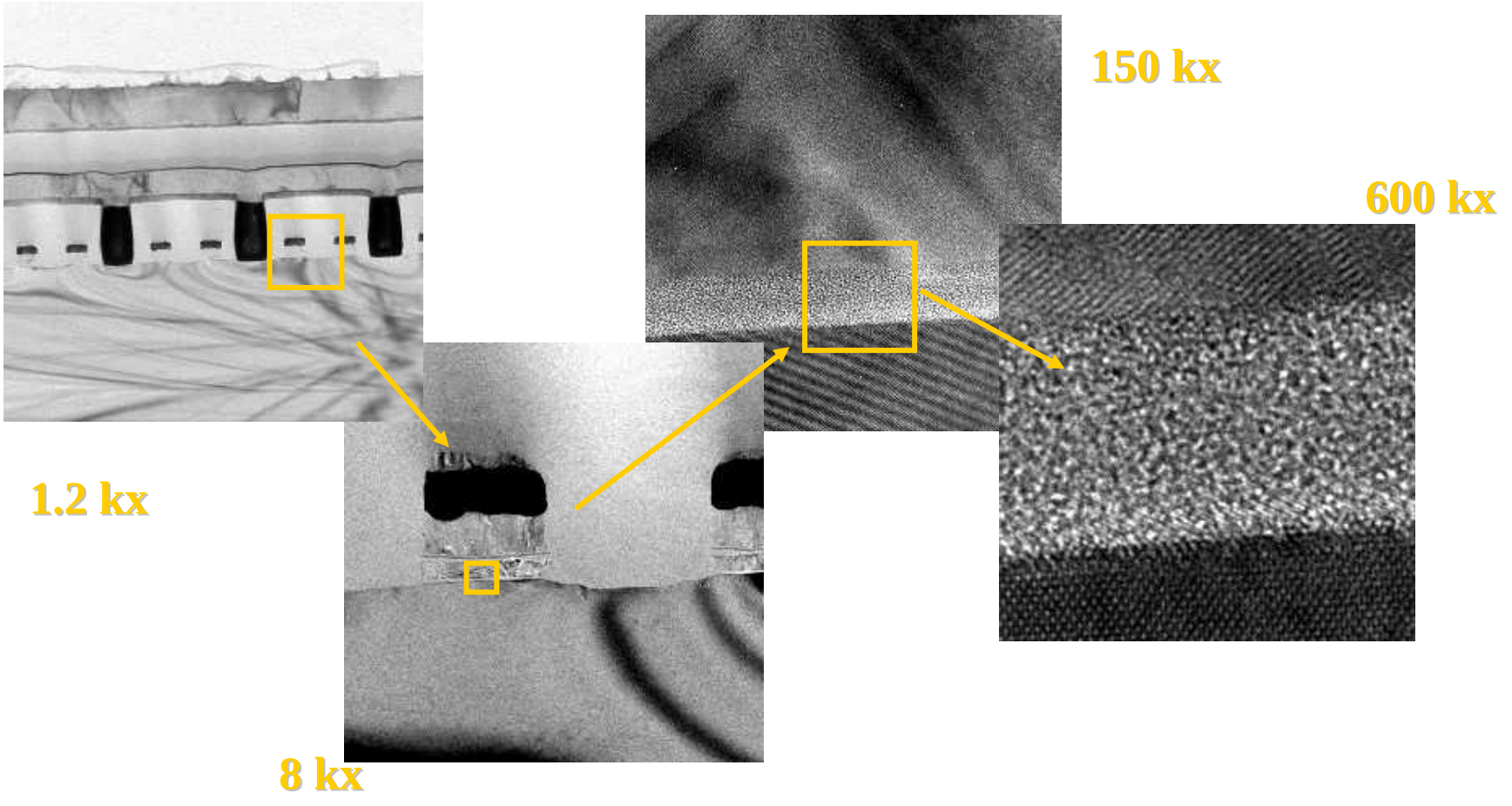
Mechanical stability

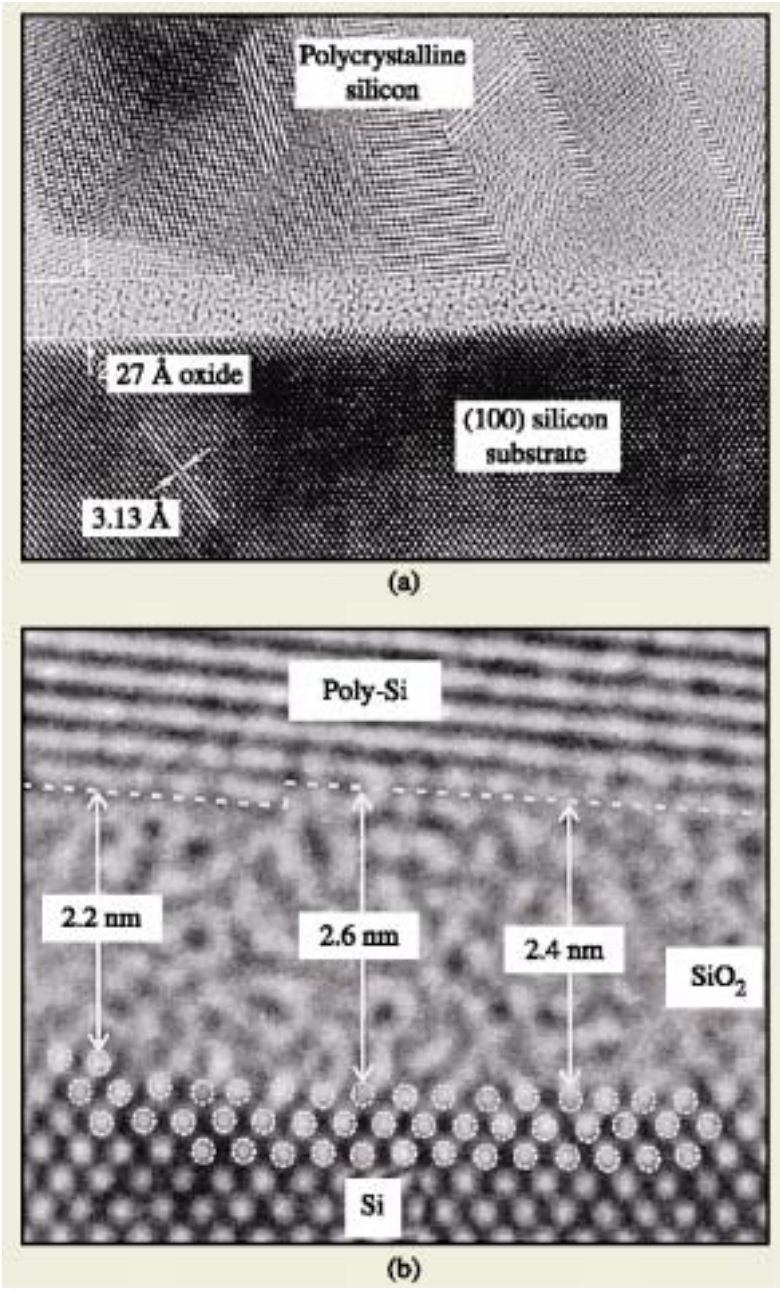
Clean environment: (Ultra) high vacuum

Specimen preparation: very very thin

In general HREM is needed for studying nano-materials.

CTEM BF and HRTEM

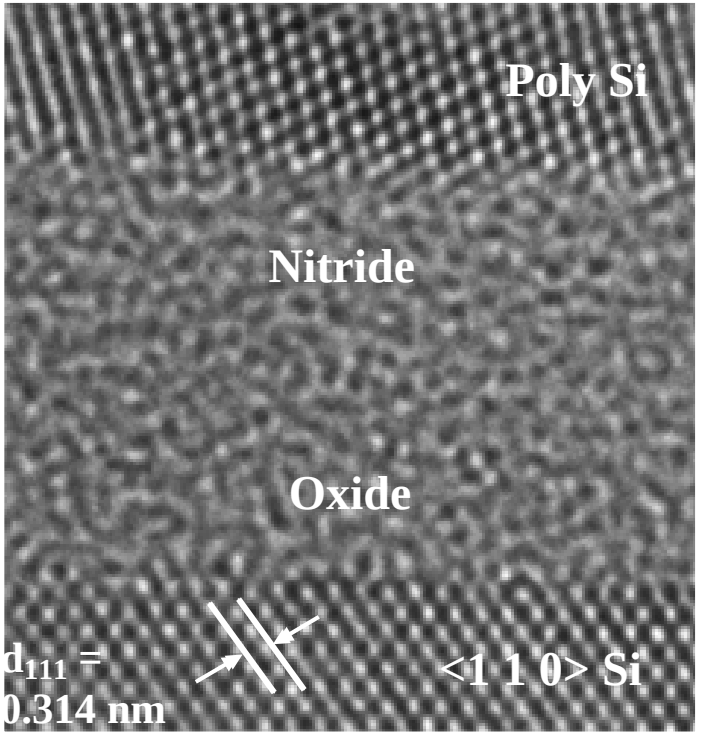


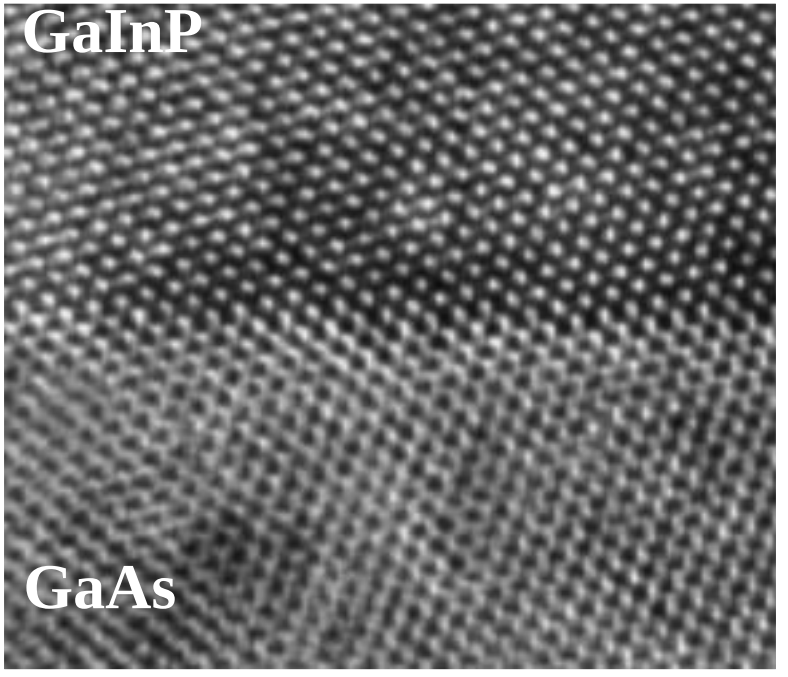


HRTEM for oxide thickness Measurement in MOS structure

Cross-sectional high-resolution transmission electron microscope (HRTEM) images for MOS structure with (a)~2.7 nm and (b) ~2.4 nm image. The poly-Si grains are easily noticeable in (a); the Si/SiO_2 and poly-Si/SiO_2 interface are shown in (b). On a local, atomic scale, thickness variation of ~2-3 Å are found which are a direct result of atomic silicon steps at both interfaces.

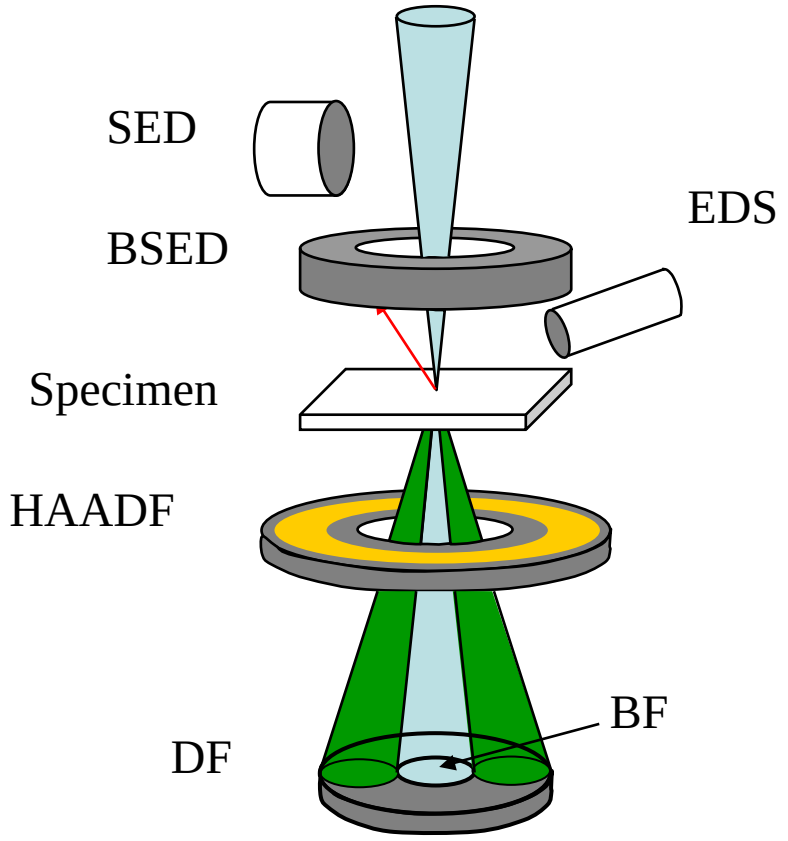
HREM Image — Interface



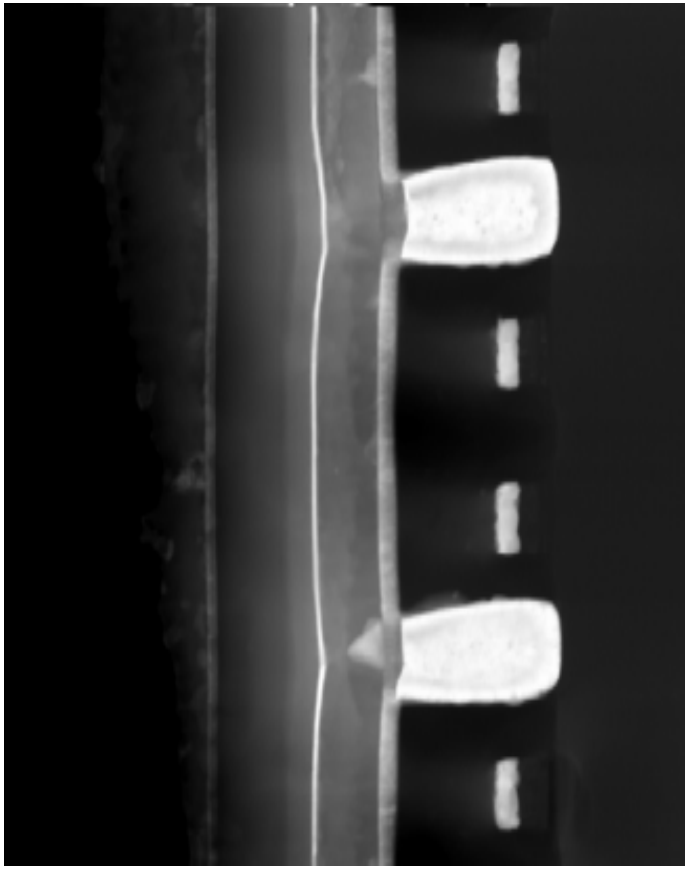


Fundamentals of STEM

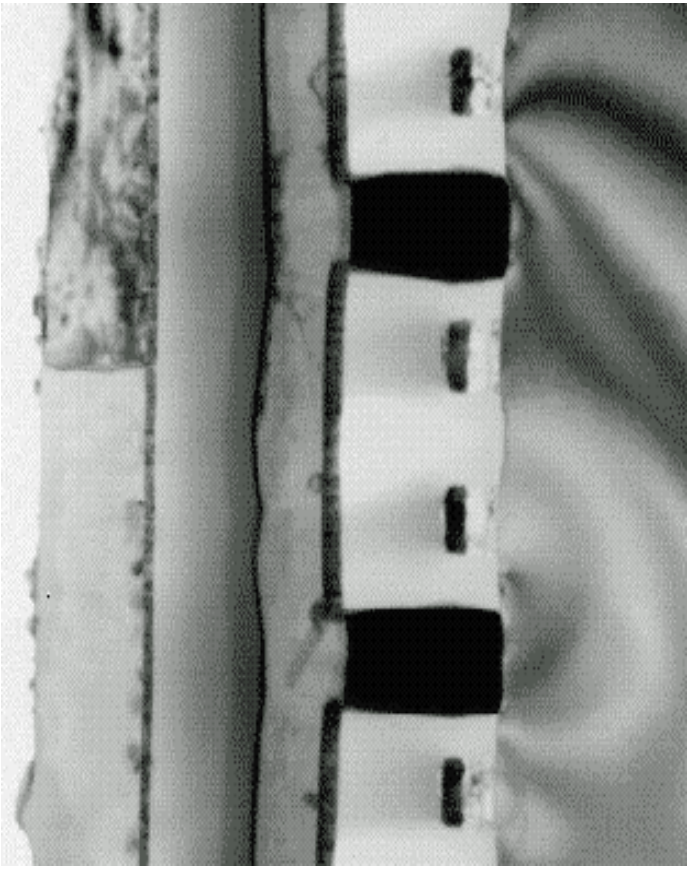
- More detectors than a SEM below the specimen, which collect beam transmitted, or diffracted, from the specimen
- The beam intensity variation contains the useful information about the location where beam is currently situated



STEM BF and ADF images from a semiconductor device

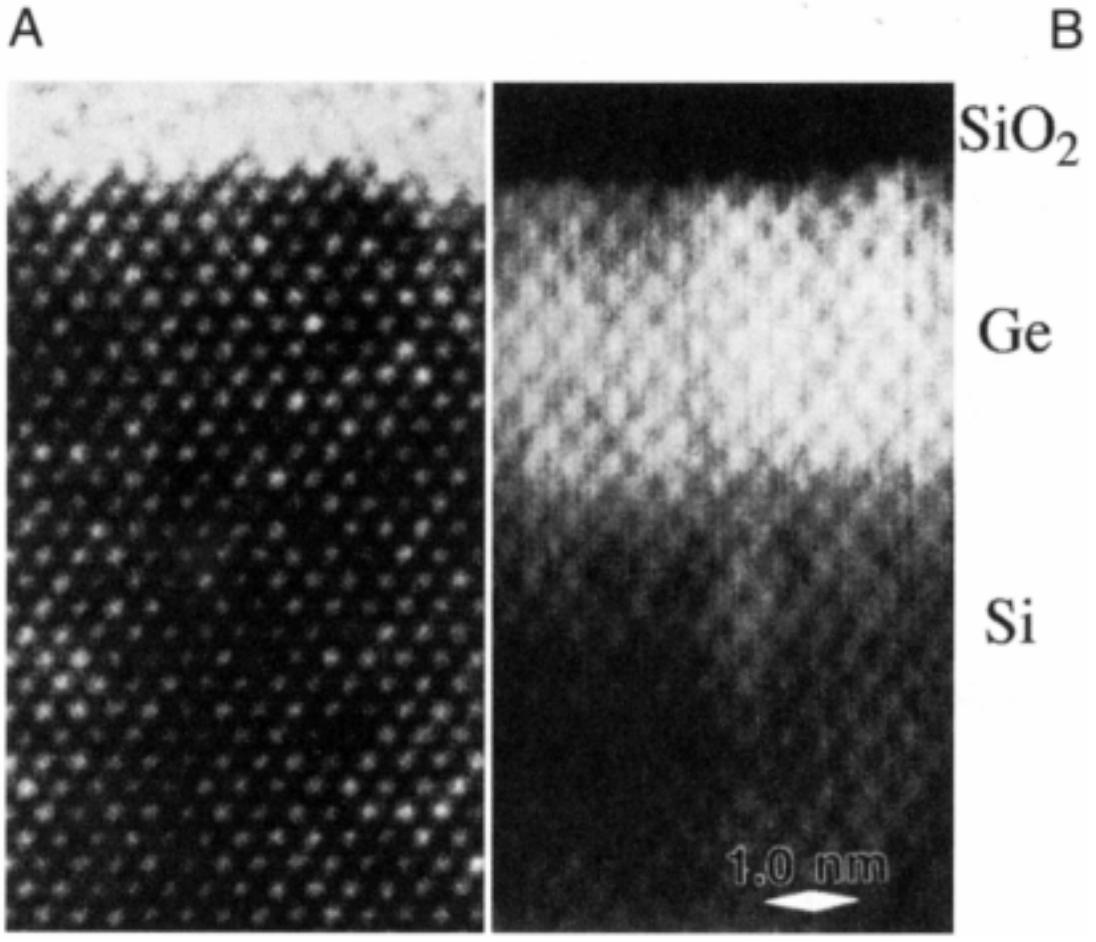


ADF



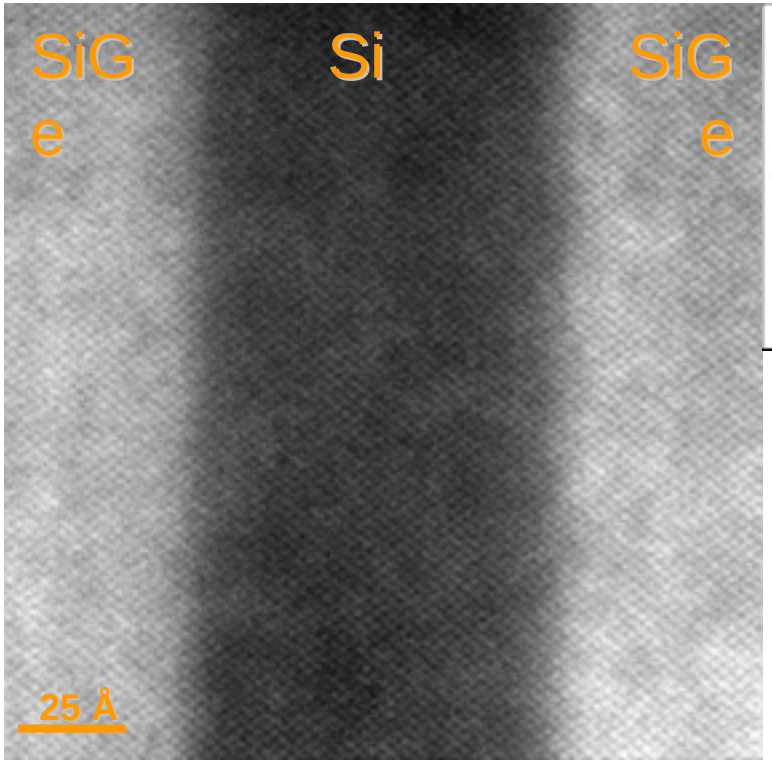
BF

HREM vs. STEM HAADF Image — Interface

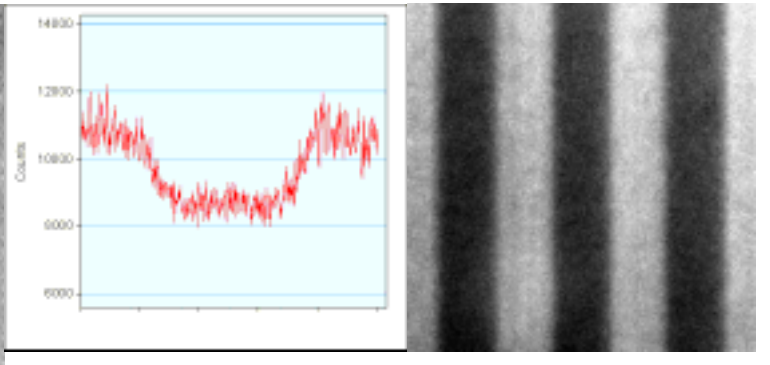


HRTEM STEM HAADF

HAADF image of SiGe alloy layers

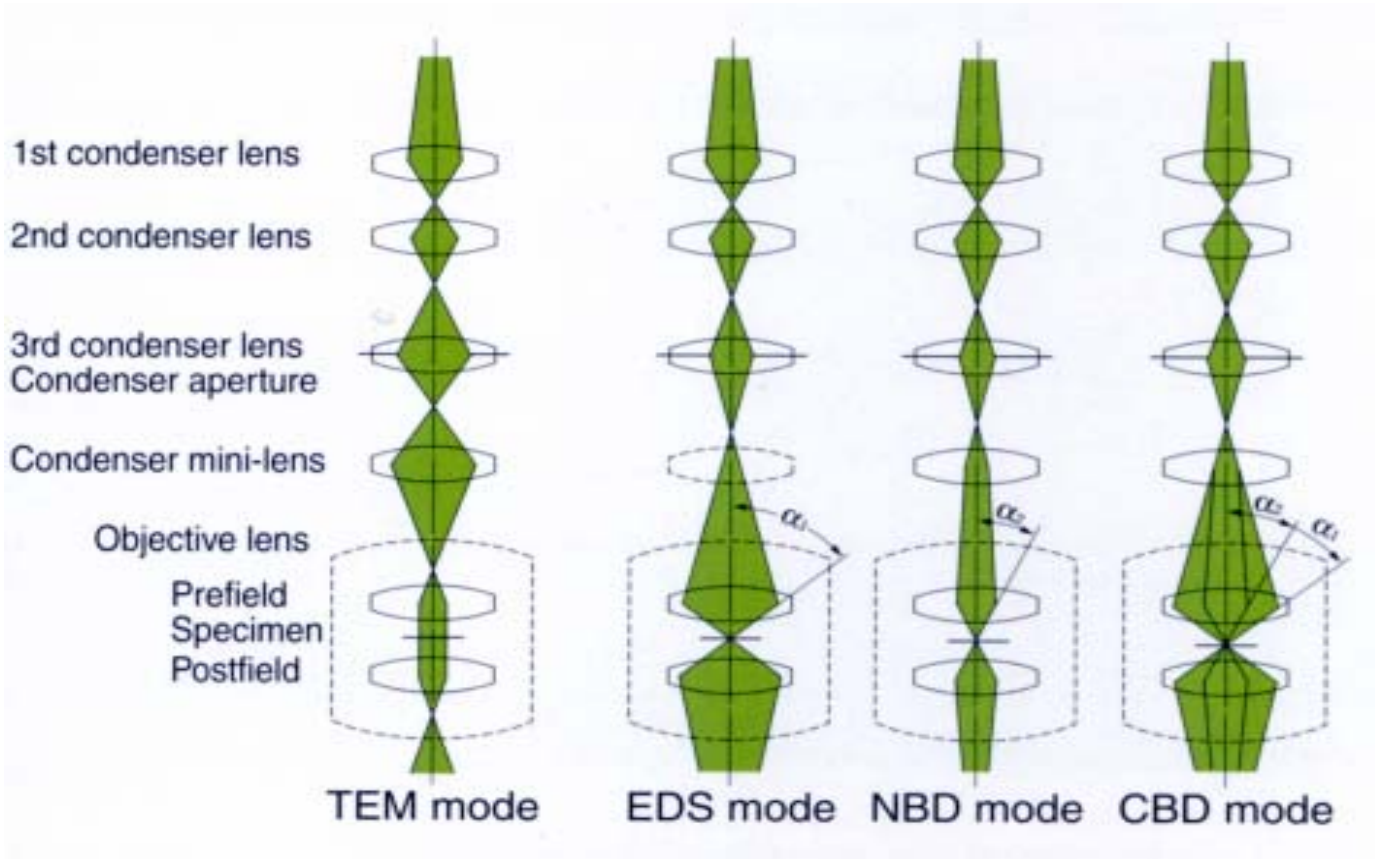


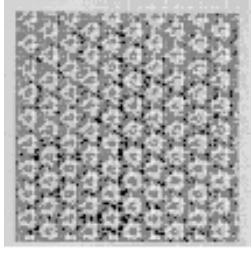
Tecnai F20 S-Twin



ADF image of $Si_{0.81}Ge_{0.19}$ alloy layers alternating with pure Si layers in a <110> orientation. Due to the Z-dependence of incoherent ADF STEM, the Ge rich layers are brighter than the pure Si. The interface between the layers is not sharp but shows a gradual decay.

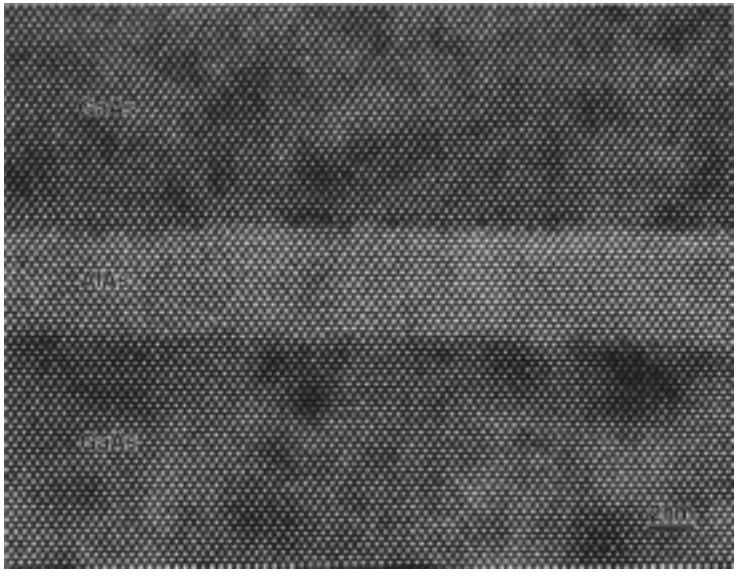
Quick Beam Select System



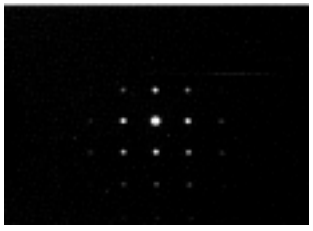


Information from TEM

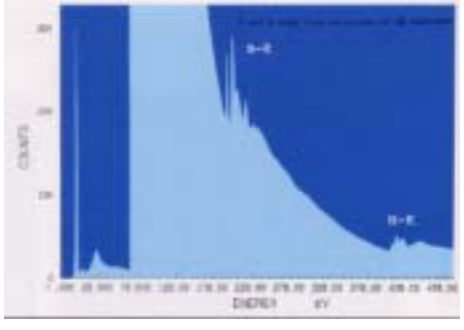
EDS



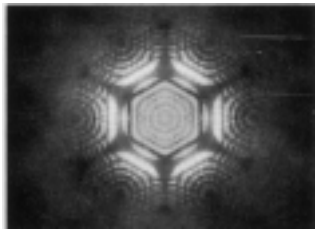
Lattice image
GaAs/AlAs



Electron Diffraction



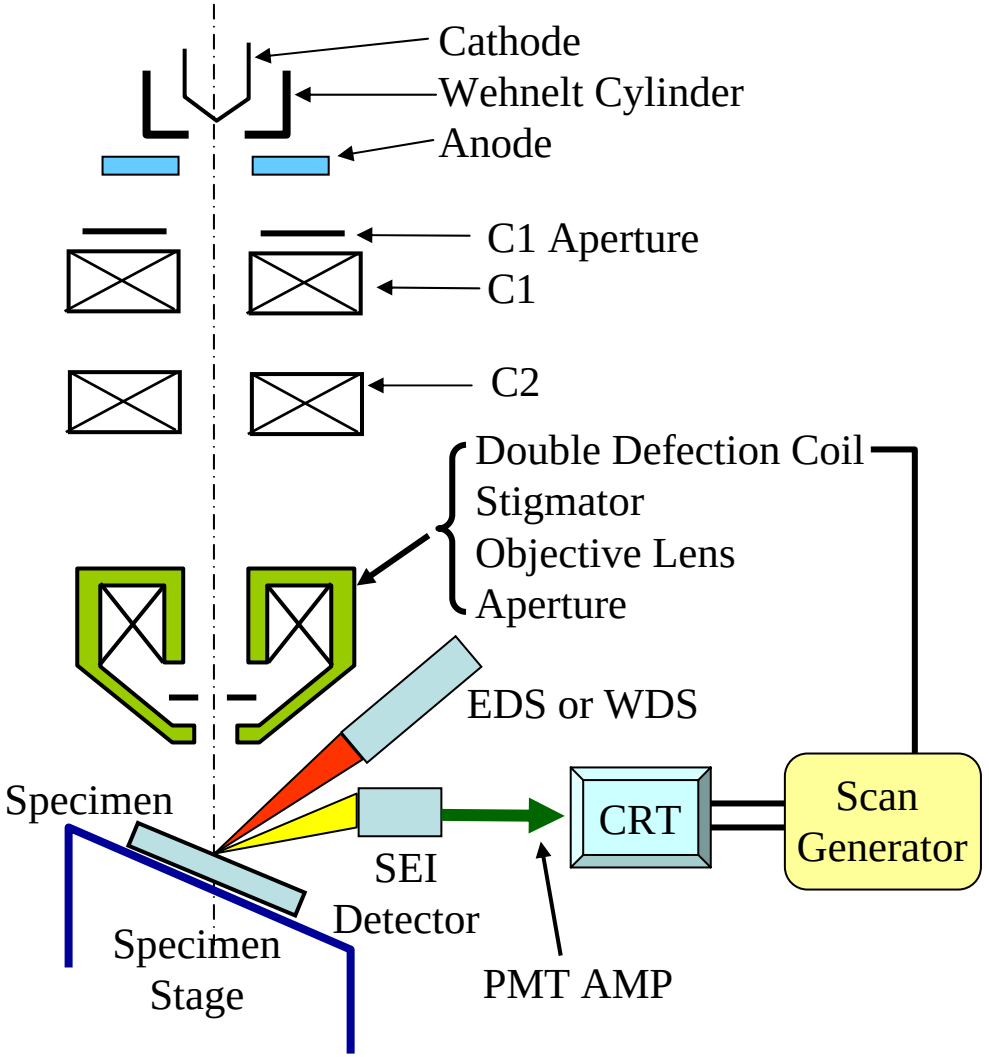
EELS or GIF



CBED

STEM+BF, HAADF →Mapping and Z-contrast image

Lens System of SEM



Scanning electron microscopy – microprobe

Beam/specimen interaction: When the specimen is thick, "semi-infinite".
Monte Carlo simulation

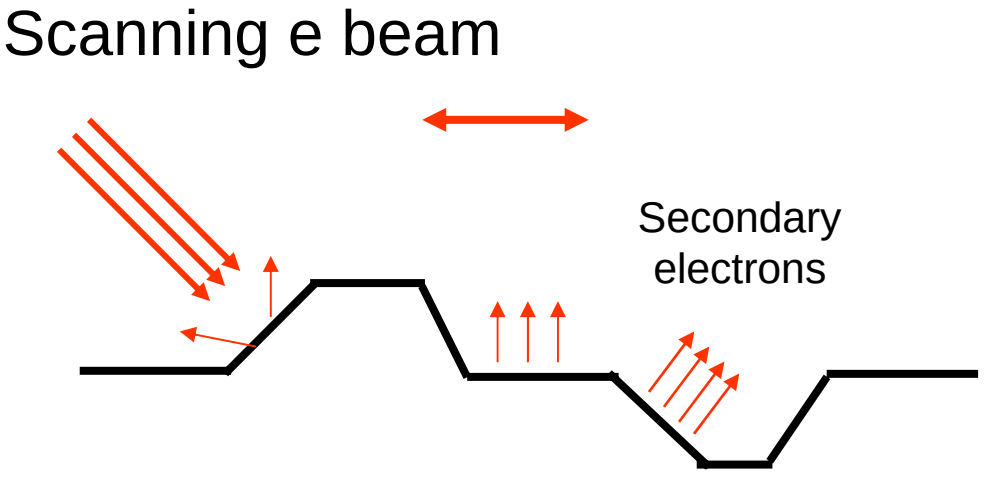
The probe forming system: (vg)
Forming a small probe is the same as forming a small spot in the image
The column

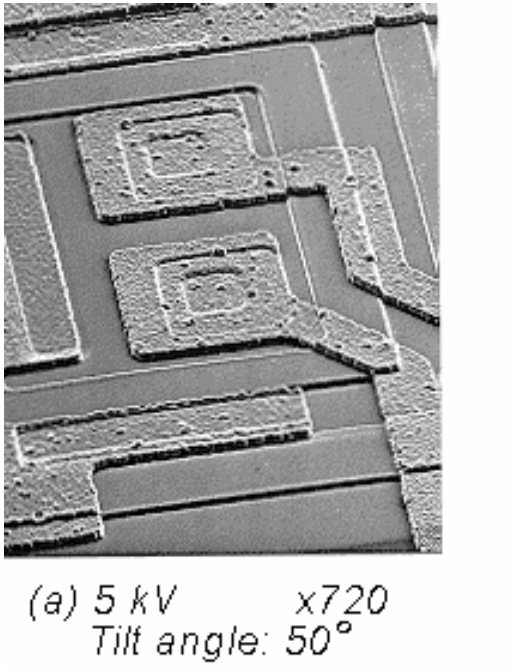
Contrast mechanism:
Secondary electrons
Back scattered electrons
Other signals

Resolution:
Low mag: limited by scan rate
High mag: limited by lens defects – same as TEM

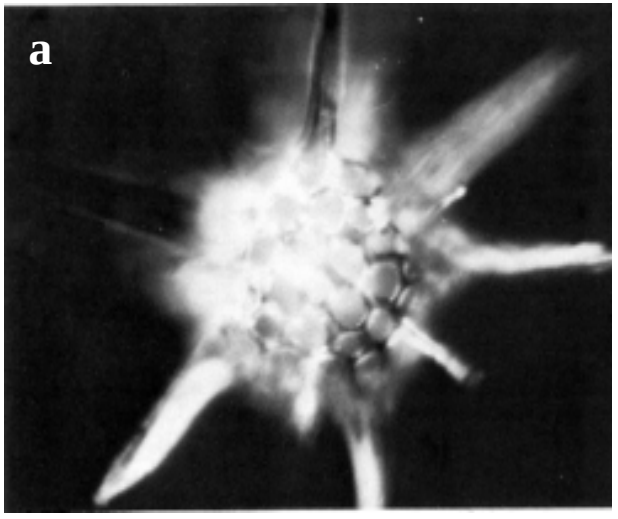
Detector

Contrast mechanism for SEM





Depth of Field or Depth of Focus



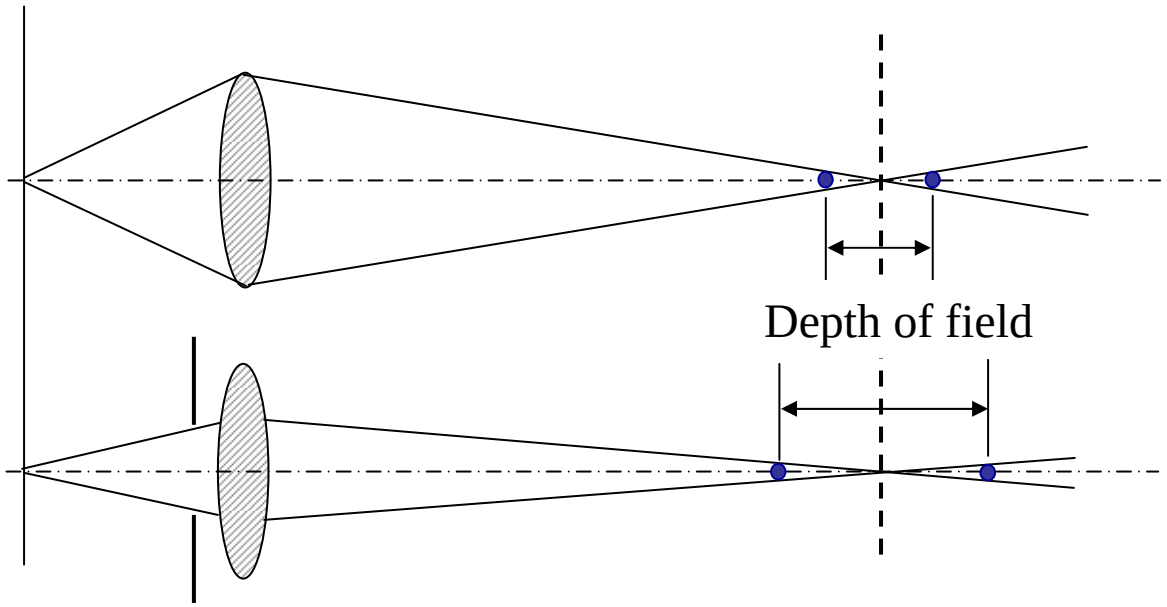
OM image

SEM image

How to increase the depth of focus of SEM image

Smaller α

(1) use smaller OBJ aperture
(2) increase Working Distance



SEM

TEM

E (kV)	10	20	30	100	200	400
λ (A)	0.122	0.0859	0.0698	0.037	0.025	0.0126
Cs (mm)		10-20			1-3	

Resolution: beam size

$r = \lambda^{3/4} Cs^{1/4}$

image point size

$r = \lambda^{3/4} Cs^{1/4}$

The instruments and techniques

- **Stationary Electron Beam**

-- **TEM: CTEM SAD/BF/CDF/WBDF, HRTEM**

-- **AEM: CBED, NBD, EDS, EELS, and EFTEM**

- **Scanning Electron Beam**

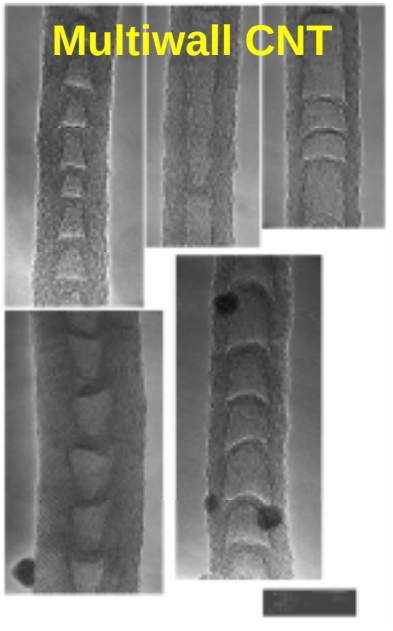
-- **STEM (BF, DF, and HAADF)**

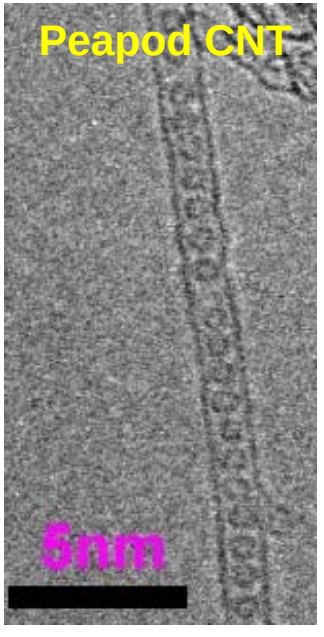
-- **SEM (SEI, BEI)**

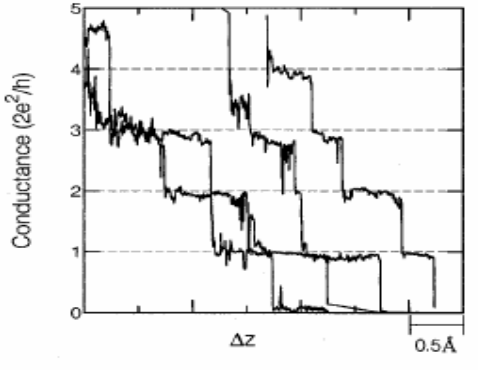
-- **SEM + WDS = EPMA**

- **Modern TEMs are all capable of HR works, but for some analytic works, attachments such as EDS and EELS must be added.**

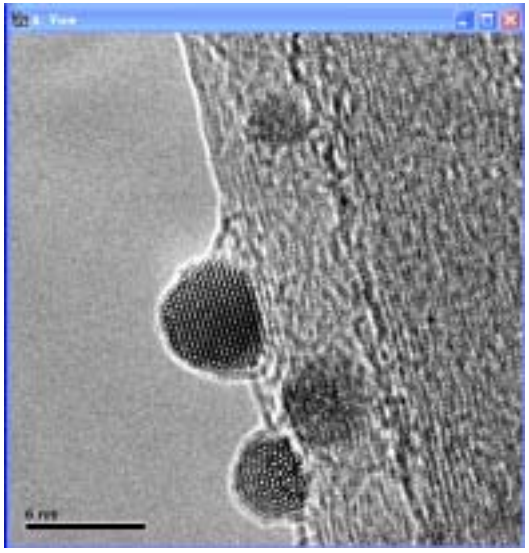
In situ studies with UHV HRTEM

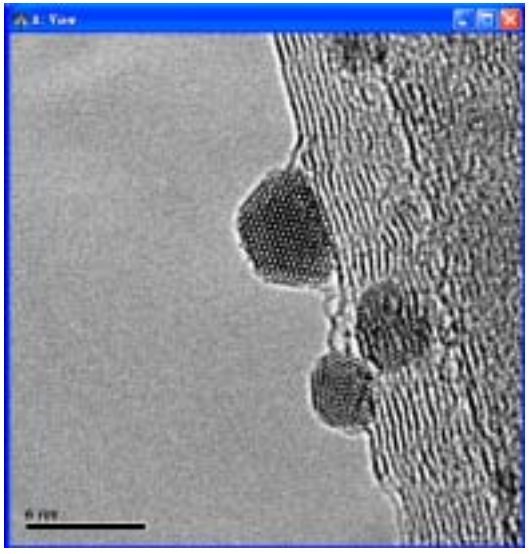


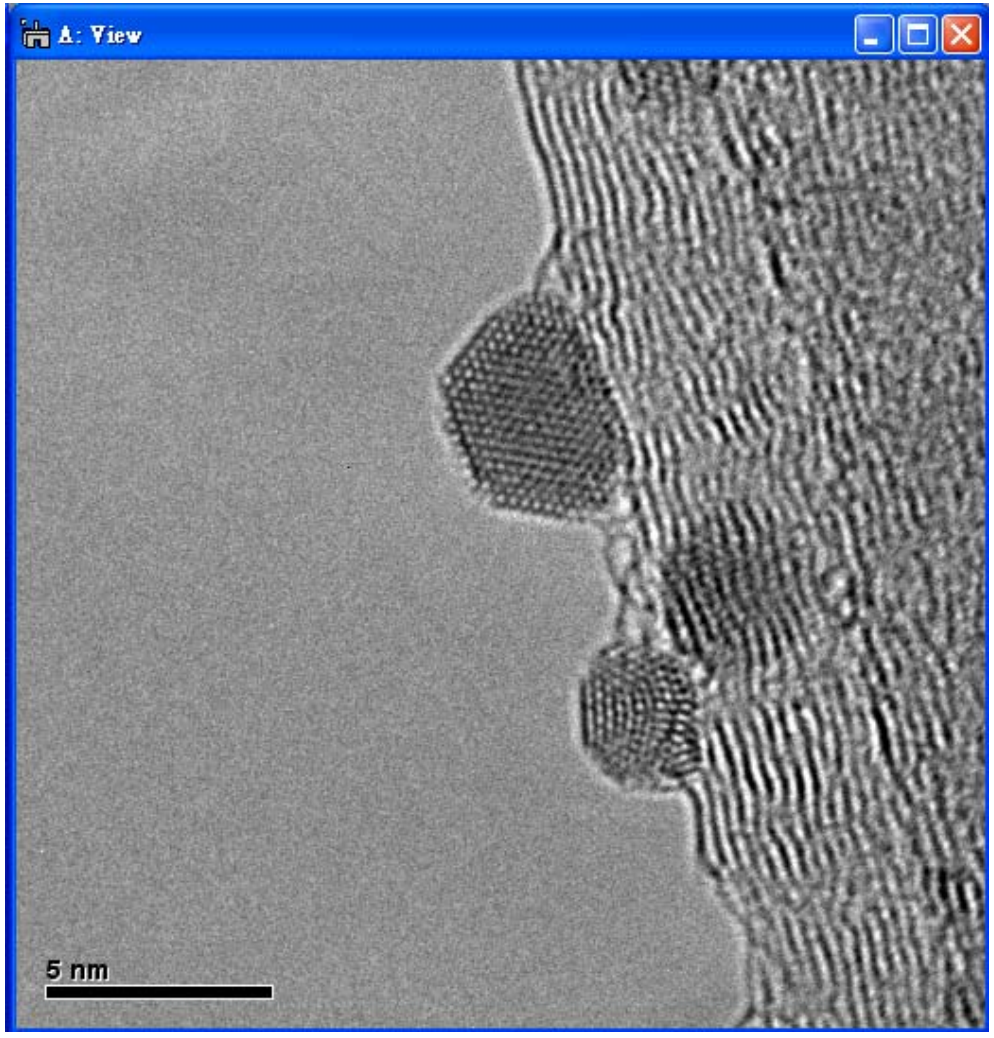




Atomic motion and recrystallization

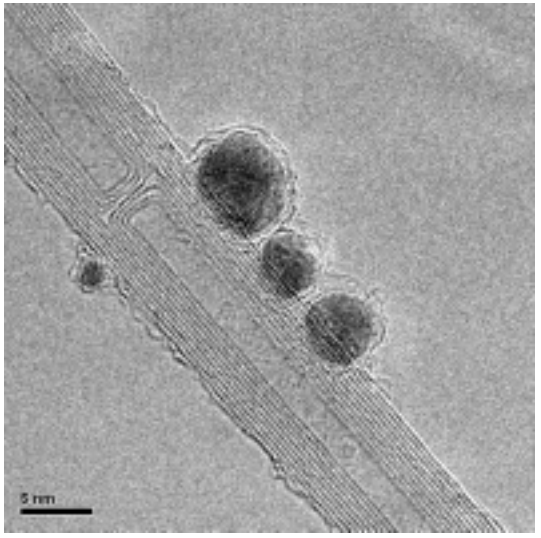


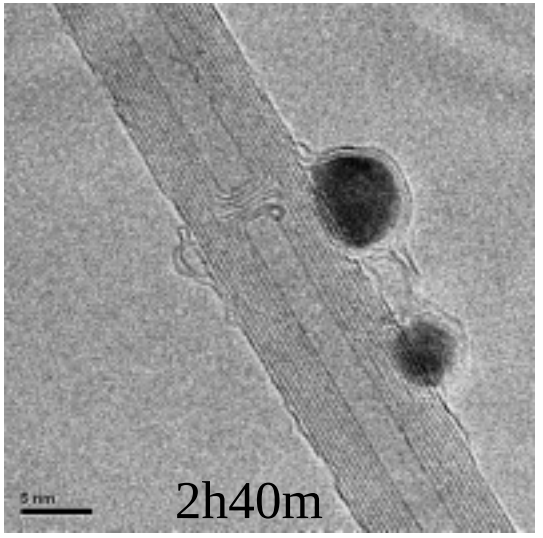


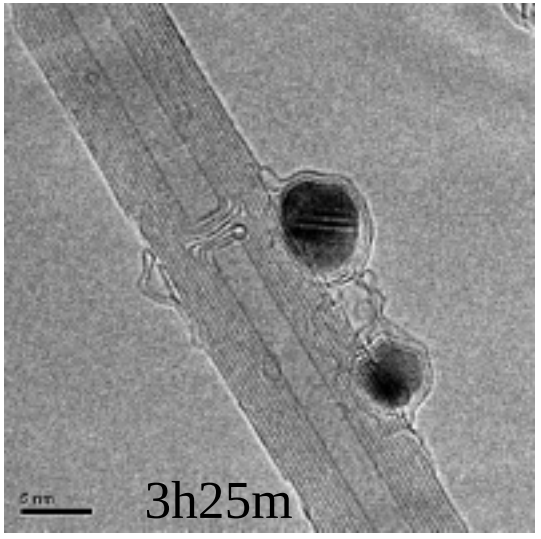


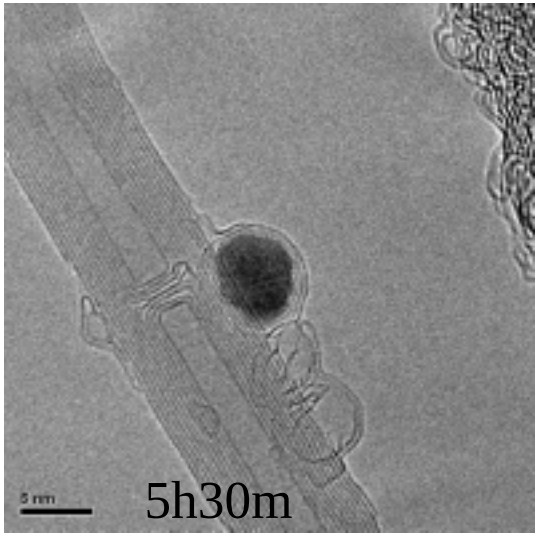
Ag clusters as catalyses

479°C

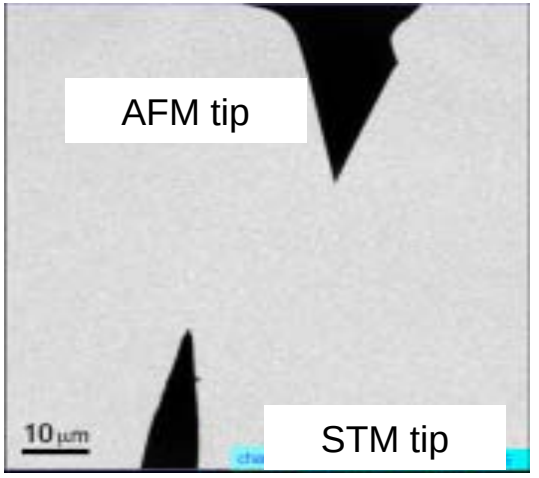


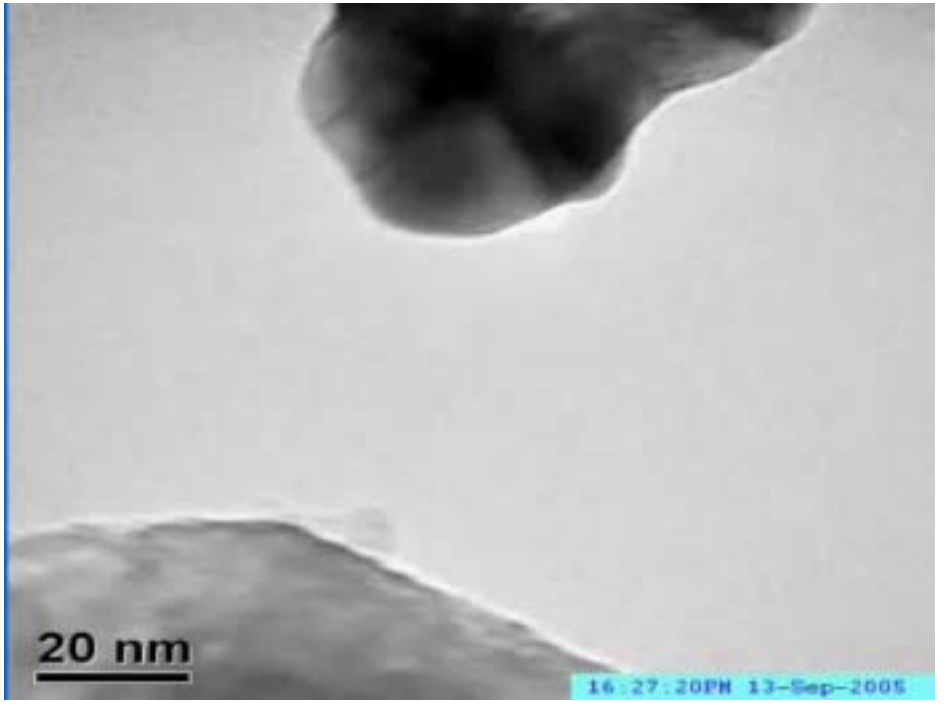


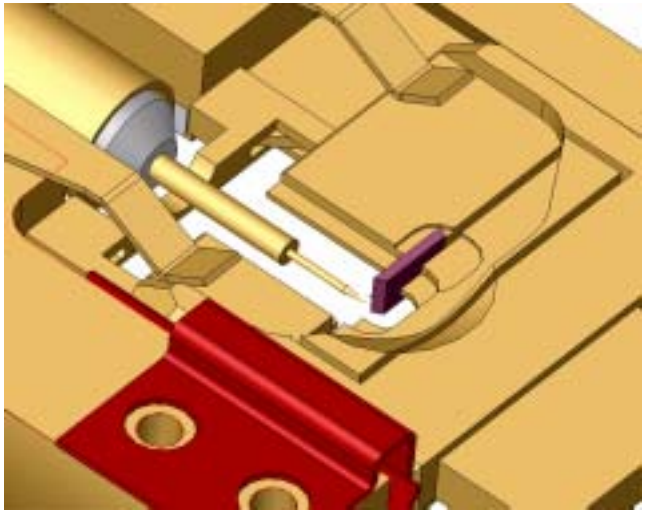




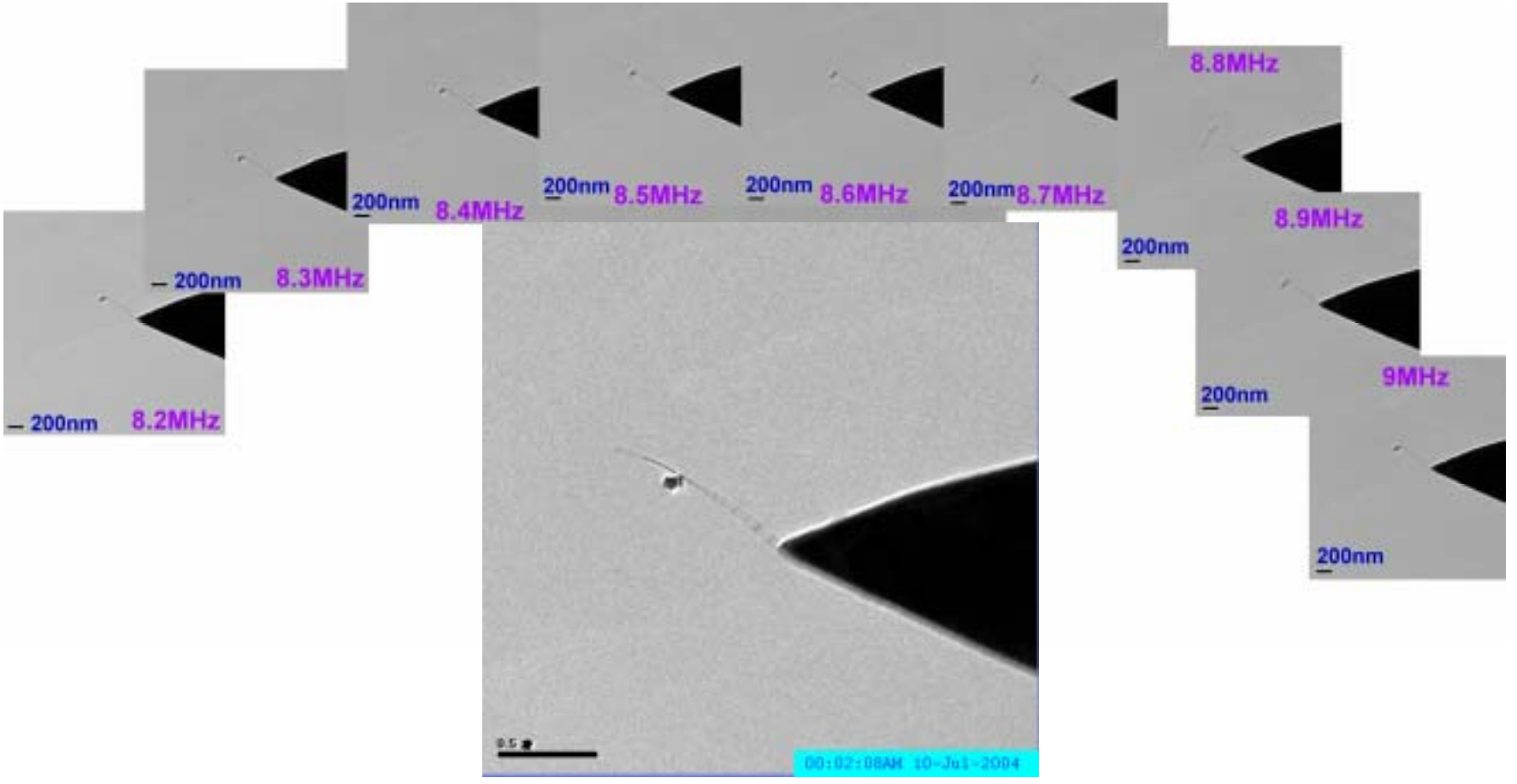
STM tip and AFM probe under TEM



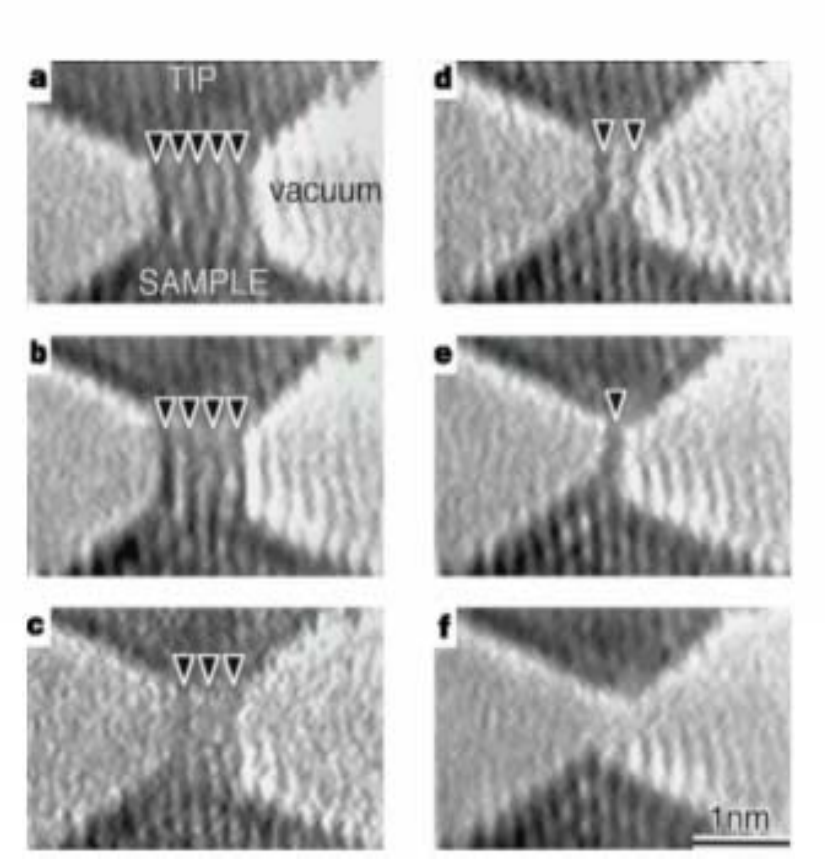


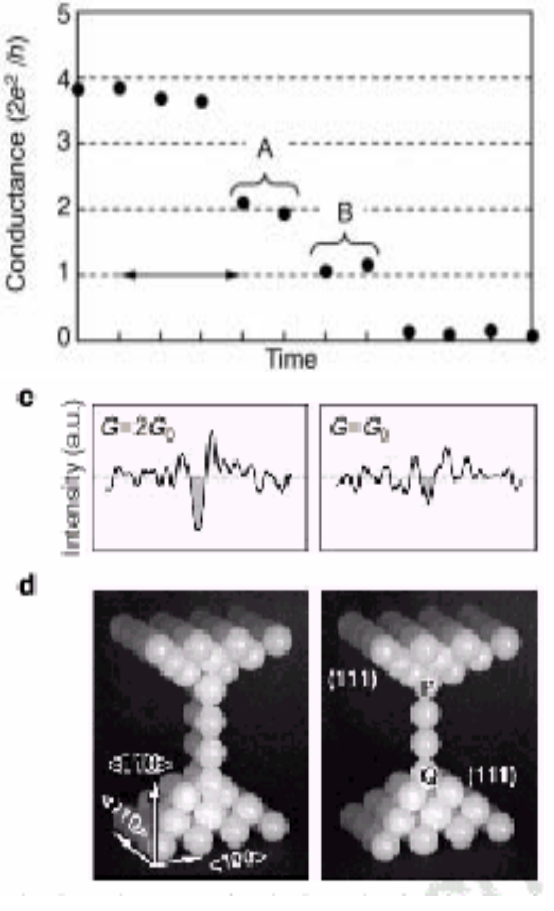


Electromechanical Resonator



Point contact of Au wire





Electrowetting