NTNU
Norwegian University of Science and Technology

TMT4320 Nanomaterials
Sptember 21st, 2016

- Characterization of nanomaterials: TEM, SEM, XPS

Outline

- Introduction to Electron Microscopy
- Transmission Electron Microscopy (TEM)
- Scanning Electron Microscopy (SEM)
- X-Ray Photoelectron spectroscopy (XPS)

What is Nano Characterization?

- What do nanomaterials look like?

  Dimensions, structure

- What are nanomaterials made of?

  Chemical composition, elemental proportions

- What are the properties of nanomaterials?
  - Physical, chemical, electromagnetic

Introduction to Electron Microscopy (EM) (1)

What is microscopy?

- Microscopy is any technique for producing visible images of structures or details too small to be seen by the human naked eye.

Introduction to Electron Microscopy (EM) (2)

Electron microscopes (EM)

Light (optical) Microscope

Scanning Electron Microscopes (SEM)

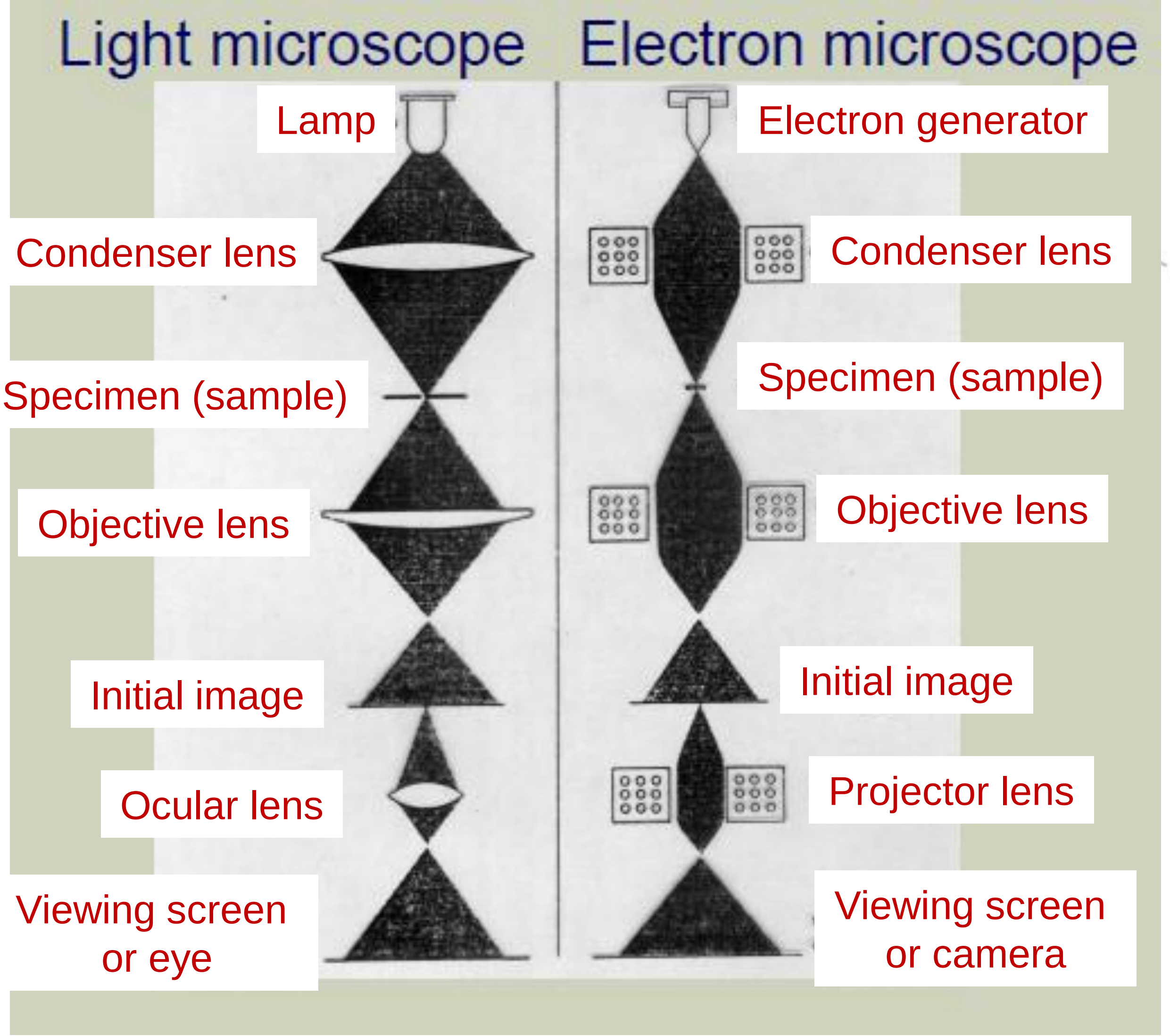
Transmission Electron Microscopes (TEM)

Electron Microscopy (EM)

Definitions

- Electron microscopes are specially designed to allow the interaction of a high energy electron beam with the sample as a means to explore/study a material’s structure
- Electron microscopes have a greater resolving power than light microscopes, making possible to see sub-nanometer objects in finer details

Similarity light - electron microscope (EM)



Why we use Electrons?

1. Easy to produce high brightness electron beams (heating a metal surface such as tungsten)

2. Electrons are easy to manipulate

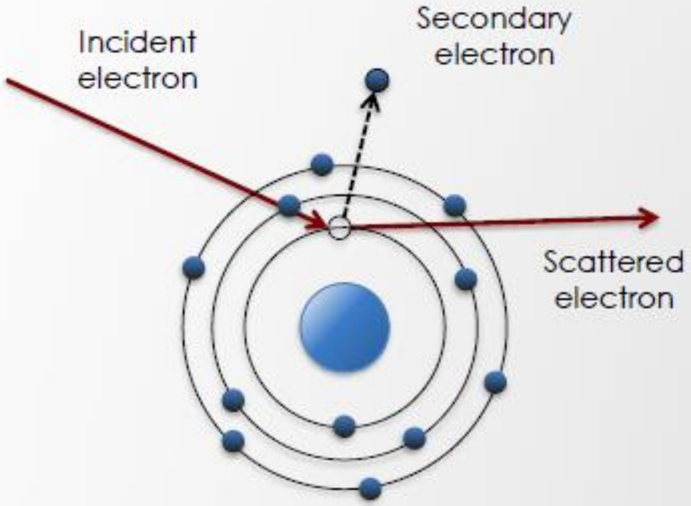
3. High energy electrons have a short wavelength (*see Nanostructures and Nanomaterials pp 441-445*)

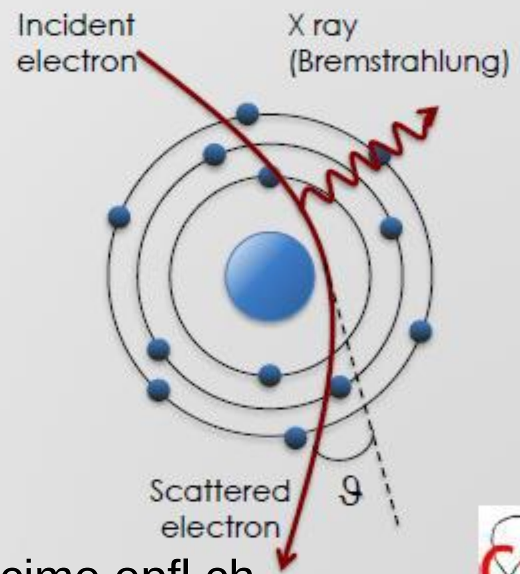
4. Interact strongly with matter

Interaction of electrons with matter

Inelastic Scattering

- An incident electron ejects a bound electron and scatters with an energy lowered by the electron bound energy.
- The ejected electrons having low energies (5-50 eV) are called secondary electrons (SE) and carry information about the surface topography
- The incident electron can be scattered by Coulomb interaction with the nucleus
- In the case of inelastic interaction, there is **energy transfer**, and the target atom can be ionized





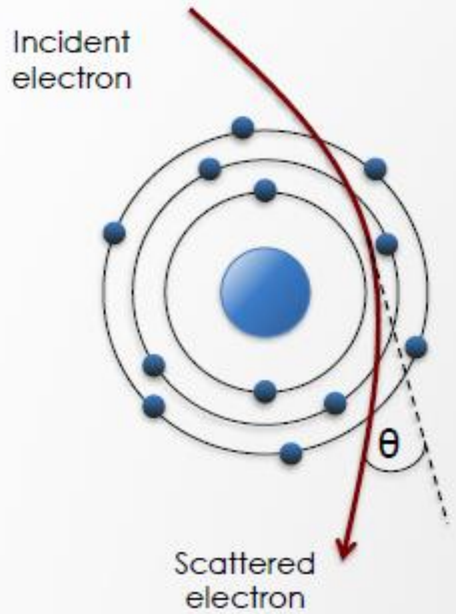
Thomas LaGrange, (April 2016) Slides available at http://cime.epfl.ch

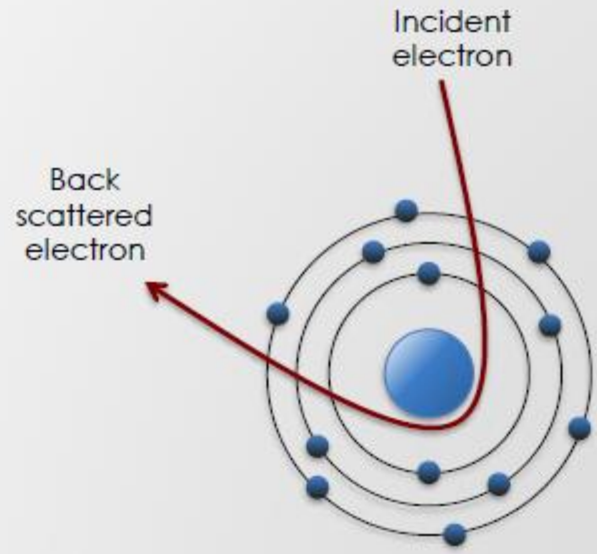
Interaction of electrons with matter

Elastic scattering

No energy transfer

- Low angle diffusion: Coulomb interaction with the electron cloud.
- High angle diffusion, or back scattering: Coulomb interaction with nucleus.
- Atom is not ionized.

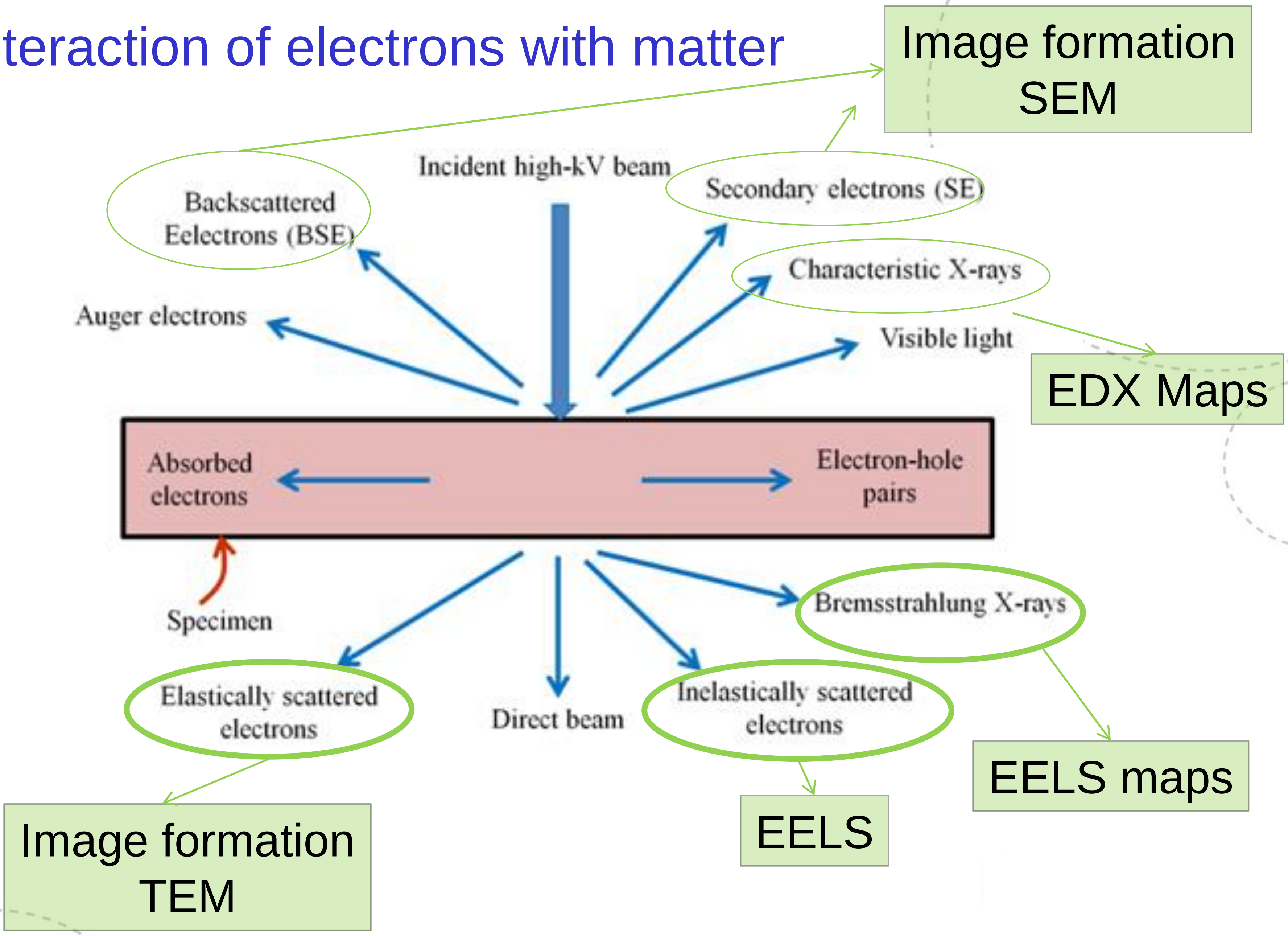




Rutherford scatter
Z-contrast

Thomas LaGrange, (April 2016) Slides available at http://cime.epfl.ch

Interaction of electrons with matter



Interaction of electrons with matter

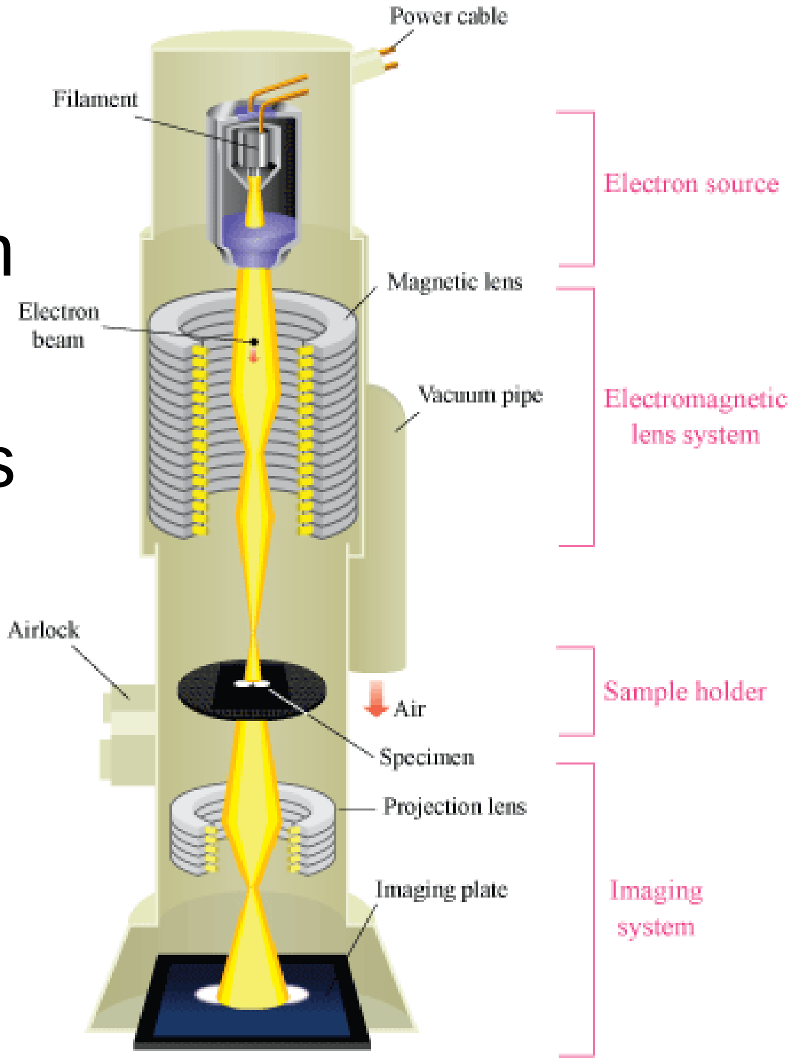
Definitions

❖ Secondary electrons (SE): electrons generated as a result of the ionization of the specimen atoms. SE are generated as a consequence of other radiations such as ions, electrons or photons with sufficiently high energy to produce the ionization.

❖ Backscattered electrons (BSE): high-energy electrons originating from the electron beam, that are reflected or back-scattered out of the specimen interaction volume by elastic scattering interaction with specimen atoms.

Transmission Electron Microscopy TEM

- ❖ A beam of electrons is transmitted through an ultra thin Specimen (sample)
- ❖ Sample preparation depends on the type of the material.
- ❖ The sample should allow electrons to pass through

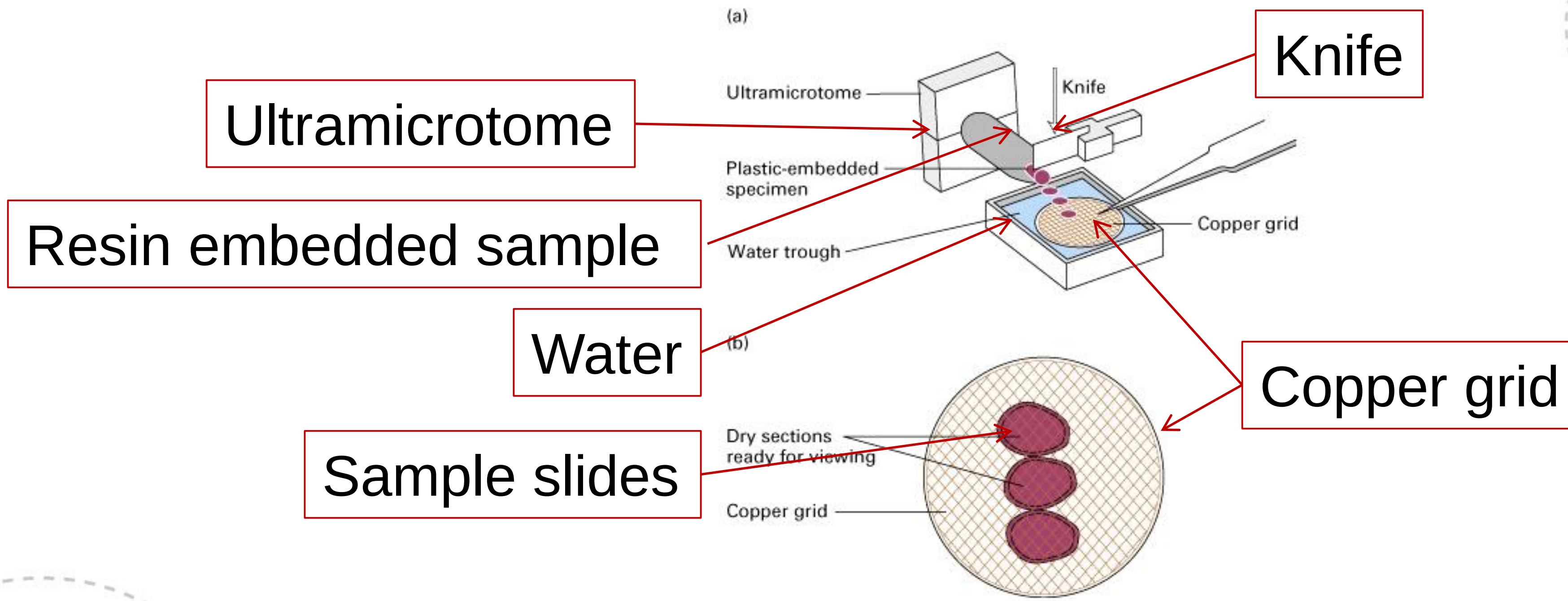


http://www.hk-phy.org/atomic_world/tem/tem02_e.html

Sample preparation for TEM imaging examples

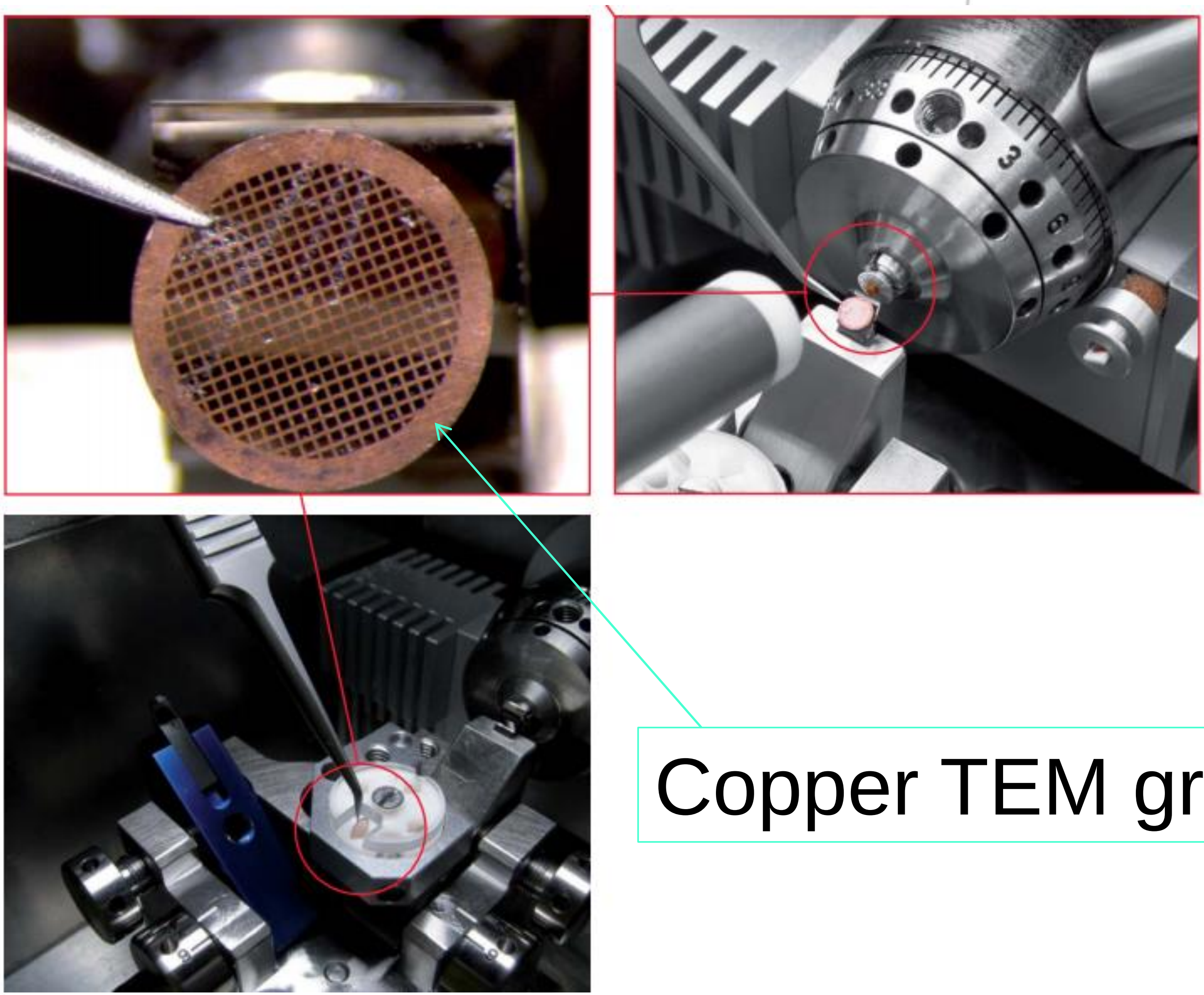
Preparation of thin films for TEM imaging

- Sample thickness < 100 nm
- The sample undergoes the following steps
  - It is embedded in a specific resin
  - It is cutted in ultrathin slides using an ultramicrotome
  - It is deposited on a copper grid

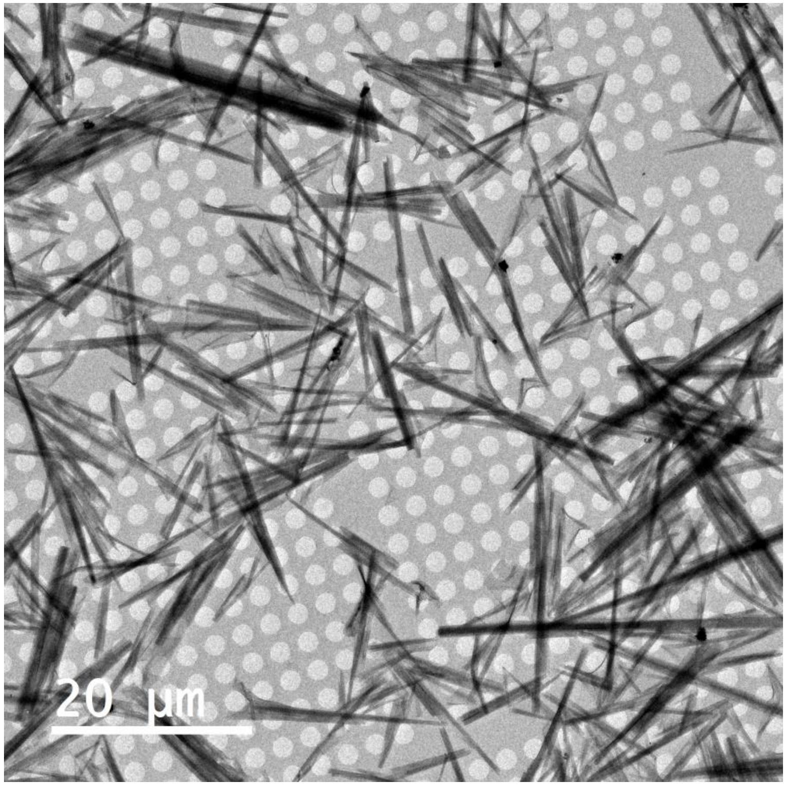


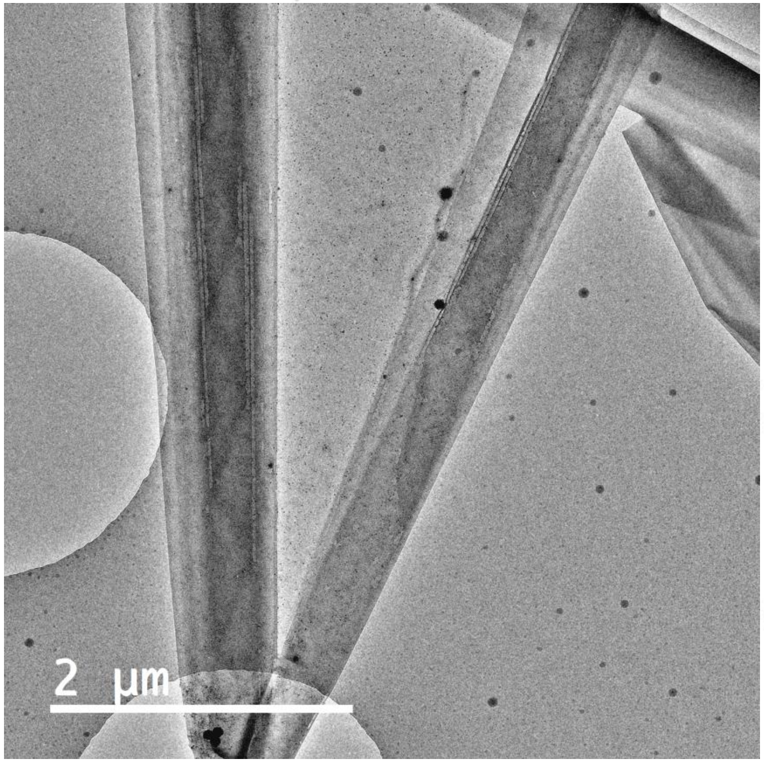
http://www.pha.jhu.edu/~ghzheng/old/webct/note1_4.htm

Leica microsystems



Copper TEM grid





Low Magnification TEM images of carbon nanoscrolls

Higher magnification

M. Benelmekki and JH. Kim (submitted paper)

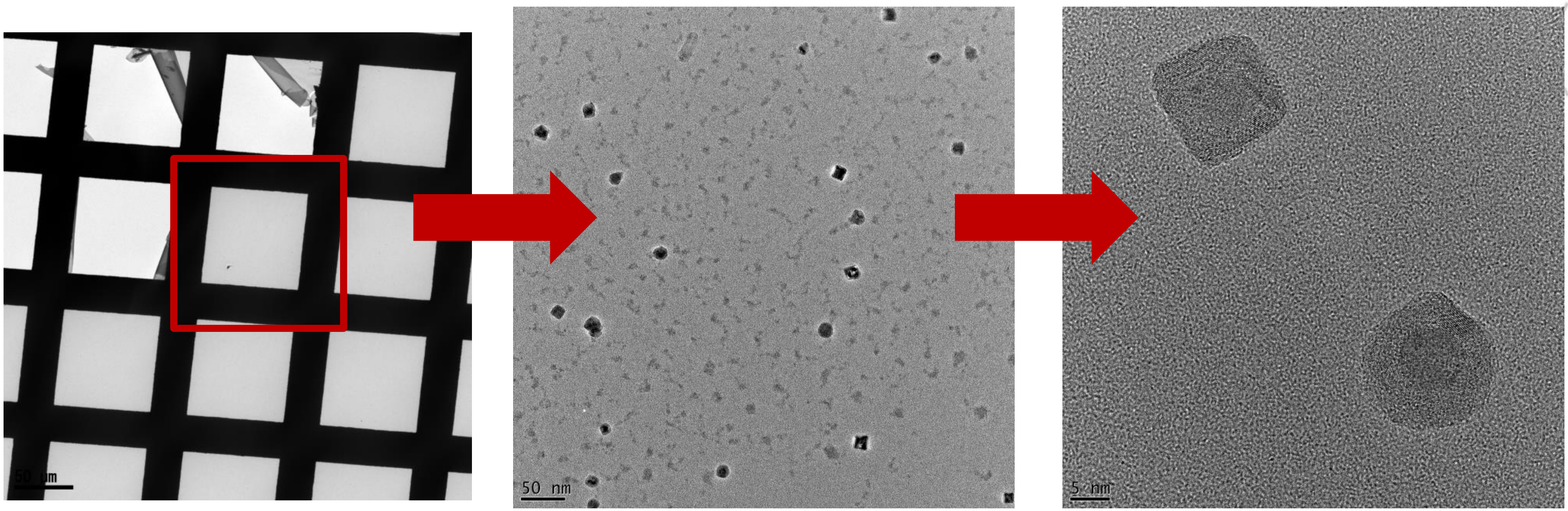
Preparation of nanoparticle sample

- NPs in suspension:

Suspension is dropped on TEM grid and the grid is tried

- Vapour phase deposition:

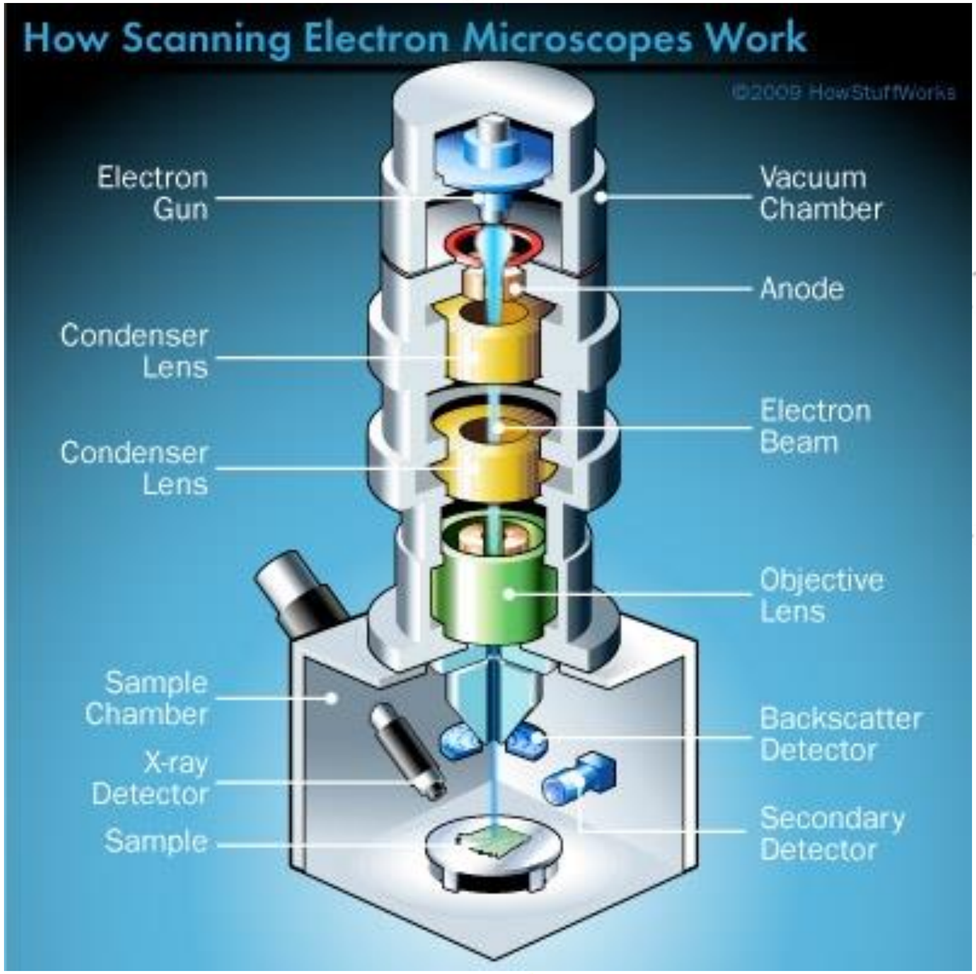
NPs are deposited directly on TEM grid



Scanning Electron Microscopy SEM

❖ Image formation is because of the secondary and back-scattered Electrons

❖ Samples are dehydrated and made conductive.



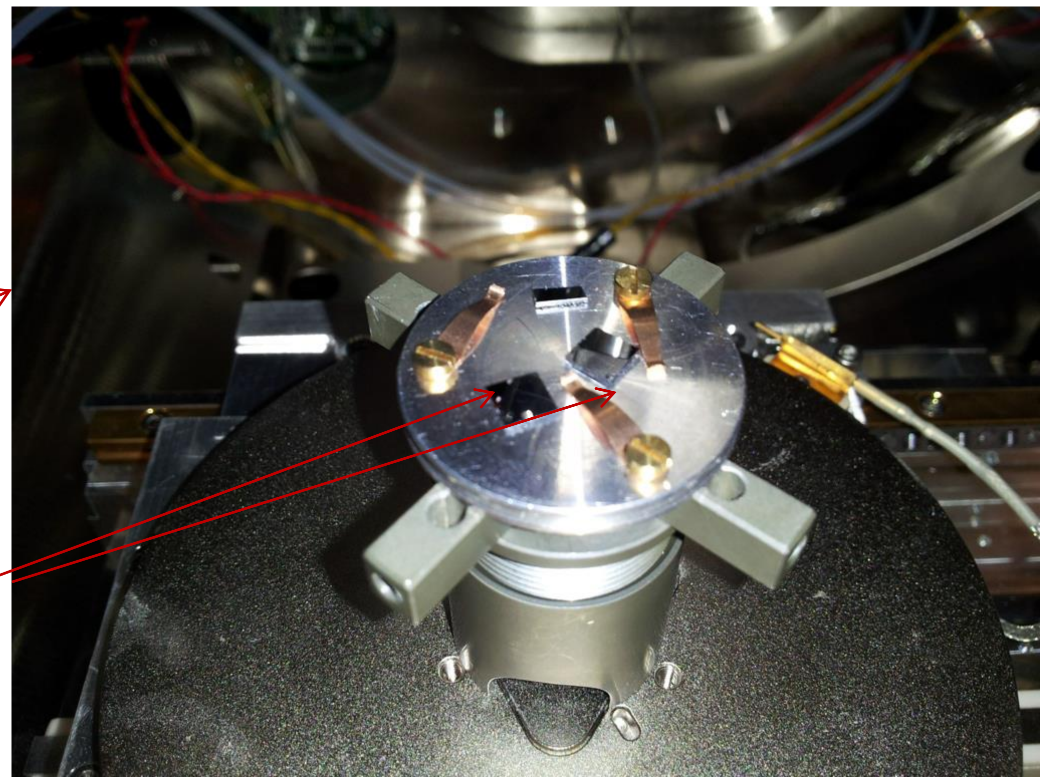
http://science.howstuffworks.com/scanning-electron-microscope2.htm

Sample preparation and example

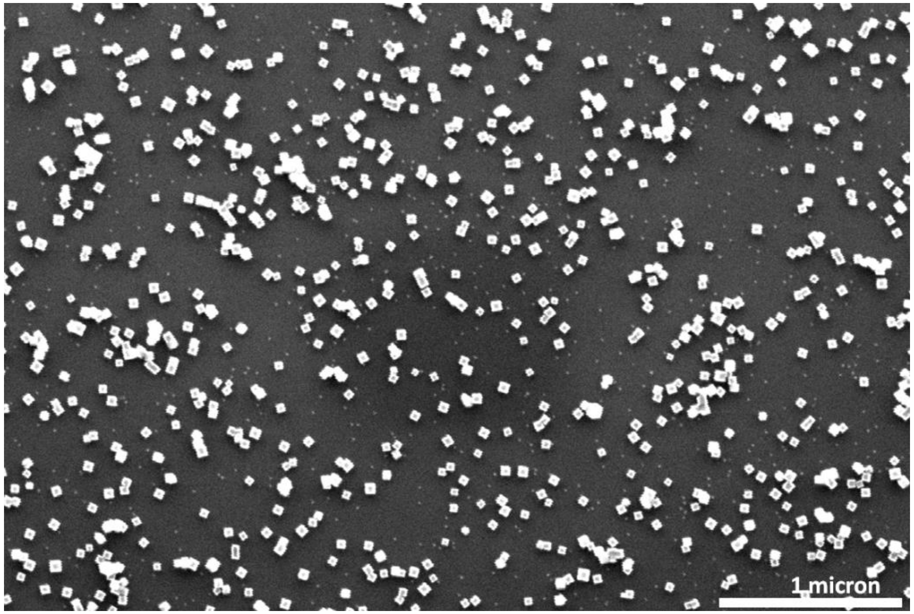
- Film imaging doesn’t require any special preparation
- Suspension of NPs is dropped on the surface of a solid substrate
- Substrates are preferably conductive to avoid charging effects

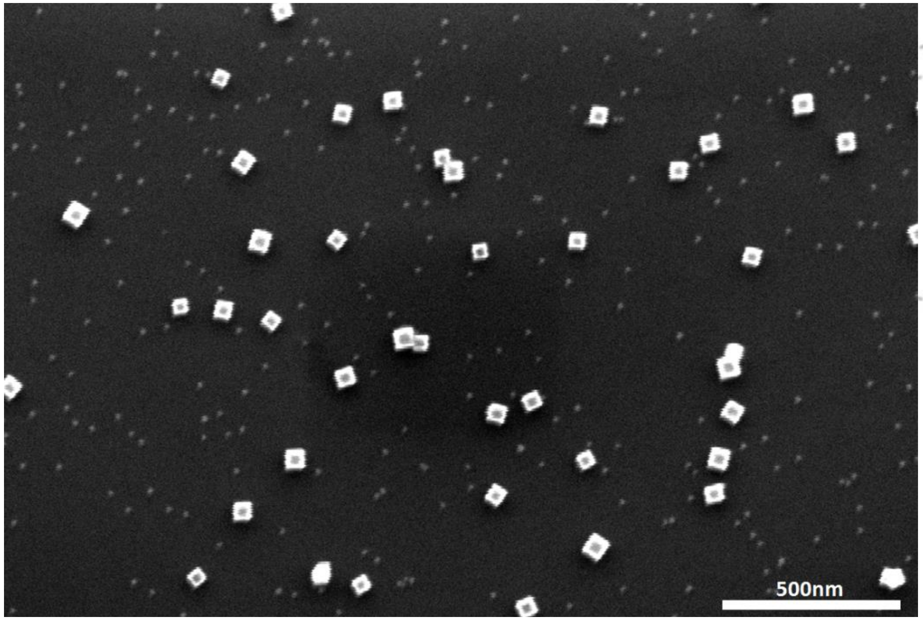
SEM chamber

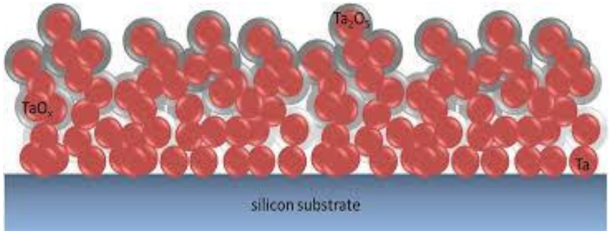
NPs deposited on Si Substrates



SEM images of Fe Nanoparticle deposited on Silicon (Si) substrate

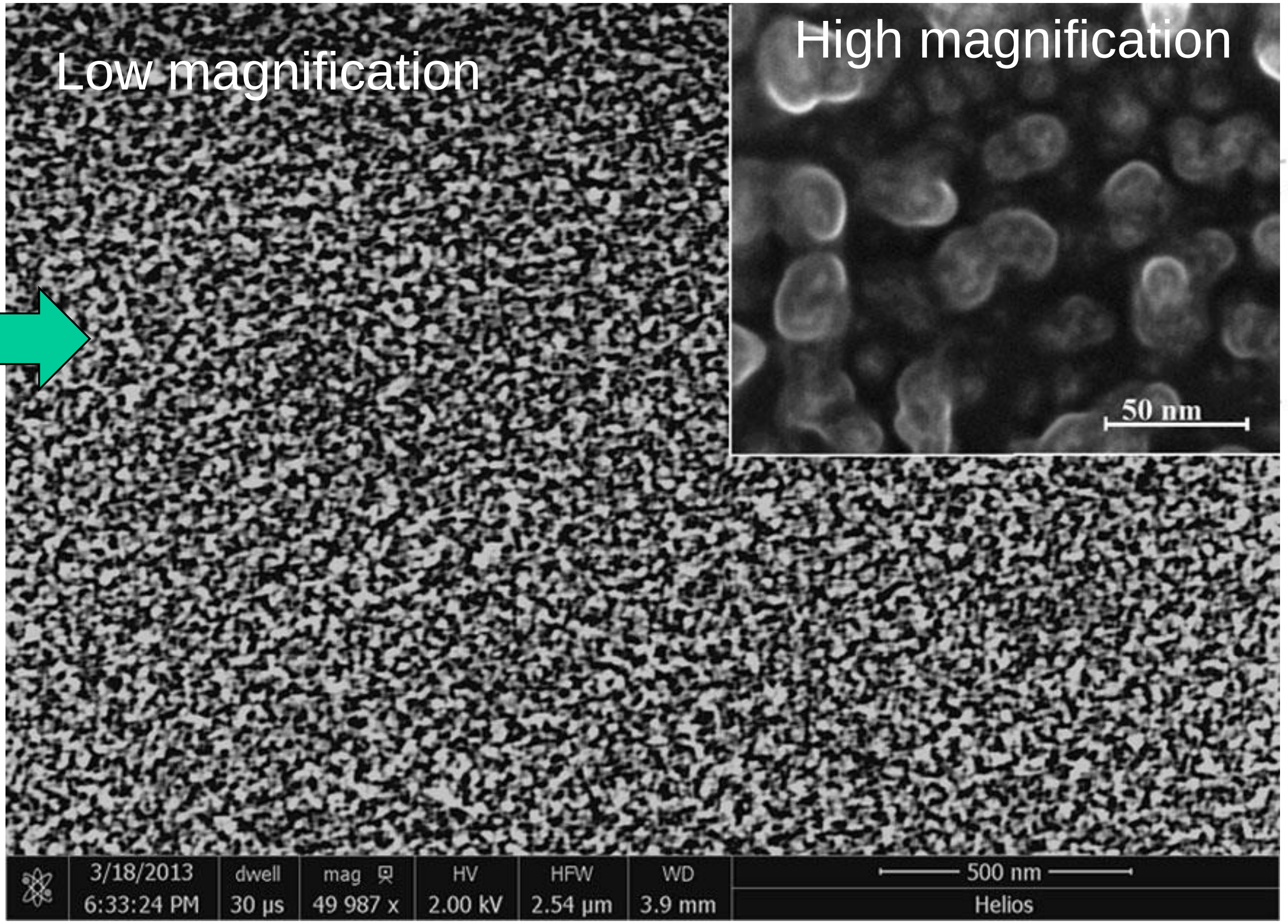






SEM images of porous Tantalum (Ta) film

Film deposited
from Ta NPs
Using magnetron-
Sputtering inert-gas-
condensation



J Nanopart Res (2014) 16:2373

Introduction to X-Ray Photoelectron Spectroscopy (XPS)

Definition

- XPS is a surface-sensitive spectroscopic technique that measures quantitatively:
  - The elemental composition of the material,
  - Chemical states and electronic states of the elements within the material
- XPS technique operates at Ultra-High-Vacuum (UHV) $\leq 10^{-9}$ Torr

How it works?

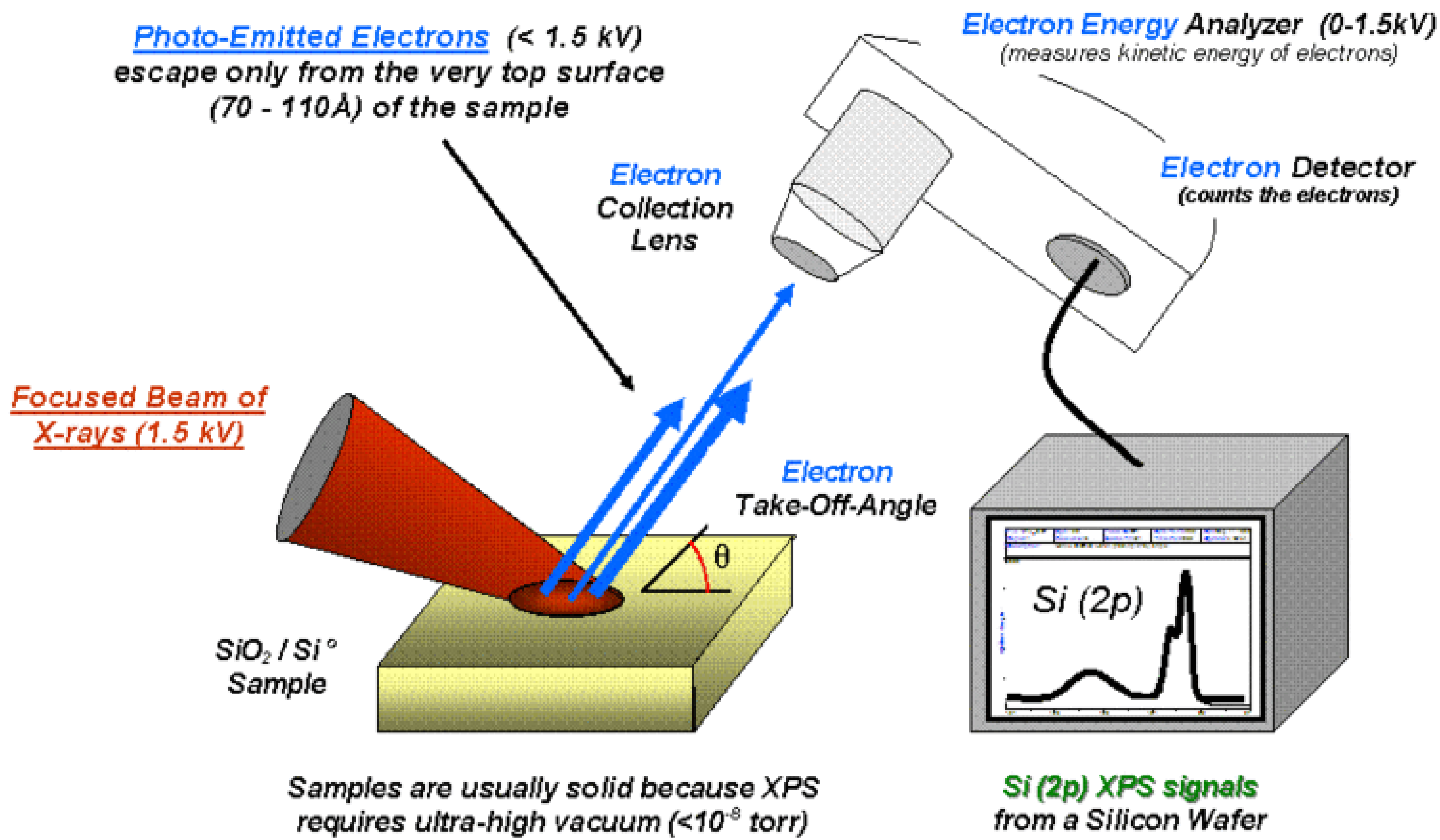
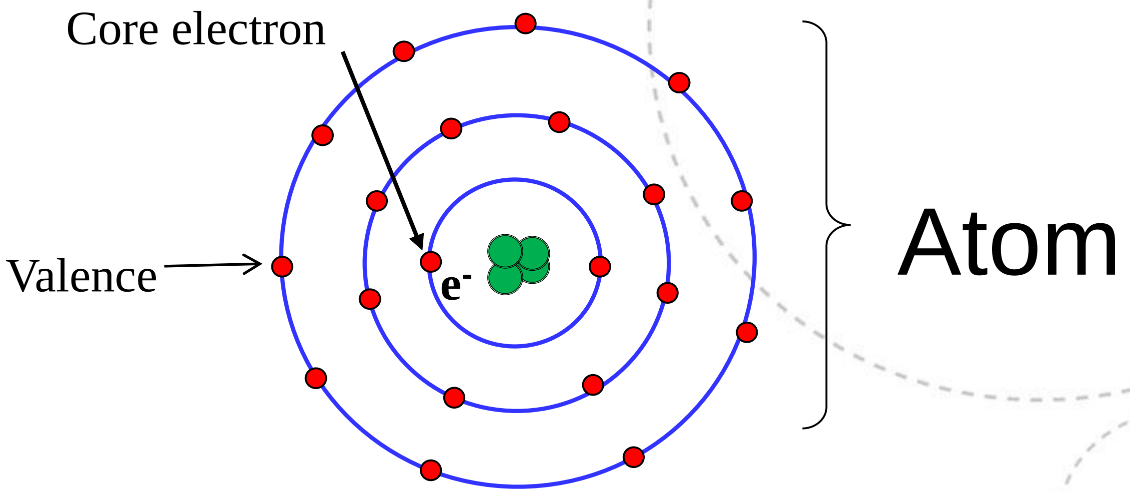


Photo-Emitted Electrons (< 1.5 kV)
escape only from the very top surface
(70 - 110Å) of the sample
Electron Energy Analyzer (0-1.5kV)
(measures kinetic energy of electrons)
Electron Collection Lens
Electron Detector
(counts the electrons)
Focused Beam of X-rays (1.5 kV)
Electron Take-Off-Angle
θ
SiO2 / Si°
Sample
Si (2p)
Samples are usually solid because XPS requires ultra-high vacuum (<10-8 torr)
Si (2p) XPS signals from a Silicon Wafer

How it works?

- ✓ The X-Rays irradiate the sample surface, hitting **the core electrons (e^-) of the atoms**
- ✓ The X-Rays penetrate the sample to a depth on the order of a micrometer
- ✓ Useful e^- signal is obtained only from a depth of around 1 to 10 nm on the surface.
- ✓ The X-Ray source produces photons with specific energies:
  - MgKα photon with an energy of 1253.6 eV
  - AlKα photon with an energy of 1486.6 eV
- ✓ Normally, the sample will be irradiated with photons of a single energy (MgKα or AlKα). This is known as a monochromatic X-Ray beam.

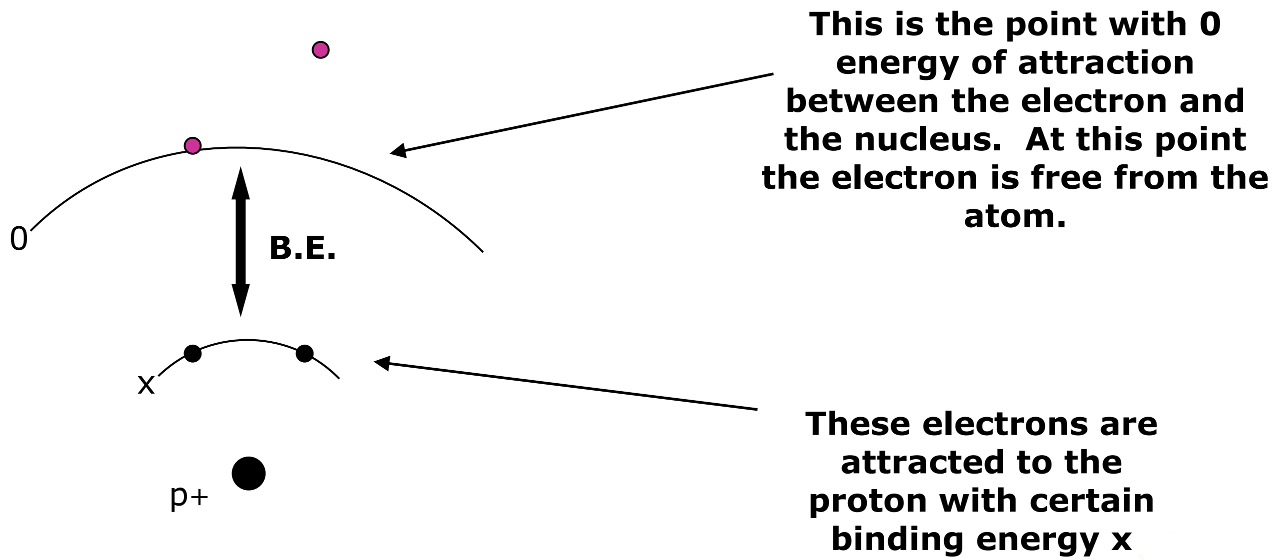
Why the Core Electrons?



- The core electrons are local close to the nucleus and have Binding Energies (BE) characteristic of their particular element.
- An electron near the Fermi level is far from the nucleus, moving in different directions all over the place, and will not carry information about any single atom.
- The core e-s have a higher probability of matching the energies of AlKα ((1486.6eV) and MgKα (1253.6 eV)

Binding Energy (BE)

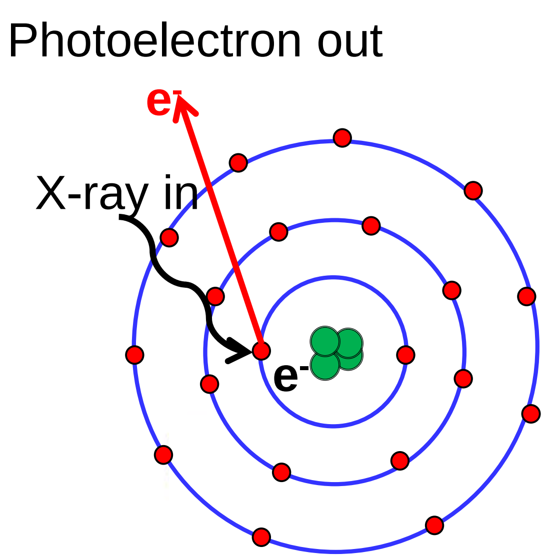
The Binding Energy (BE) is characteristic of the core electrons for each element. The BE is determined by the attraction of the electrons to the nucleus. If an electron with energy x is pulled away from the nucleus, the attraction between the electron and the nucleus decreases and the BE decreases. Eventually, there will be a point when the electron will be free of the nucleus.



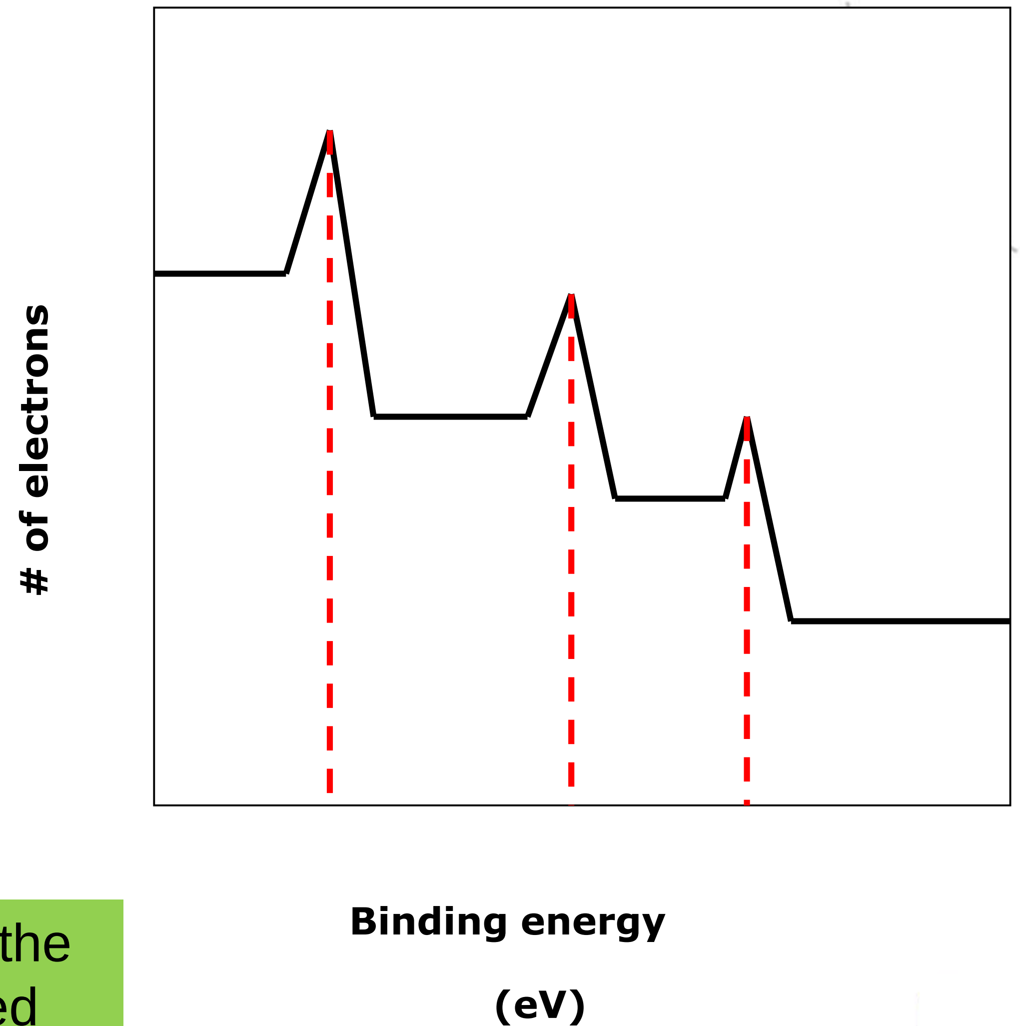
Equation

$$\boxed{\text{BE (eV)} = h\nu - \text{KE} - \phi}$$

- ✓ KE: Kinetic Energy (measure in the XPS spectrometer)
- ✓ hv: photon energy from the X-Ray source (controlled)
- ✓ Φ : spectrometer work function. It is a few eV, it gets more complicated because the materials in the instrument will affect it. Found by calibration.
- ✓ BE: is the unknown variable



What we obtain?

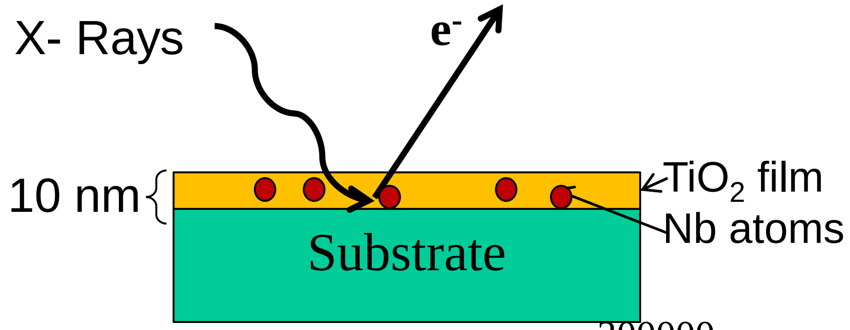


There are tables with the BE already assigned to each element.

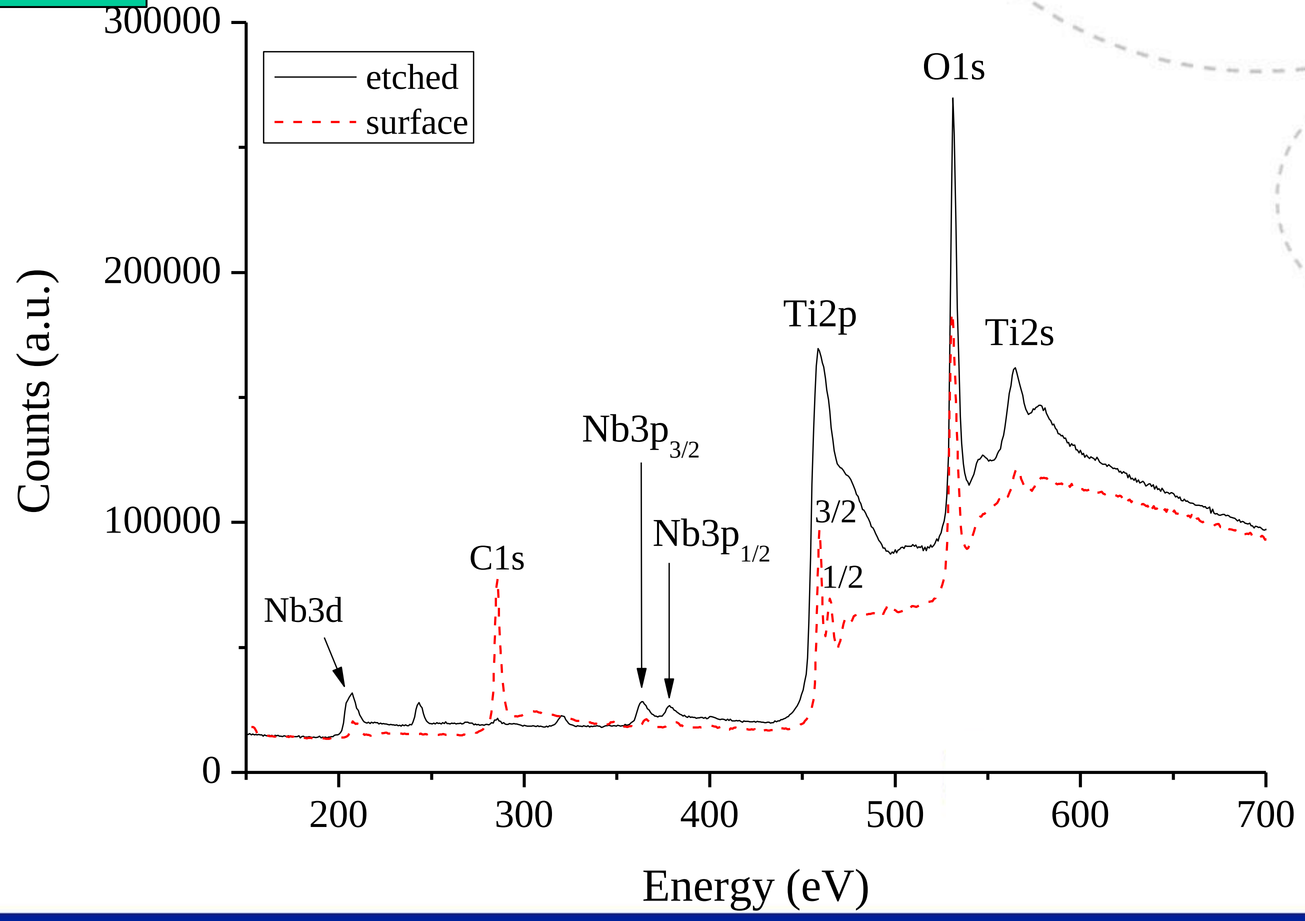
Why Does XPS Need Ultra High Vacuum (UHV)?

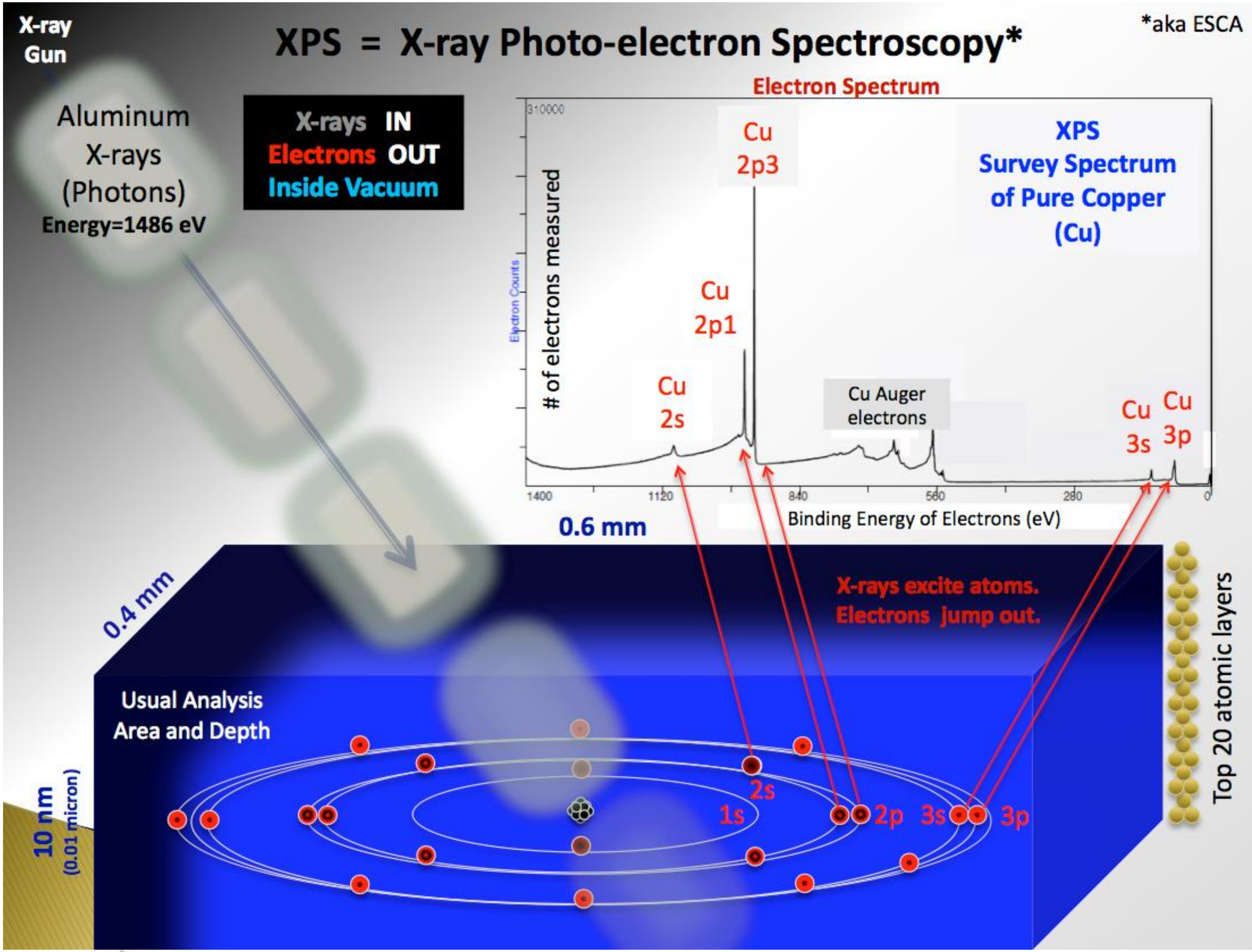
- Contamination of surface
  - **XPS is a surface sensitive technique** **(**Contaminates will produce an XPS signal and lead to incorrect analysis of the surface of composition).
- Analysis chamber pressure is $\leq 10^{-9}$ Torr
- Removing contamination
  - To remove the contamination the sample surface is etched with argon ions (Ar^+).
  - heat and oxygen can be used to remove hydrocarbons

Why Does XPS Need Ultra High Vacuum (UHV)?



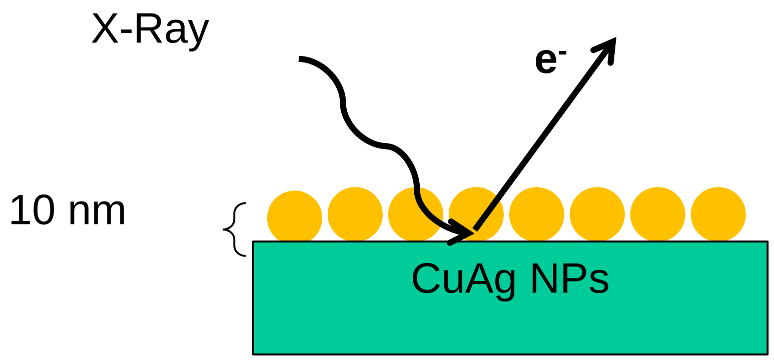
XPS spectra (surveys): TiO_2:Nb film on Si substrate; effects of Ar surface eaching





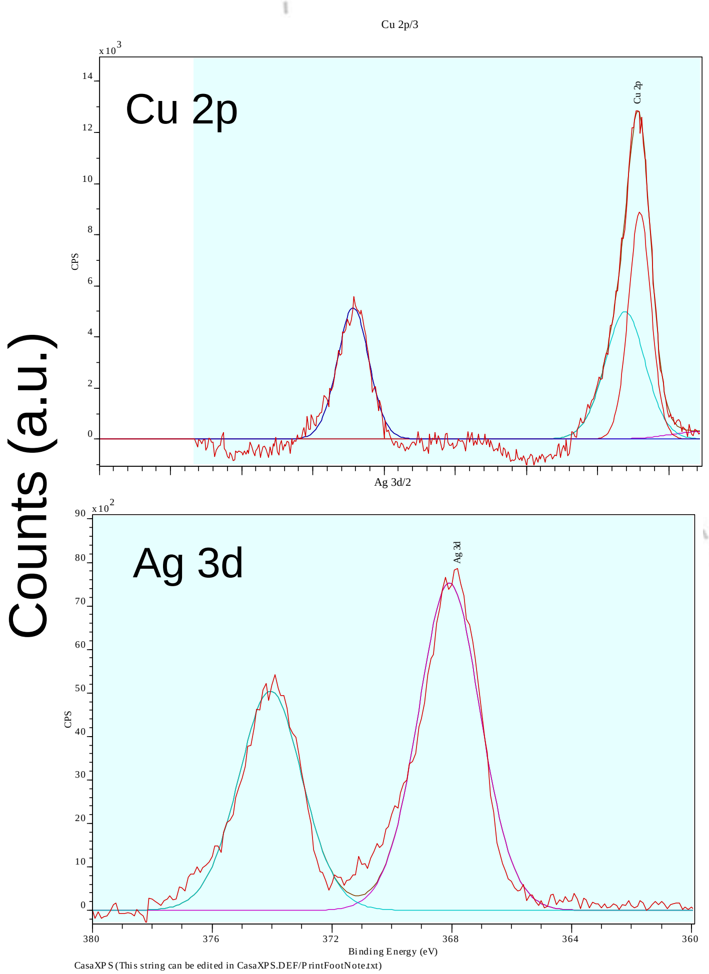
X-ray Gun
XPS = X-ray Photo-electron Spectroscopy*
*aka ESCA
Aluminum X-rays (Photons)
Energy=1486 eV
X-rays IN
Electrons OUT
Inside Vacuum
Electron Spectrum
310000
Cu 2p3
XPS Survey Spectrum of Pure Copper (Cu)
Cu 2p1
Cu 2s
Cu Auger electrons
Cu 3s
Cu 3p
# of electrons measured
Electron Counts
1400
1120
840
560
280
0
Binding Energy of Electrons (eV)
0.6 mm
0.4 mm
X-rays excite atoms.
Electrons jump out.
Usual Analysis Area and Depth
10 nm
(0.01 micron)
1s
2s
2p
3s
3p
Top 20 atomic layers

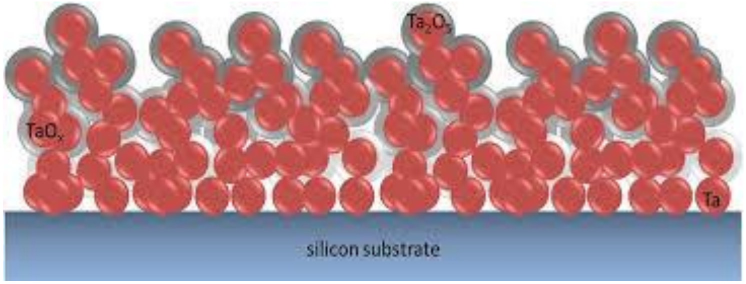
XPS & Chemical Composition (example)



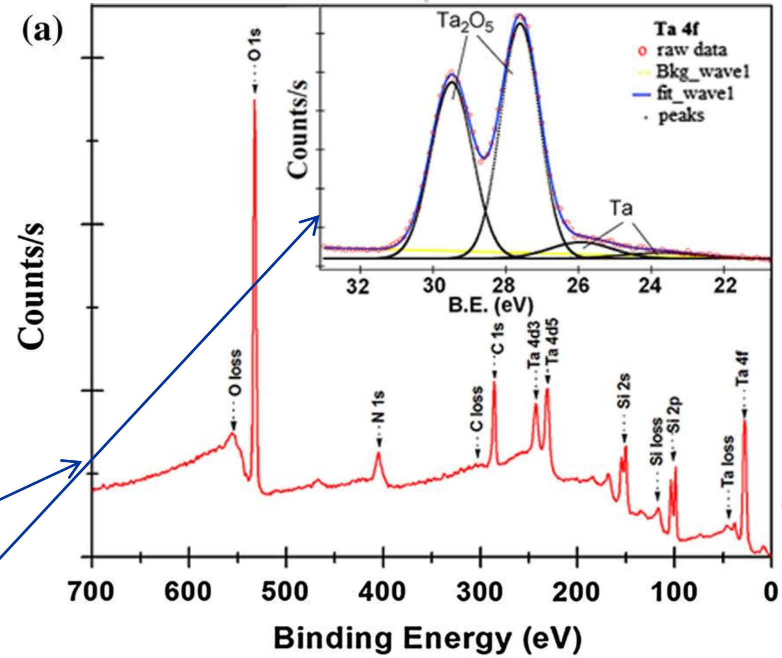
Analysing the peak area
of each material,
we can determine
the chemical composition of
the nanoparticles

Cu68Ag32 (atomic%)



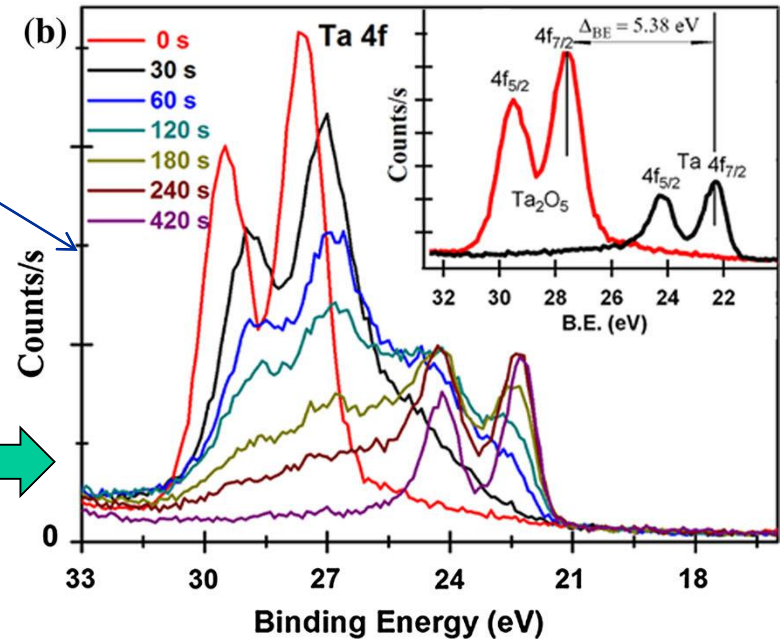


Ta film formed from NPs



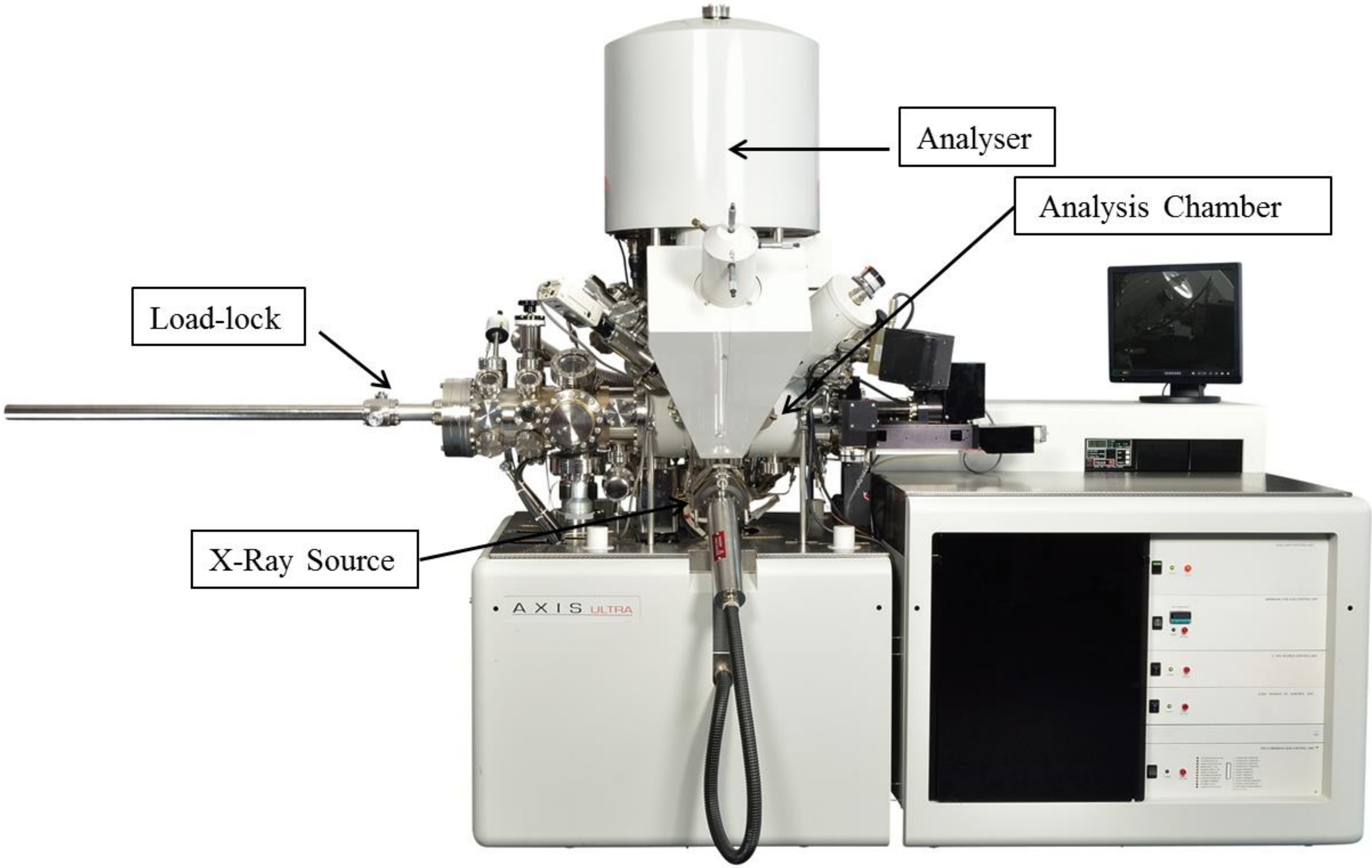
General spectrum= survey

Ta 4f core level spectra

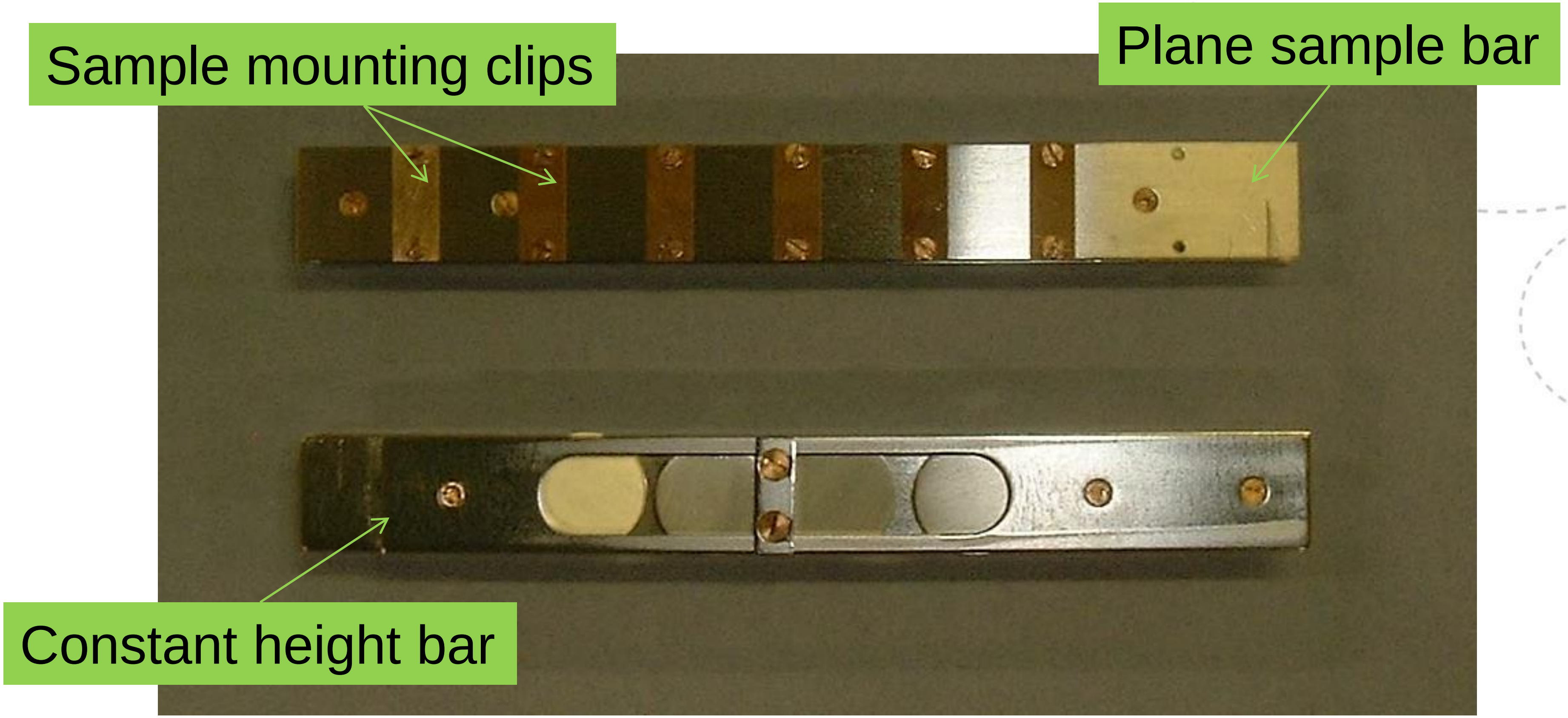


Depth profiling measurements
Argon etching

X-Ray photoelectron spectroscopy system *Kratos Axis UltraDLD 39-306* equipped with mono AlKα source

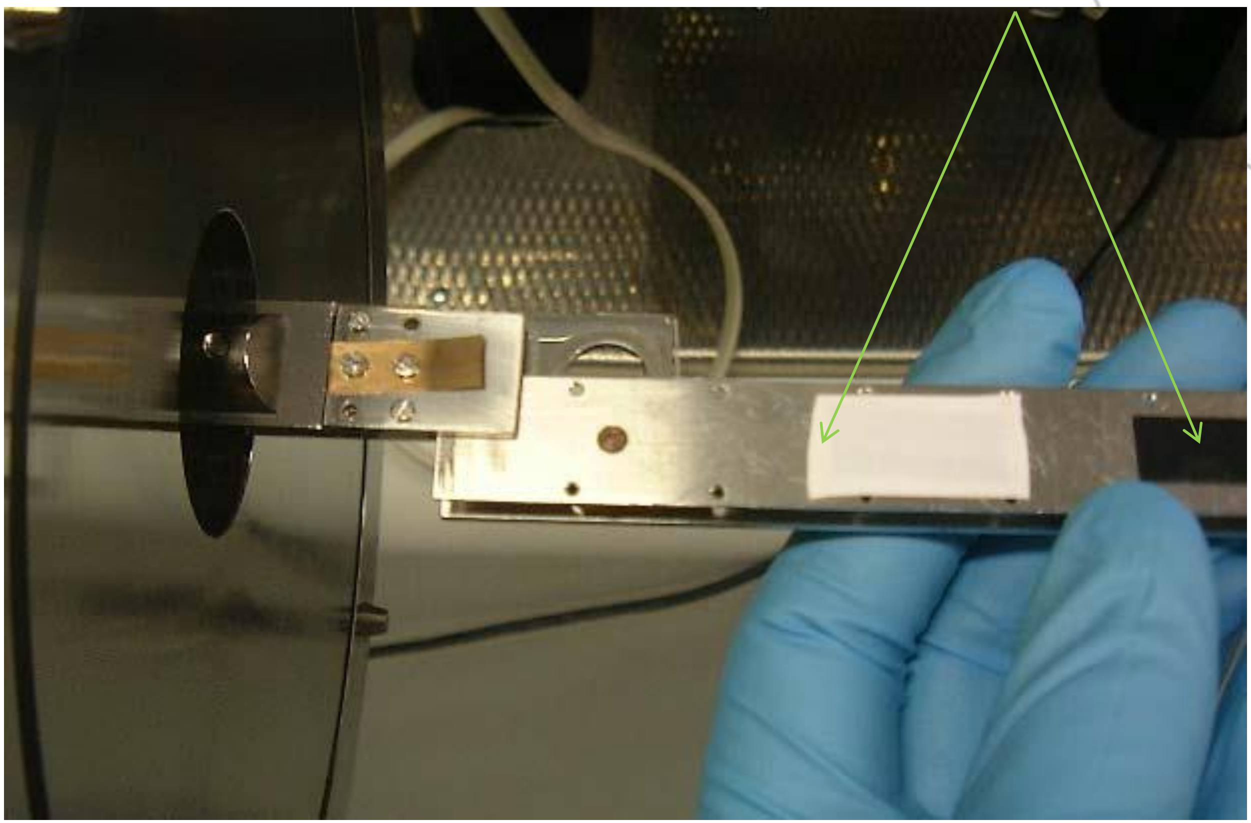


Sample preparation



Kratos Axis UltraDLD

Samples are mounted on the bar



Kratos Axis UltraDLD

Summary

TEM: A beam of electrons is transmitted through a thin sample, and interacting with the sample as it passes. An image is formed from the interaction of the electrons transmitted through the sample. Preparation of the sample is required to allow the transmission of the electrons

SEM: Sample surface is imaged by scanning it with a high-energy beam of electrons in a raster scan pattern. No special preparation of the sample is required. The **electrical conductivity** of the sample is necessary to avoid sample charging

XPS: Spectra are obtained by irradiating a material with a beam of x-rays. The kinetic energy (KE) of electrons that escape from the top 0 to 10 nm of the material is monitored. The photoelectrons generated from atomic core level shells and emitted from the sample are counted and analysed for their KE.

TEM, SEM, XPS operate under vacuum

Technical acronyms

NPs: Nanoparticles
EM: Electron Microscopy
TEM: Transmission Electron Microscope
HRTEM: High Resolution Transmission Electron Microscope
STEM: Scanning Transmission Electron Microscope
SEM: Scanning Electron Spectroscopy
EELS: Electron Energy Loss Spectroscopy
XPS: X-ray Photoelectron Spectroscopy
SE: Segundary Electrons
BSE: Back Scattered Electrons
EDX: Energy Dispersive X-ray spectroscopy
KE: Kinetic Energy
BE: Binding Energy

Next lecture

Characterization of nanomaterials:
XRD, SAXS, SPM