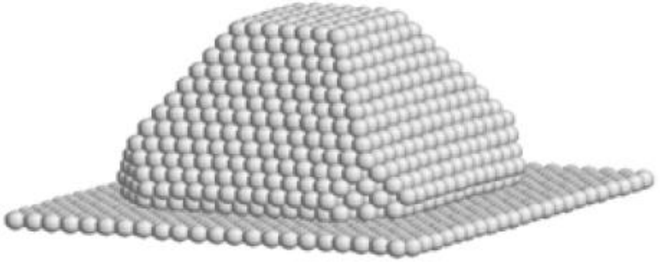
NTNU

Norwegian University of Science and Technology

TMT4320 Nanomaterials
Septemeber 26th, 2016

- TNN5:Characterization of nanomaterials: STM, AFM, XRD, SAXS



Last week

- Bottom-up synthesis: Physical/Vapour phase methods
  - Mechanisms
  - Flame Spray Pyrolysis (FSP)
  - Pulsed Layer Deposition (PLD)
  - Magnetron-sputtering based Inert-gas-condensation
- Characterization of nanomaterials: TEM, SEM and XPS

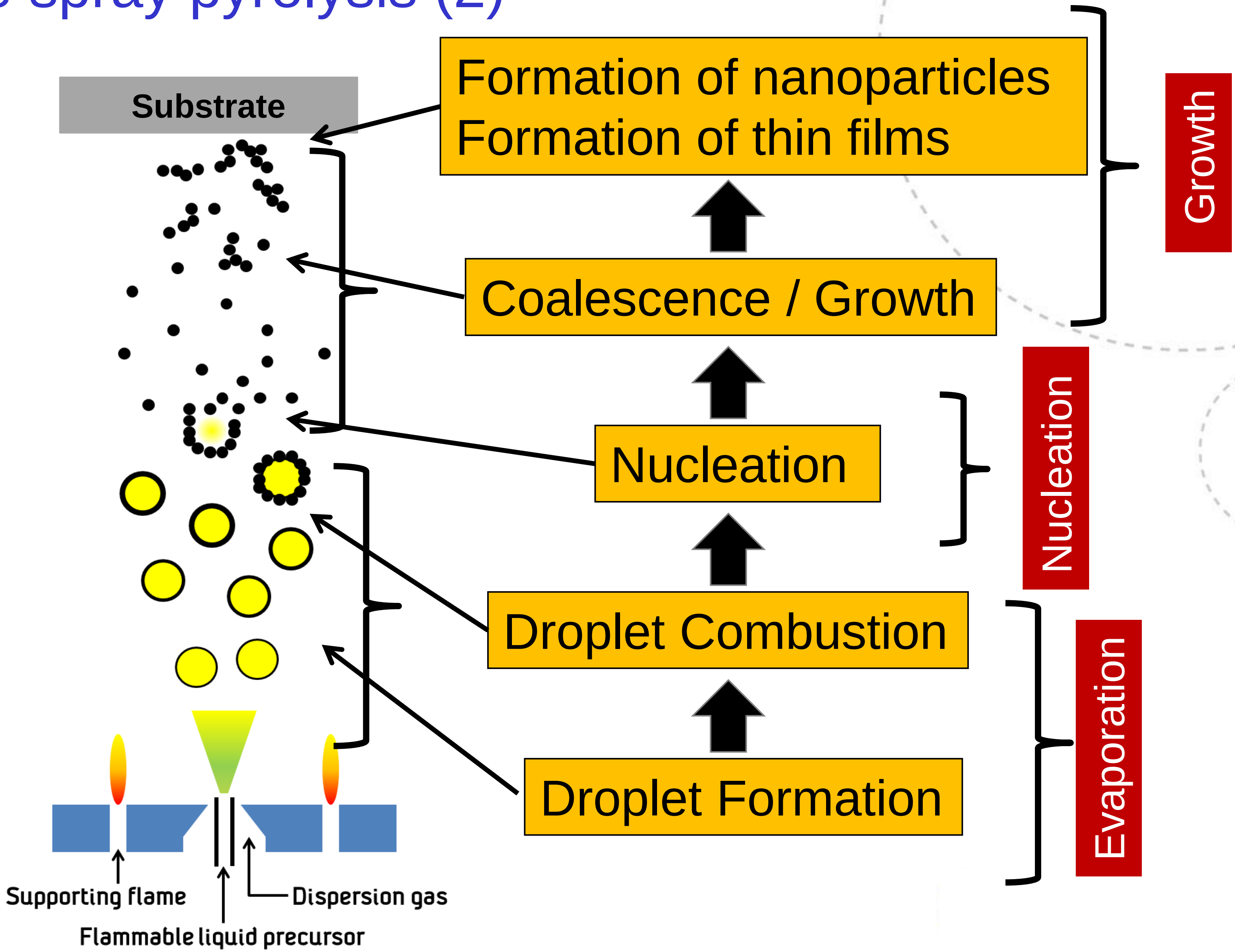
Last week

- Bottom-up synthesis: Physical/Vapour phase methods
    - Mechanisms
        - Driving force → pressure difference → growth rate equation
        - Evaporation techniques: Thermal, Pulsed laser ablation, electron beam and sputtering

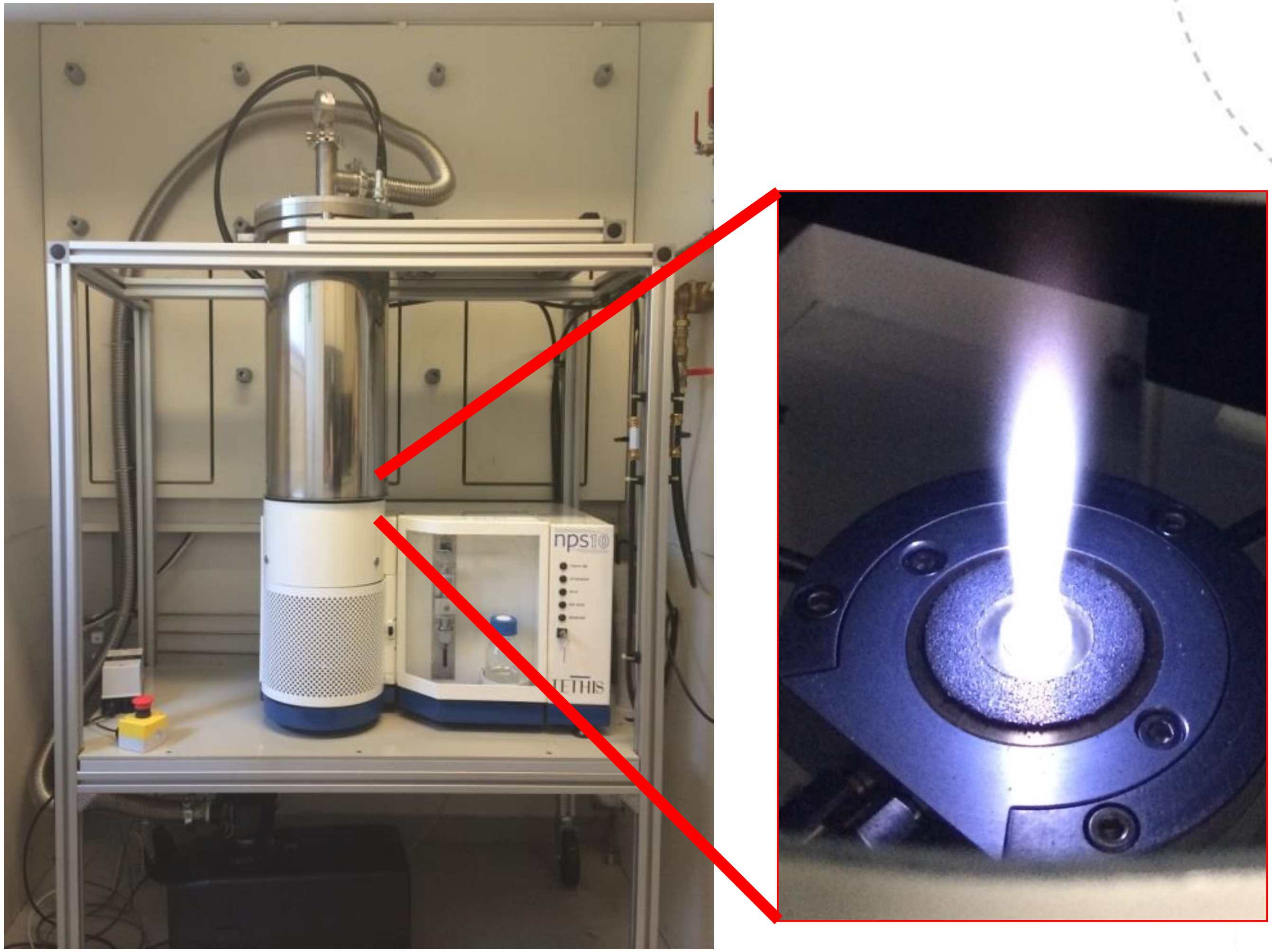
Last week

- Bottom-up synthesis: Physical/Vapour phase methods
  - Flame Spray Pyrolysis (FSP)
    - High T flame process for synthesis of metal oxide nanoparticles

Flame spray pyrolysis (2)



Flame spray pyrolysis at NTNU-campus (SINTEF)



Last week

- Bottom-up synthesis: Physical/Vapour phase methods
  - Flame Spray Pyrolysis (FSP)
    - High T flame process for synthesis of metal oxide nanoparticles
    - Examples of SnO_2, Fe_2O_3, TiO_2, …
    - Advantages:
      - Versatile and scalable
      - Nanoparticles are fully oxidized and crystalline.
    - Disadvantage:
      - Polydispersity of nanoparticle size distribution

Last week

- Bottom-up synthesis: Physical/Vapour phase methods
  - Pulsed Layer Deposition (PLD)
    - In a PLD high power pulsed laser beam is focused to strike a target of the desired materials. The material is then vaporised and deposited as a film on a substrate facing the target. Process in ultra high vacuum or in the presence of gas

Concept of PLD (1)

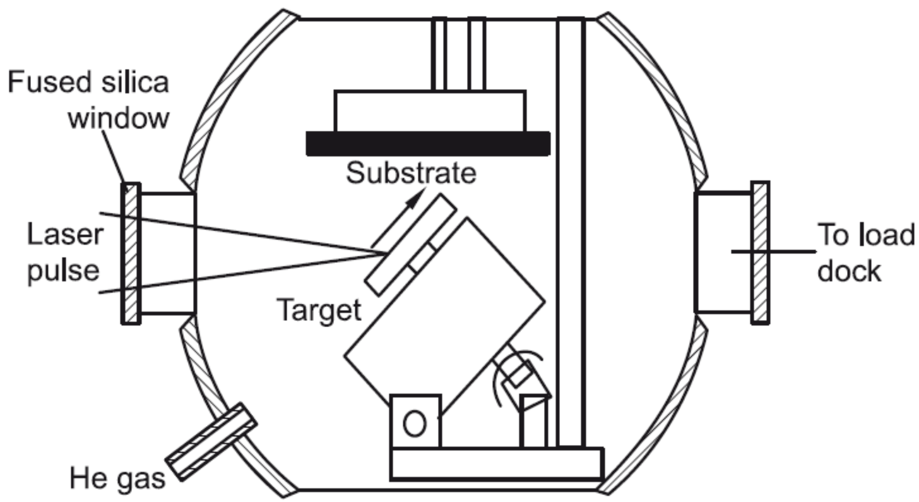


Fig. 3.3 Schematic of a laser ablation chamber equipped with a rotating target holder.

PLD stages

- Laser ablation of target
- Plasma generation
- Film nucleation and growth

- The laser-target interaction: electromagnetic energy is converted into electronic excitation and then into thermal/mechanical energy to cause ablation
- A plume: atoms, molecules, e^-, ions, clusters, particles, molten globules
- The plume expands with hydrodynamic flow characteristics

Last week

- Bottom-up synthesis: Physical/Vapour phase methods
  - Pulsed Layer Deposition (PLD)
    - In a PLD high power pulsed laser beam is focused to strike a target of the desired materials. The material is then vaporized and deposited as a film on a substrate facing the target. Process in ultra high vacuum or in the presence of gas
    - Main advantage is the homogenous evaporation when compared with other PVD techniques.

Last week

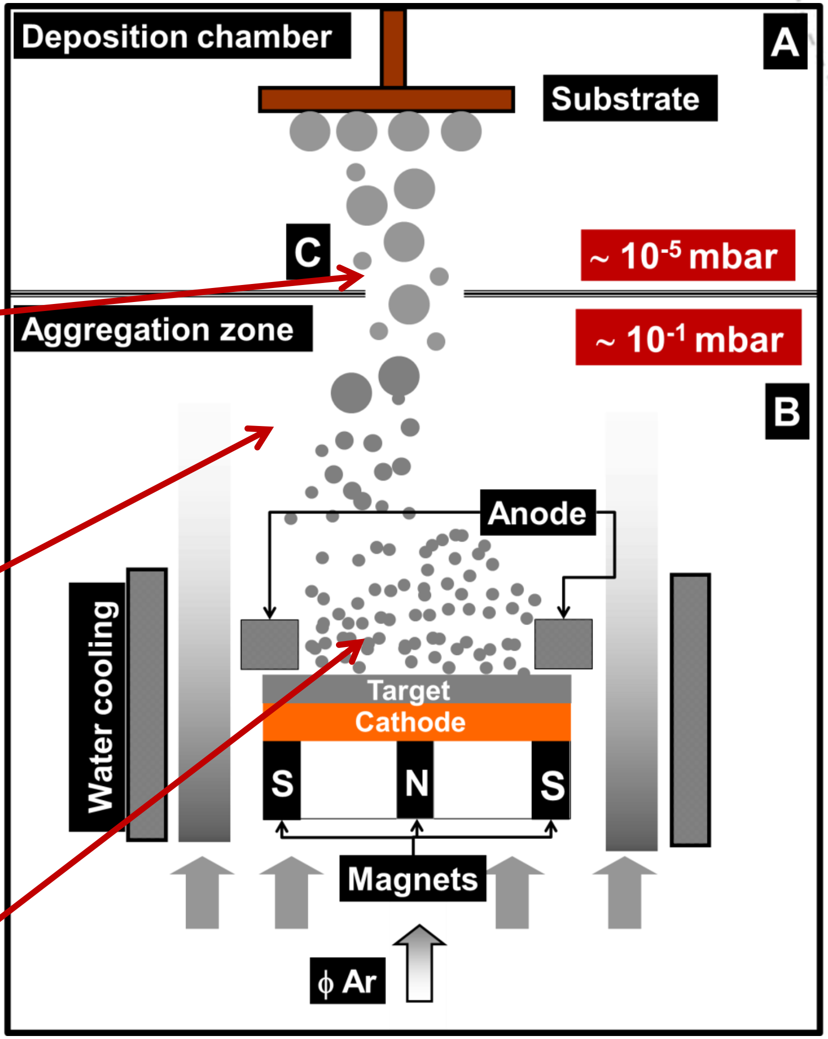
- Bottom-up synthesis: Physical/Vapour phase methods
  - Magnetron-sputtering based Inert-gas-condensation
    - Bombardment with high-velocity ions of an inert gas

Concept of Sputtering (Nanoparticle deposition)

Aperture

Aggregation zone: Nucleation and growth of NPs

Plasma zone



Particle pathway towards deposition chamber

Last week

- Bottom-up synthesis: Physical/Vapour phase methods
  - Magnetron-sputtering based Inert-gas-condensation
    - Bombardment with high-velocity ions of an inert gas
    - Binary nanoparticles formation
      - Factors: bond strength, surface energies, atomic radii, electronegativity and charge transfer
      - Example: FeAl and SiAg
      - Parameters controlling size, morphology and yield: plasma density, flux of Ar gas, pressure differential

Last week

- Bottom-up synthesis: Physical/Vapour phase methods
  - Mechanisms
  - Flame Spray Pyrolysis (FSP)
  - Pulsed Layer Deposition (PLD)
  - Magnetron-sputtering based Inert-gas-condensation
- **Characterization of nanomaterials: TEM, SEM and XPS**

Last week

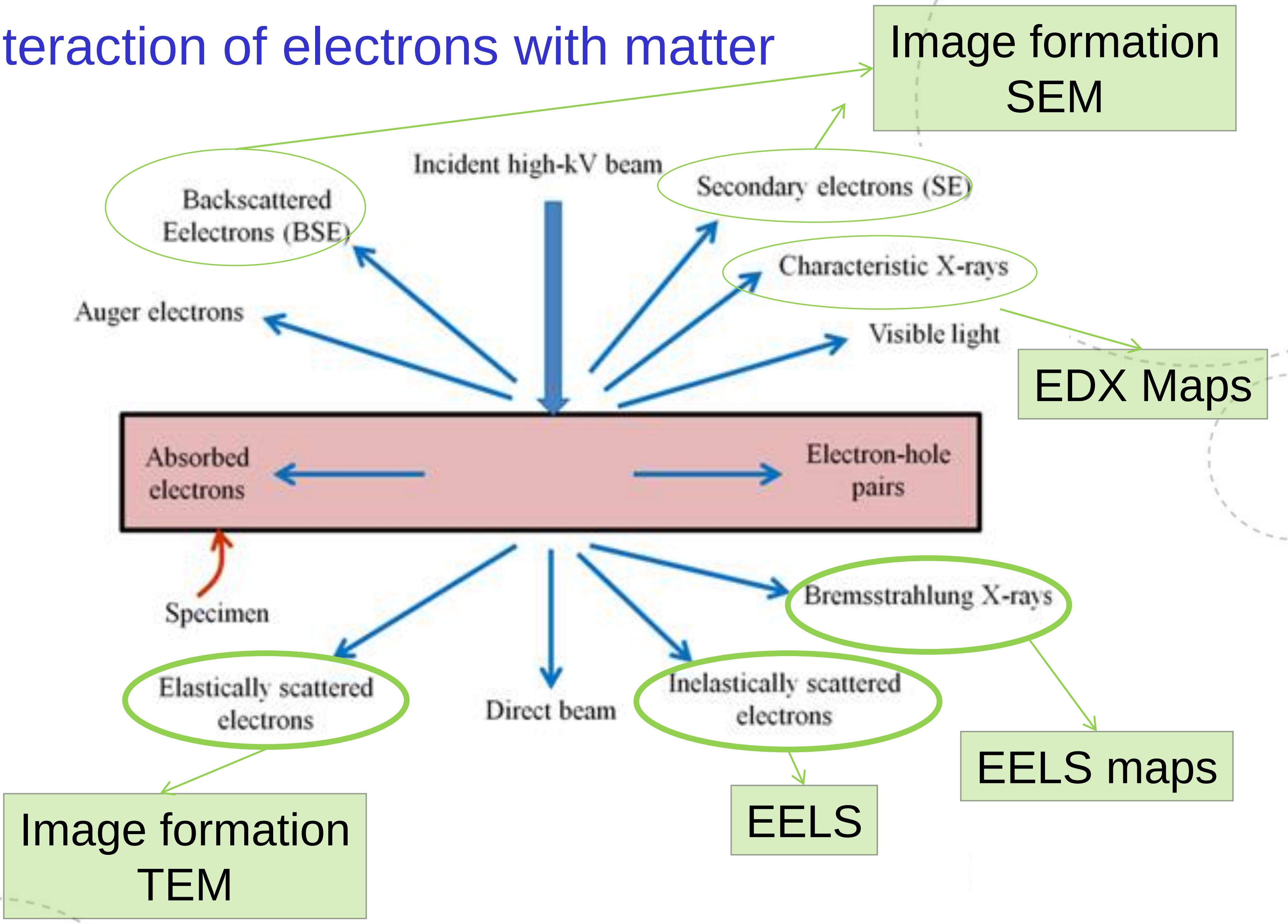
- Characterization of nanomaterials: TEM, SEM and XPS
  - Transmission Electron Microscopy (TEM)
  - Scanning Electron Microscopy (SEM)
  - X-Ray Photoelectron spectroscopy (XPS)

Last week

- Characterization of nanomaterials: TEM, SEM and XPS

  - Electron Microscopy
    - Designed to allow interaction between high energy electron beam and samples to study structure. Larger resolutions than light microscopes
    - Interaction with electrons: secondary electrons and backscattered electrons

Interaction of electrons with matter



Last week

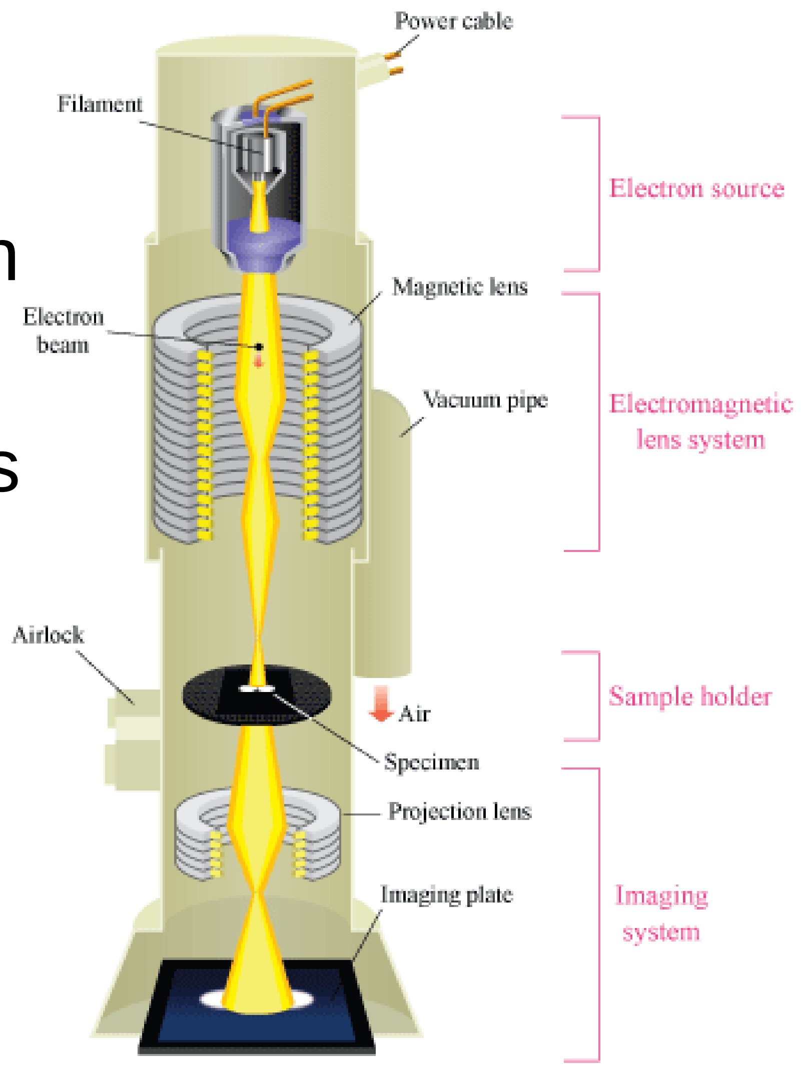
- Characterization of nanomaterials: TEM, SEM and XPS
  - Electron Microscopy
    - Designed to allow interaction between high energy electron beam and samples to study structure. Larger resolutions than light microscopes
    - Interaction with electrons: secondary electrons and backscattered electrons
    - TEM, SEM, STEM, EDX, EELS
  - Transmission Electron Microscope
    - Sample preparation

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.

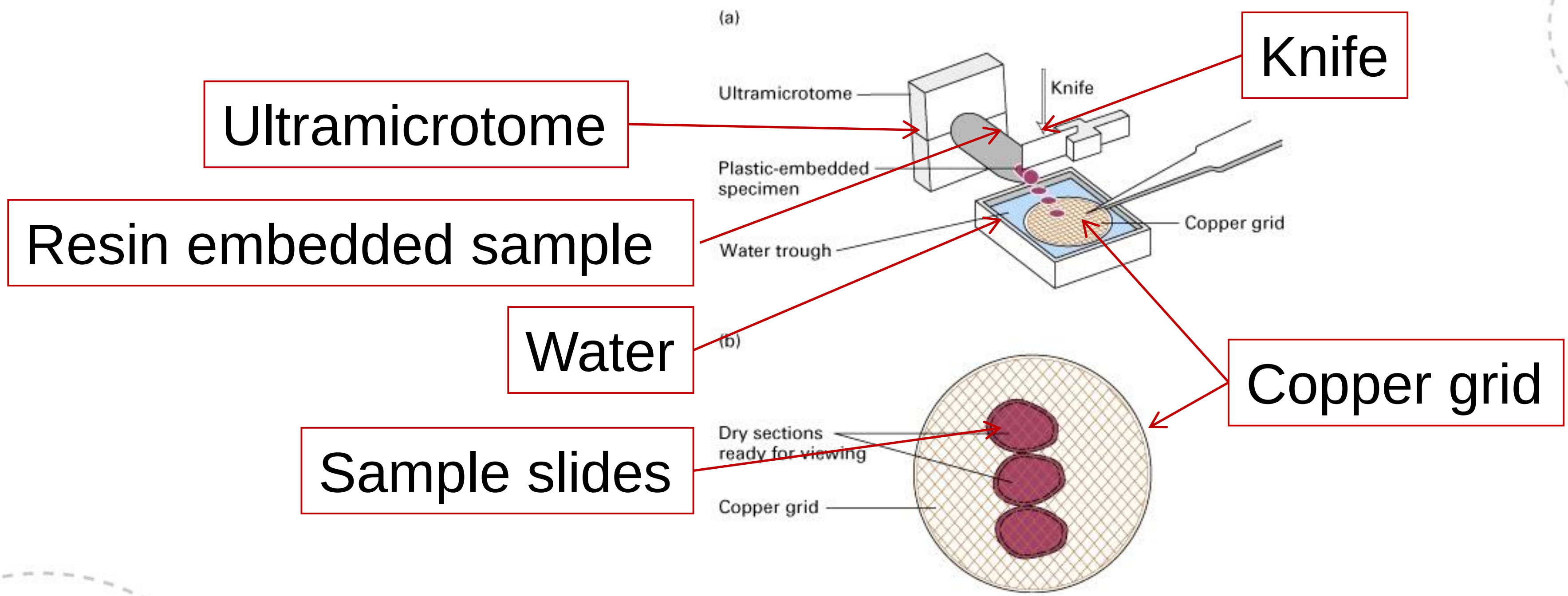
❖ The sample should allow electrons to pass through



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

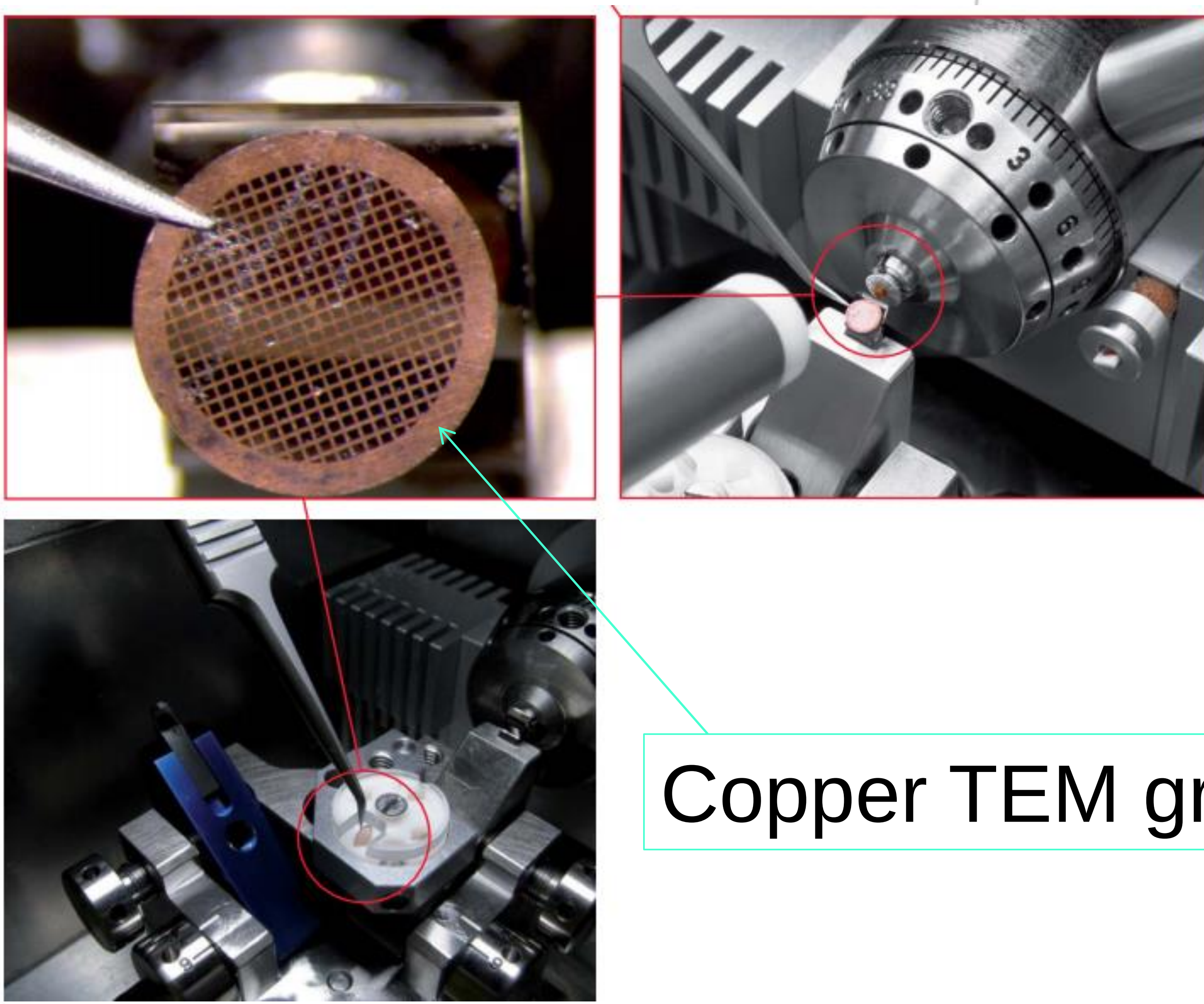
Preparation of thin films for TEM imaging

- 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

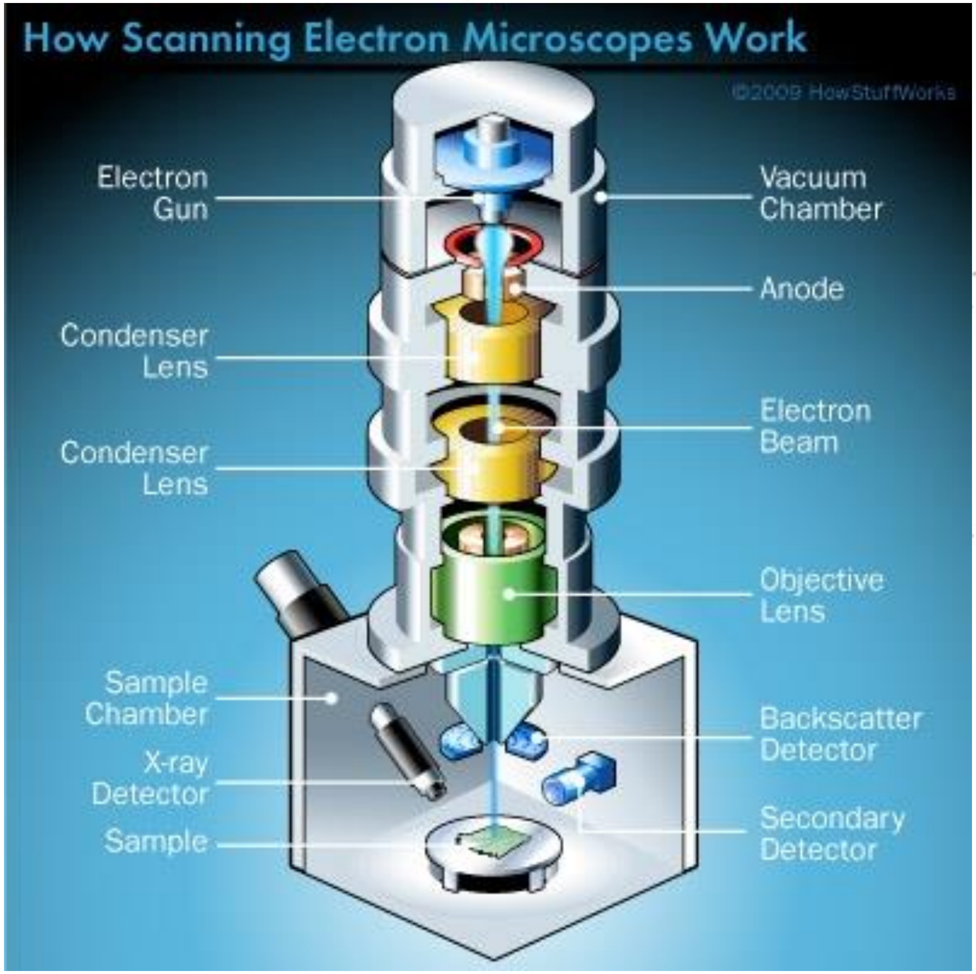
Last week

- Characterization of nanomaterials: TEM, SEM and XPS

  - Electron Microscopy
    - Designed to allow interaction between high energy electron beam and samples to study structure. Larger resolutions than light microscopes
    - Interaction with electrons: secondary electrons and backscattered electrons
    - TEM, SEM, STEM, EDX, EELS
  - Transmission Electron Microscope
    - Sample preparation
  - Scanning Electron Microscope
    - Sample preparation

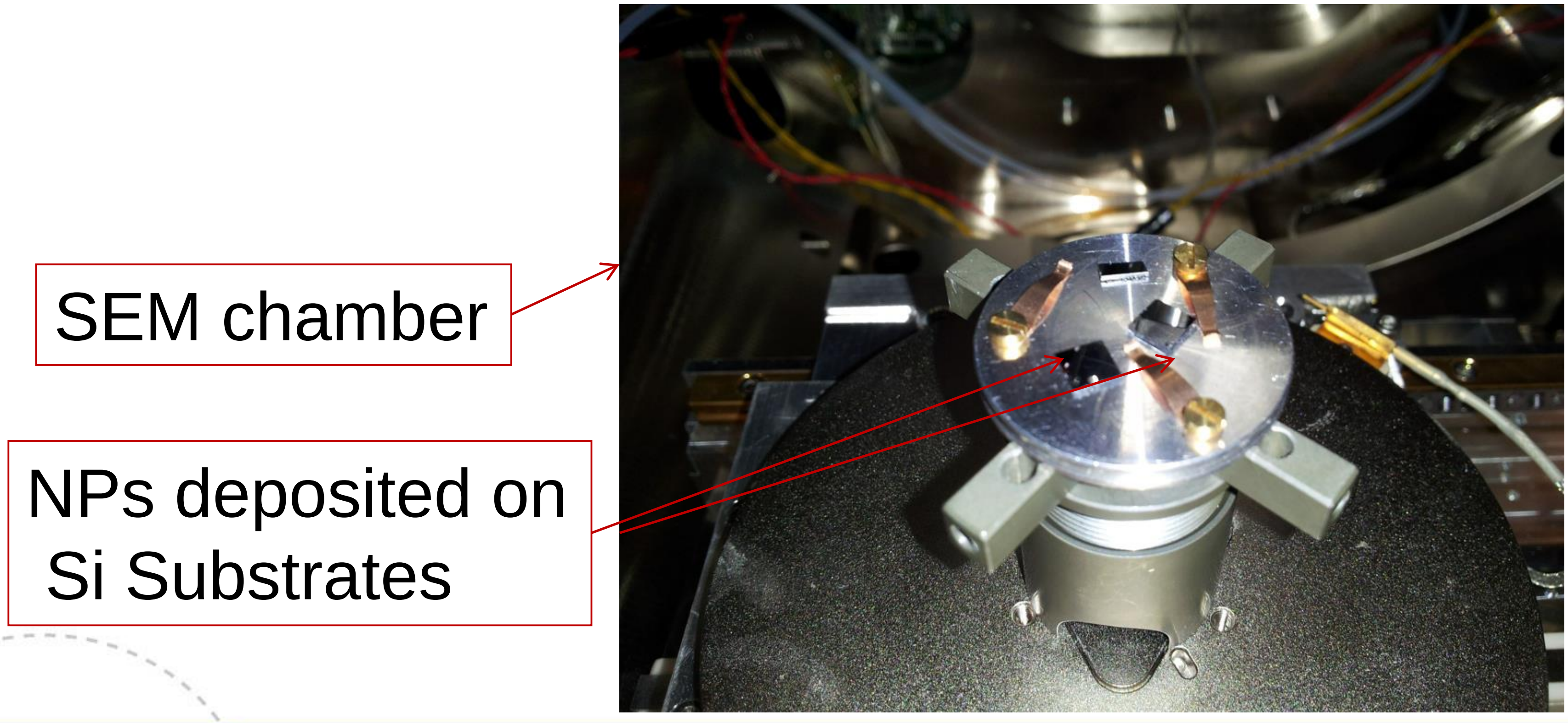
Scanning Electron Microscopy SEM

- ❖ 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

- 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



Last week

- Characterization of nanomaterials: TEM, SEM and XPS
  - X-Ray Photoelectron spectroscopy (XPS)
    - Surface-sensitive technique to measure elemental composition, chemical and electonic states
    - Ultra-High-Vacuum (UHV) ≤ 10^{-9} Torr
    - How it works?
      - X-Rays hit core electrons, penetrate about 1 µm (useful information of 1-10 nm on surface)
      - Produces photons with specific energies

How it works?

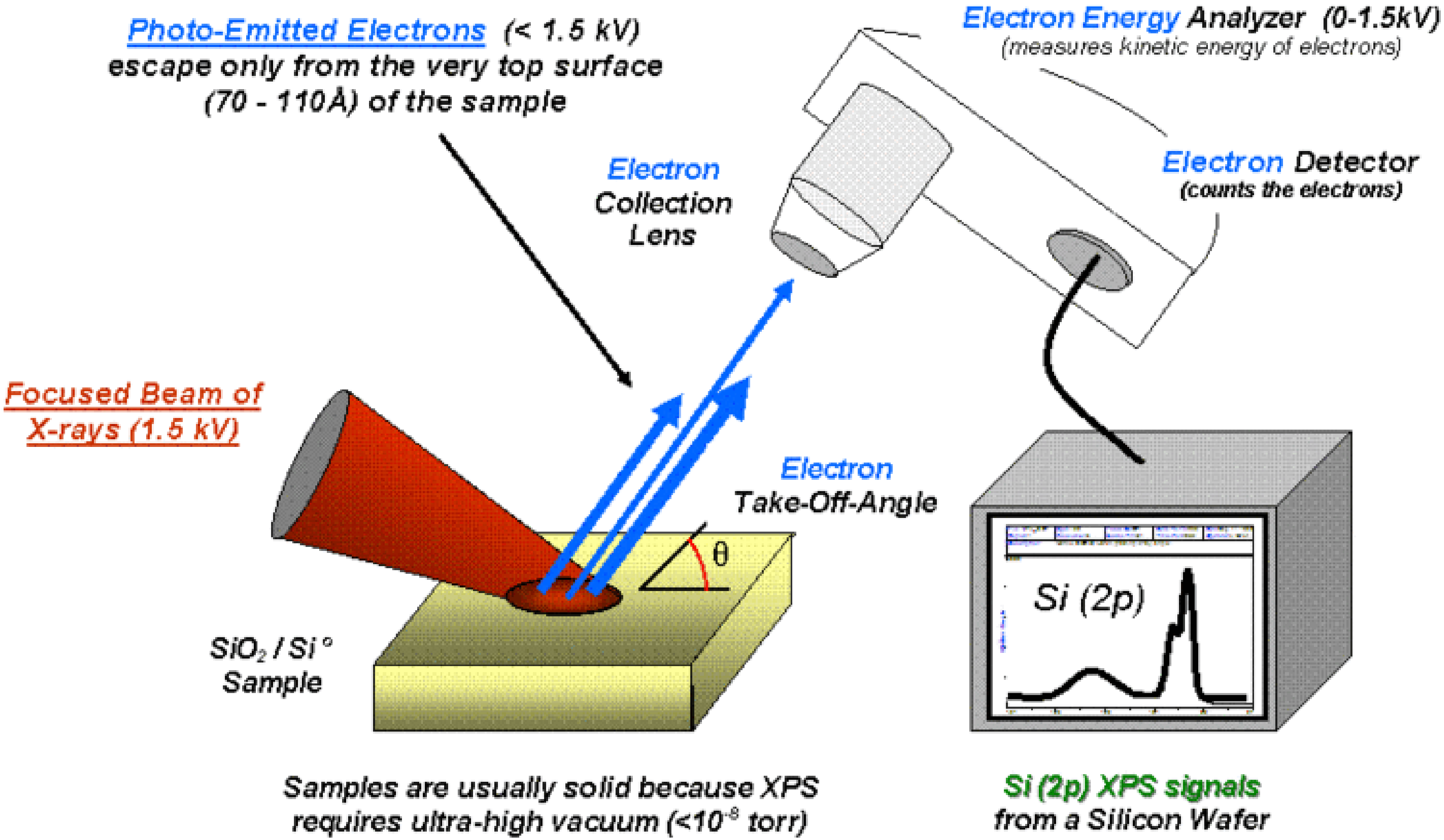
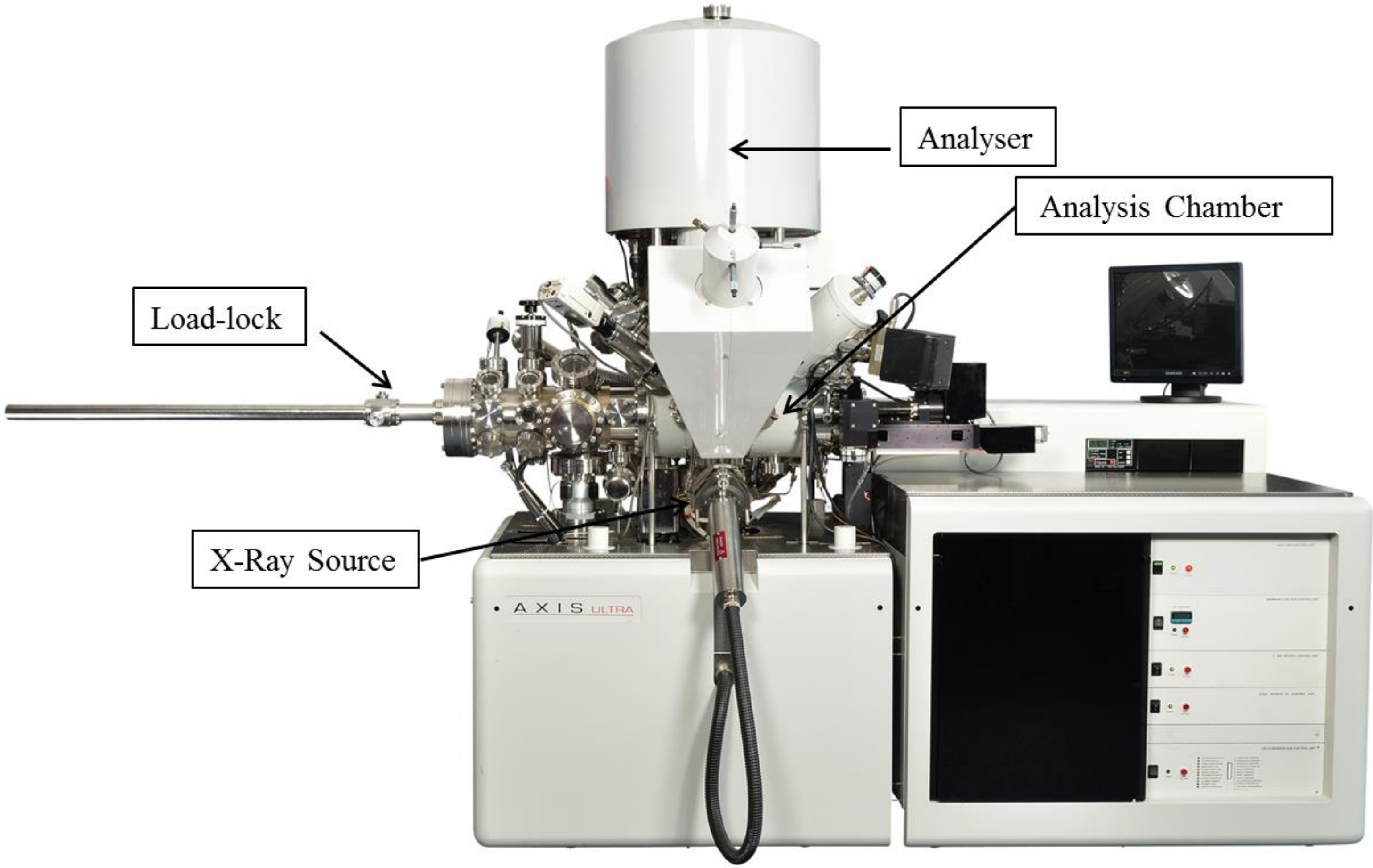
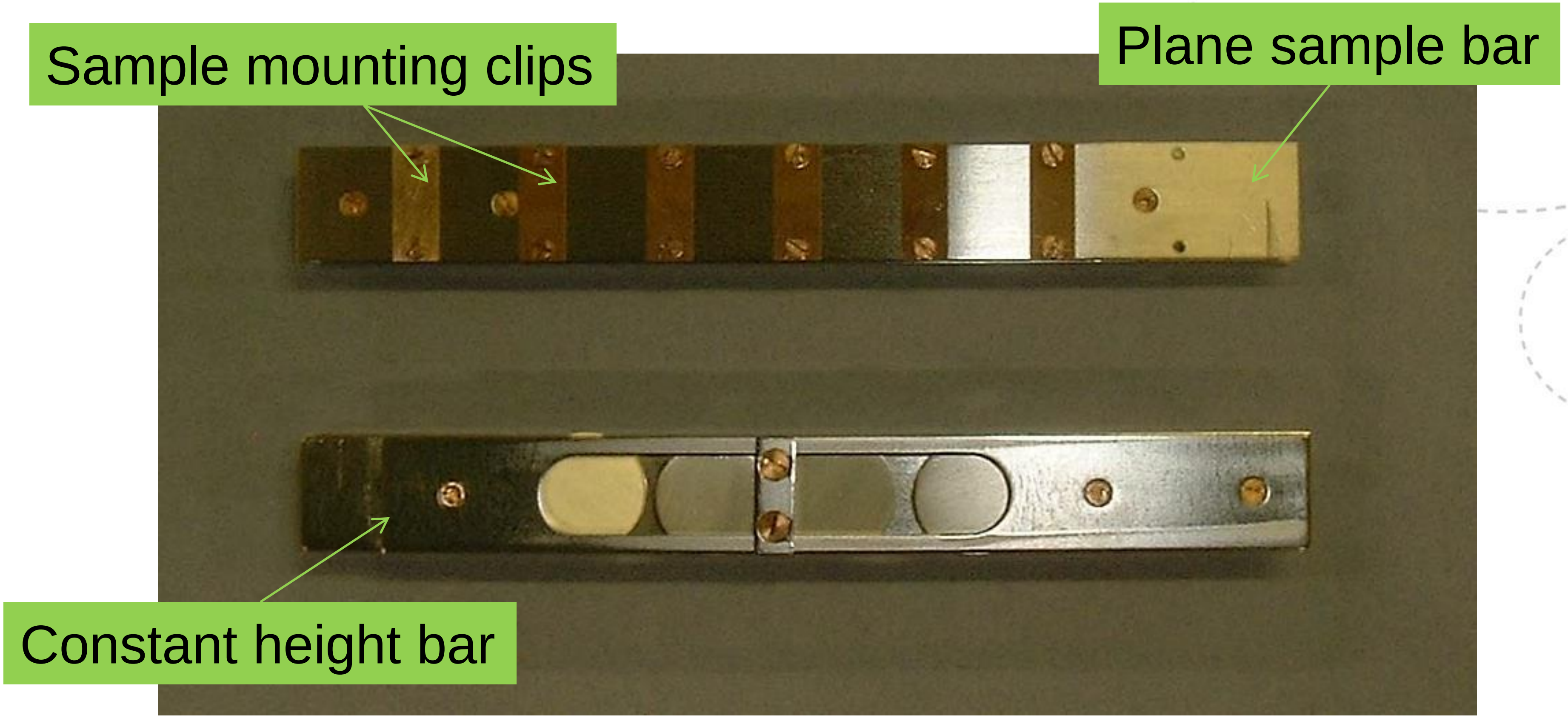


Photo-Emitted Electrons (< 1.5 kV)
escape only from the very top surface
(70 - 110Å) of the sample
Electron Energy Analyzer (0-1.5kV)
(measures kinetic energy of electrons)
Electron Collection Lens
Electron Detector
(counts the electrons)
Focused Beam of X-rays (1.5 kV)
Electron Take-Off-Angle
θ
SiO2 / 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

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

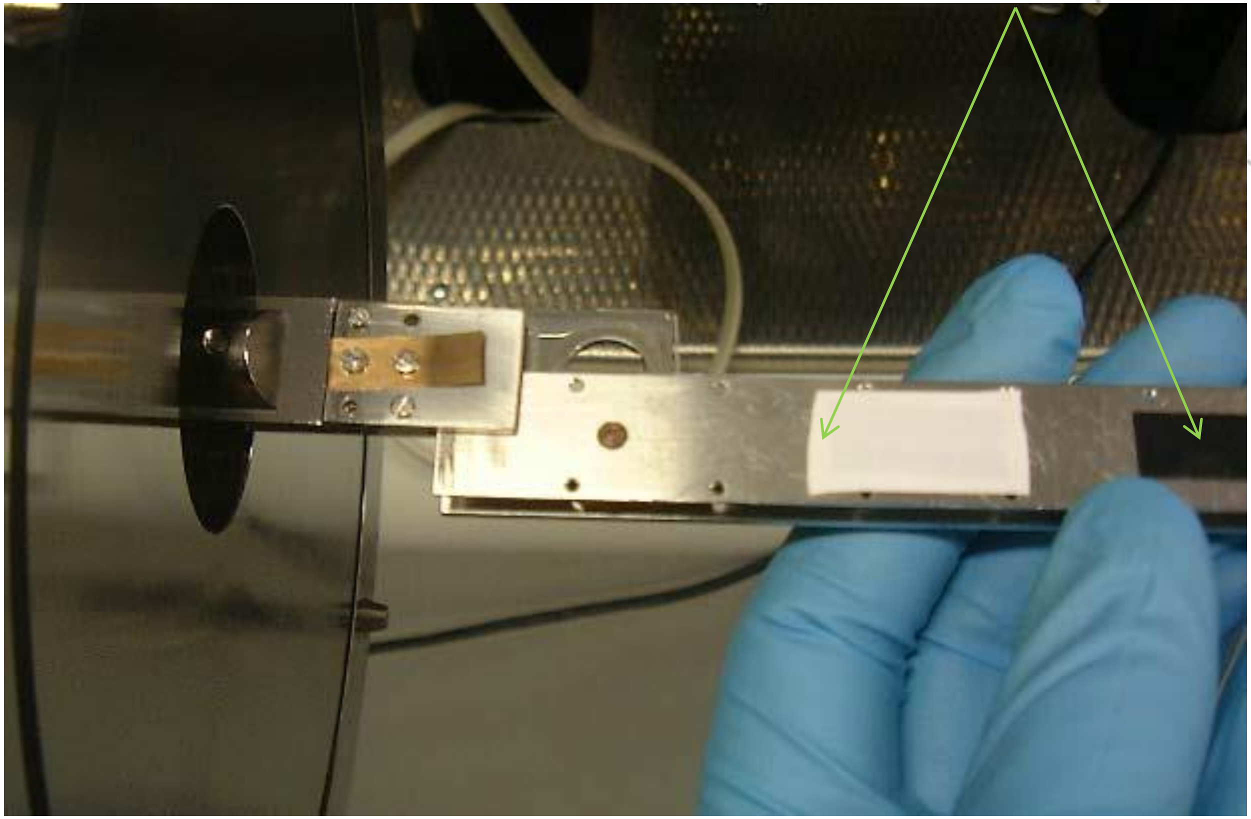


Sample preparation



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.

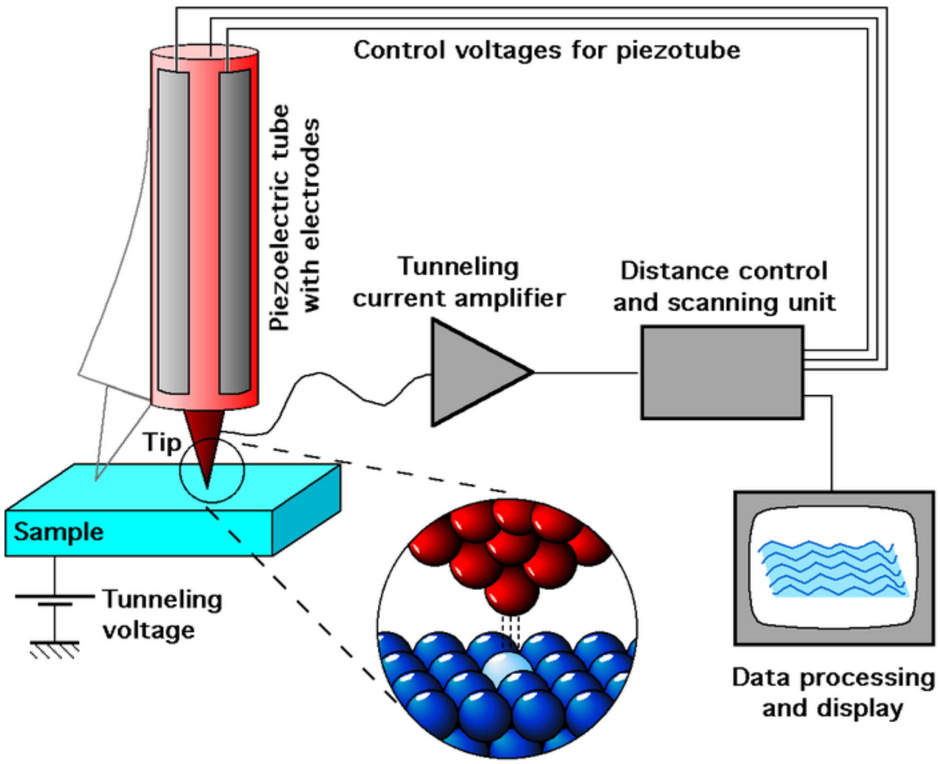
TEM, SEM, XPS operate under vacuum

Characterization of nanomaterials

- STM: Scanning Tunneling Microscope
- AFM: Atomic Force Microscope
- EDX: Next Wednesday
- XRD
- SAXS

Scanning tunnelling microscopy (STM)

- Near-field microscopy techniques
  - Scanning tunnelling microscopy (STM)
    - For low voltages, this tunnelling current is a function of the local density of states at the Fermi level, E_f, of the sample



https://www.youtube.com/watch?v=K64Tv2mK5h4

Wikipedia

Scanning tunnelling microscopy (STM)

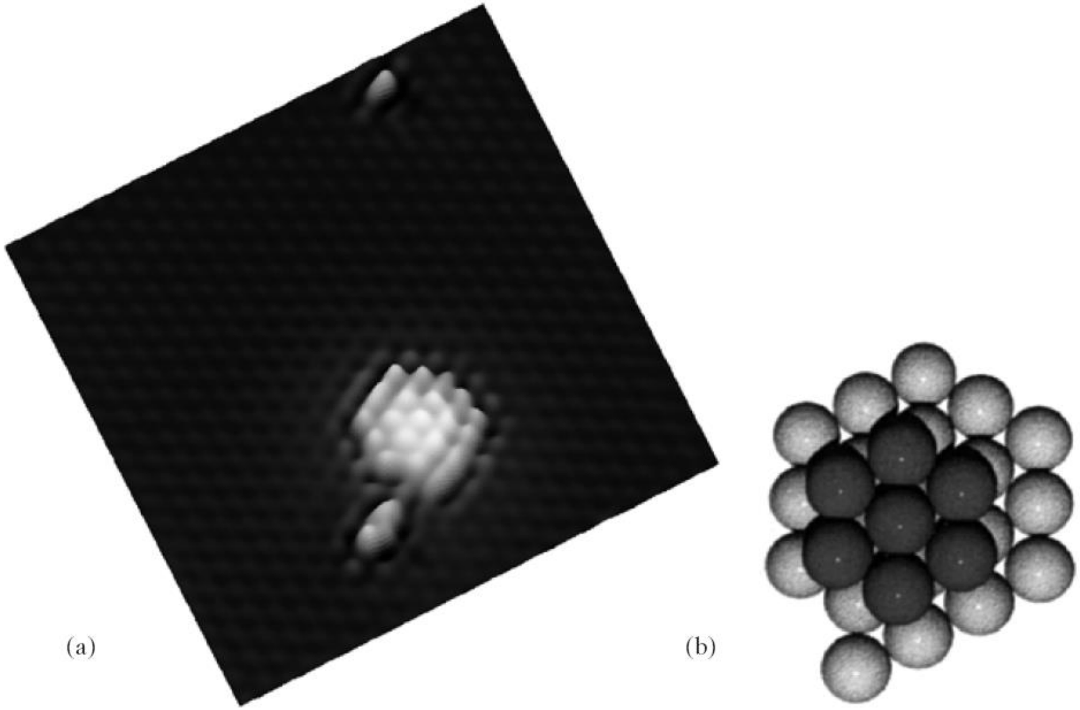
- Near-field microscopy techniques
  - Scanning tunnelling microscopy (STM) @ NTNU

http://www.ntnu.edu/nano/nanolab

Wikipedia

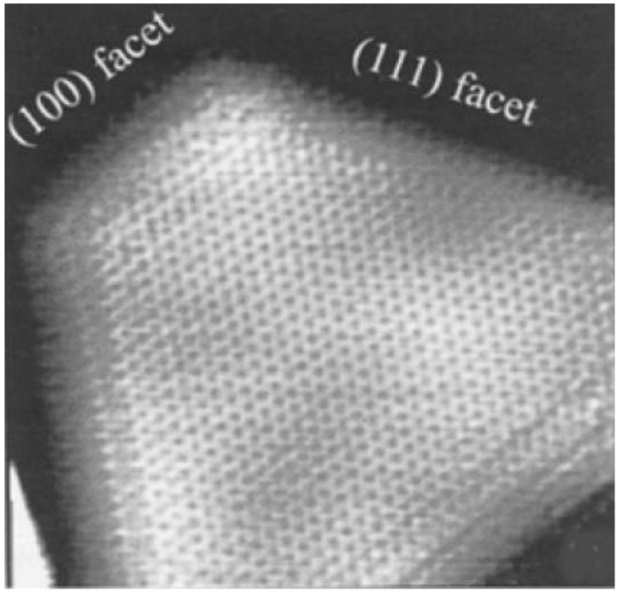
Scanning tunnelling microscopy (STM)

- Pd cluster containing 27 atoms on a MoS_2 (0001) surface
  - 20 atoms in the first layer
  - 7 atoms in the second layer



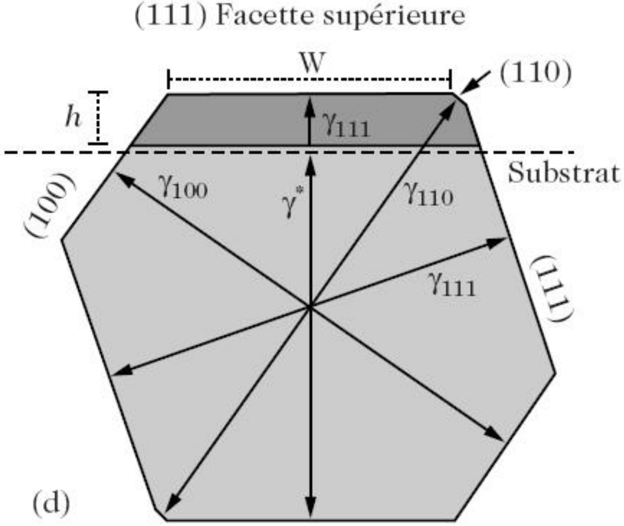
Scanning tunnelling microscopy (STM)

(c)



5 nm Pd cluster on an ultrathin layer of alumina on an NiAl (110) surface

(d)

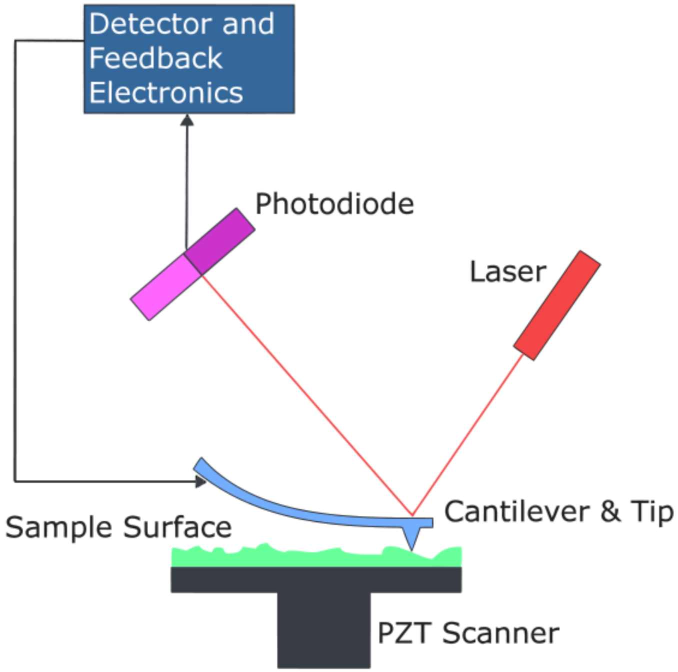


Equilibrium shape of Pd clusters on alumina

Atomic force microscopy (AFM)

- Near-field microscopy techniques
  - Atomic force microscopy (AFM)
    - Contact mode
    - Tapping mode
    - Non-contact mode

https://www.youtube.com/playlist?list=PLH4cAUjlEqR0LPdWN_8zMvf_thJCe6SmA



Wikipedia

Atomic force microscopy (AFM)

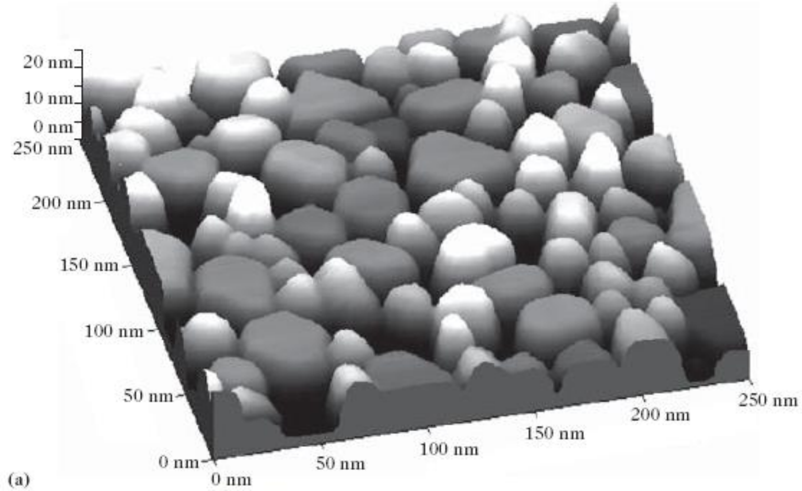
- Near-field microscopy techniques
  - Atomic force microscopy (AFM) @ NTNU

http://www.norfab.no/lab-facilities/ntnu-nanolab/

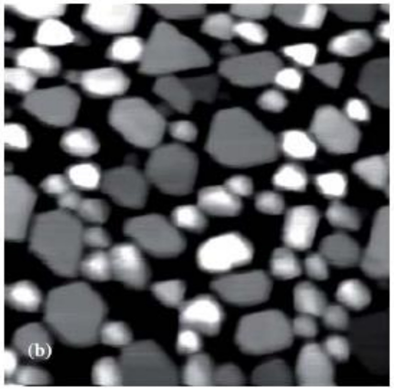
Wikipedia

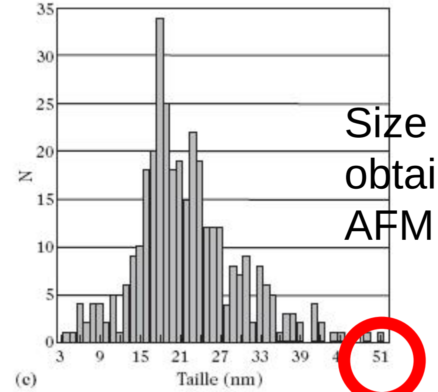
AFM vs. TEM

- Gold nanoparticels grown on mica (100)
- Particles appear bigger in the AFM images



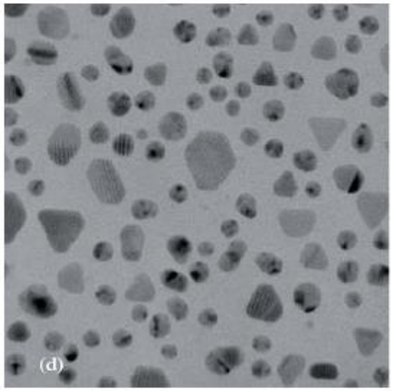
AFM image

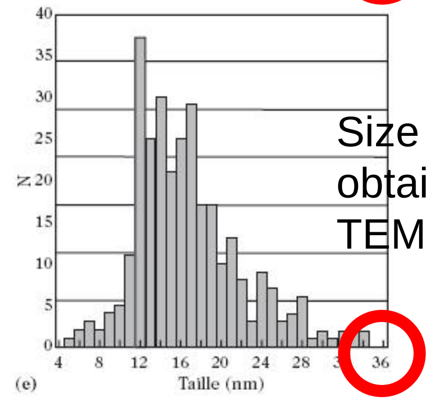




Size histogram obtained from AFM images

TEM image

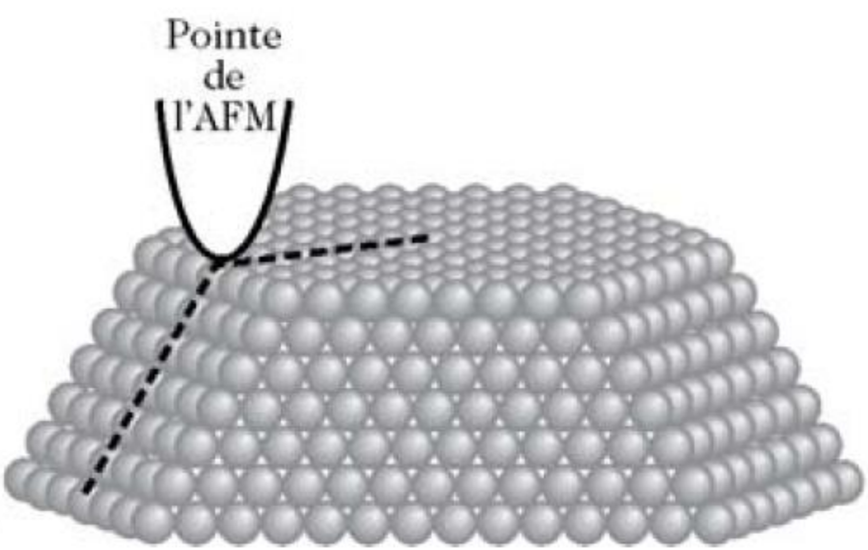


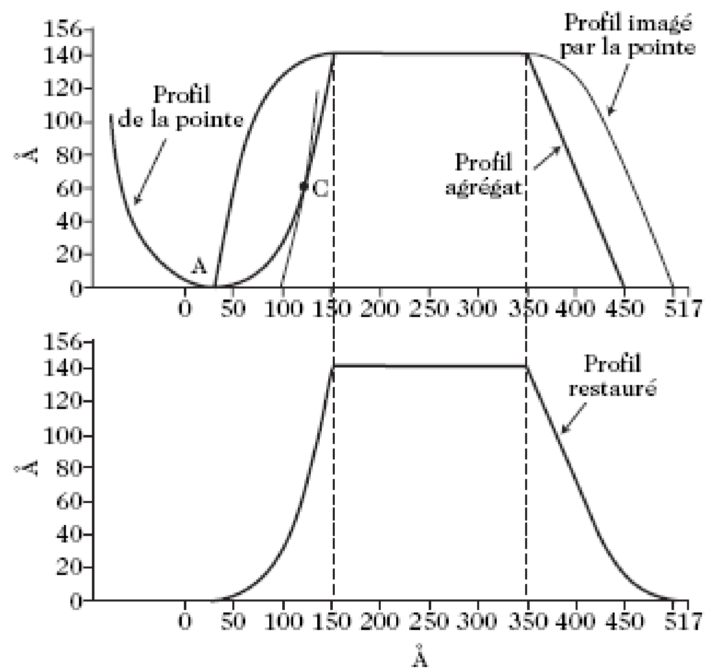


Size histogram obtained from TEM images

Convolution effect

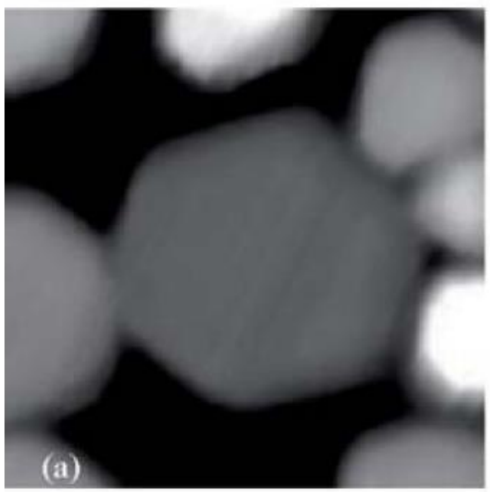
- The AFM tip shape may influence the observations
- The convolution effect increases as the radius of curvature of the tip increases and as the slopes of the facets increase
- If the shape of the tip is known the images can be partly corrected



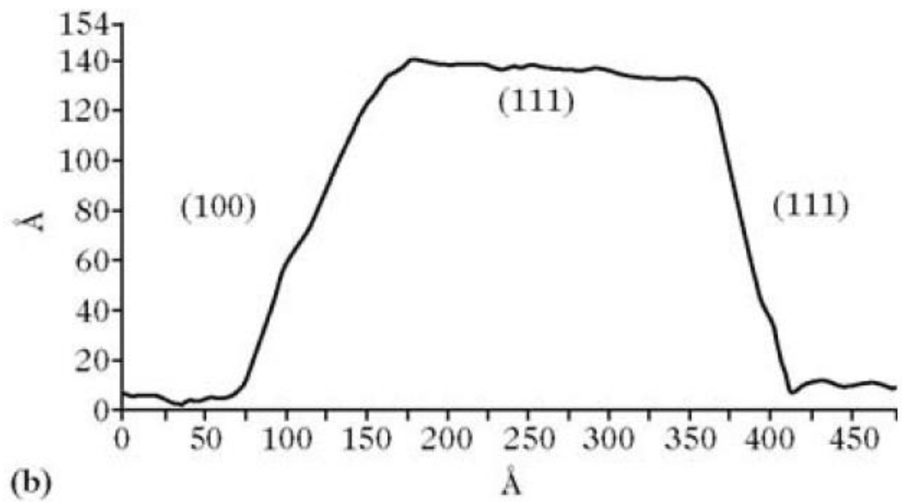


Convolution-corrected AFM

- The side faces of supported nanocrystals can be determined from the angle of the slopes
- Example
  - Gold nanoparticles supported on mica



2D AFM image of a 27-nm hexagonal particle



Profile of the particle in (**a**) in a direction perpendicular to the lateral facets, corrected for the convolution with the AFM tip

AFM vs. TEM

	SEM/TEM	AFM
Samples	Must be conductive	Insulating/Conductive
Magnification	Two-dimensional	Three-dimensional
Environment	Vacuum	Vacuum/Air/Liquid
Time for image	0.1–1 minute	1–5 minute
Horizontal resolution	0.2 nm (TEM) 5 nm (FE-SEM)	0.2 nm
Vertical resolution	n/a	.05 nm
Field of view	100 nm (TEM) 1 mm (SEM)	100 µm
Depth of field	Good	Poor
Contrast on flat samples	Poor	Good

Imaging methods

- Transmission electron microscopy (TEM) @ NTNU

TEM Gemini Centre

NTNU

Department of Physics
Department of Materials Science and Engineering

SINTEF

https://www.ntnu.edu/geminicentre/tem

Imaging methods

- Transmission electron microscopy (TEM) @ NTNU

TEM Gemini Centre
NTNU
Department of Physics
Department of Materials Science and Engineering
SINTEF

Electron Microscopy and Analysis Group Conference 2007 (EMAG 2007)
Journal of Physics: Conference Series **126** (2008) 012010

Detailed TEM characterization of $PbTiO_3$ nanorods

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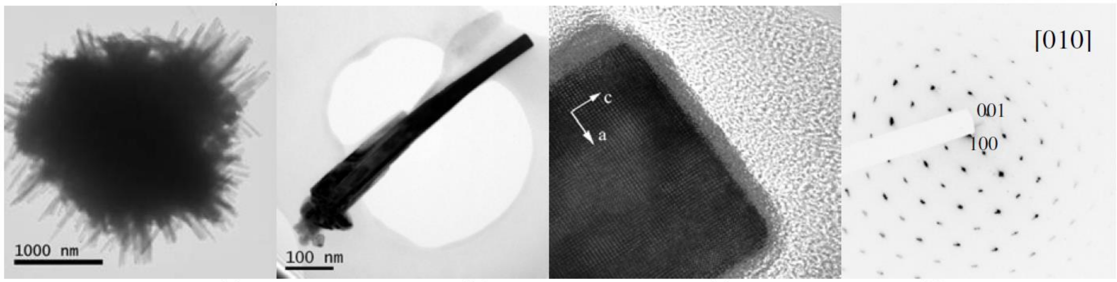


Figure 1: (a) BF image of microsphere. (b) BF image of rod with (c) HREM image of the tip and (d) SAED pattern showing a growth direction of [001].

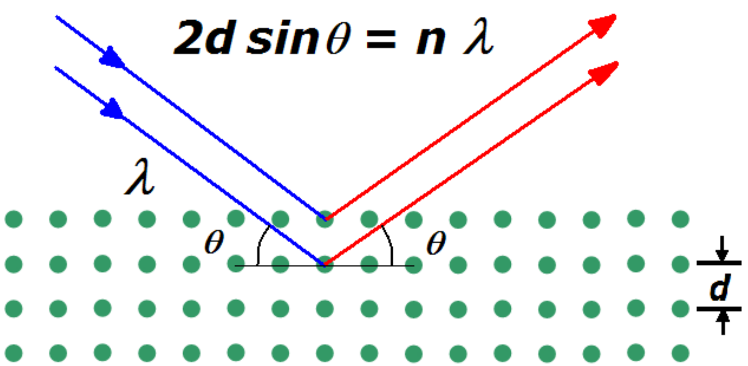
X-ray diffraction

Technique to study the structure, defects and stresses of solids

Beam of x-ray with wavelength from 0.07 to 0.2 nm is diffracted by crystalline specimen according to Bragg's law:

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

λ= X-Ray wavelength
θ = diffraction angle
d = interplanar distance



X-ray diffraction

Identify crystalline phases

Structural characteristics (cell parameters, crystallite sizes, defects, etc)

Non-destructive technique

Sample preparation is easy

Cheap

X-ray diffraction

Detection of homogenous and inhomogenous strains due to their dependence on the Bragg angle

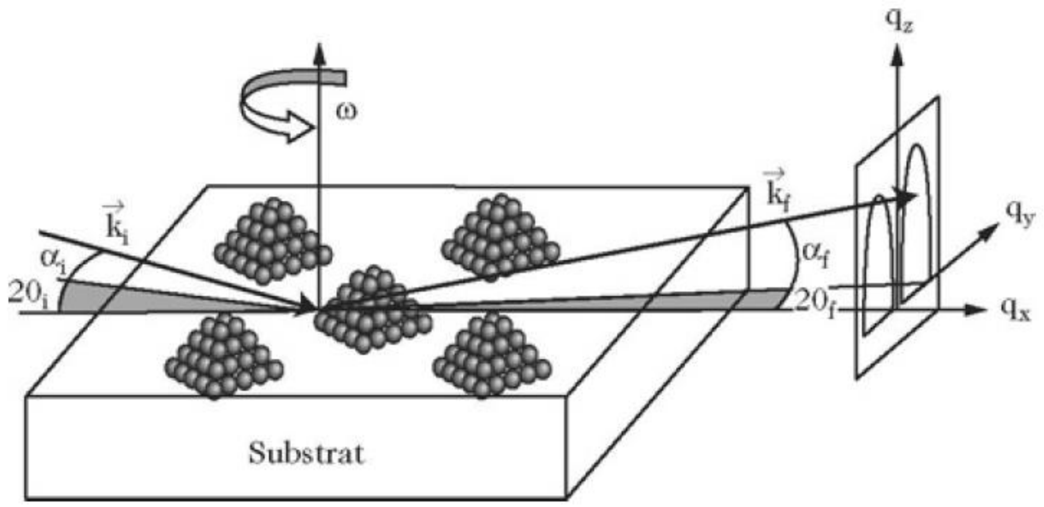
Homogeneous or uniform elastic strain shits the diffraction peaks, without change in peak profile. Shift change in the peaks means change in the lattice constants.

Inhomogeneous strains vary from crystallite to crystallite or even within a single crystallite. As XRD is an averaged information leads to peak broadening.

Peak broadening can also be due to reduction of crystallite size. This can be determined by peak profile analysis → Rietveld refinements

X-ray diffraction

- Grazing Incidence Small Angle X-Ray Scattering (GISAXS)
  - To a first approximation: average height *h*, average size *d*, average separation *D*



X-ray diffraction: instruments

Different sources : Cu, Mo, Co, synchrotron

Different sample holders: air-sensitive, shape, temperature dependent

Different detectors and filters

XRD lab at DMSE (IMT)

D8 Advance : High Temperature

Da Vinci 1

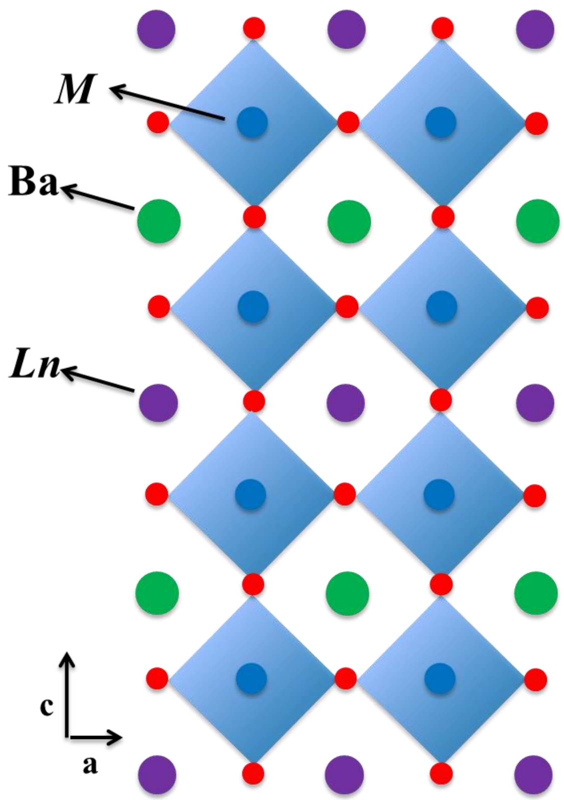
Da Vinci 2

A Unit

D8 Focus

Lay. Double Perov. vs Single Perov.

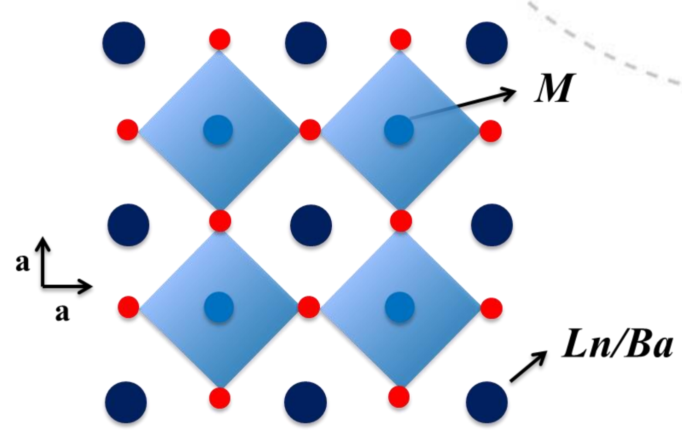
***Ln*BaM$_2$O$_6$;** *Ln* = lanthanide, Y; *M* = Co, Fe, Mn. **vs. *Ln*$_{0.5}$Ba$_{0.5}$*M*O$_3$**



***Ln*BaM$_2$O$_6$**

LDP: A-site cation order

Tetragonal



***Ln*$_{0.5}$Ba$_{0.5}$*M*O$_3$**

SP: A-site cation disorder

Cubic

Why? → Oxygen vacancies

O^{2-} ion and e^- conduction

Ba presence good for H^+ conduction

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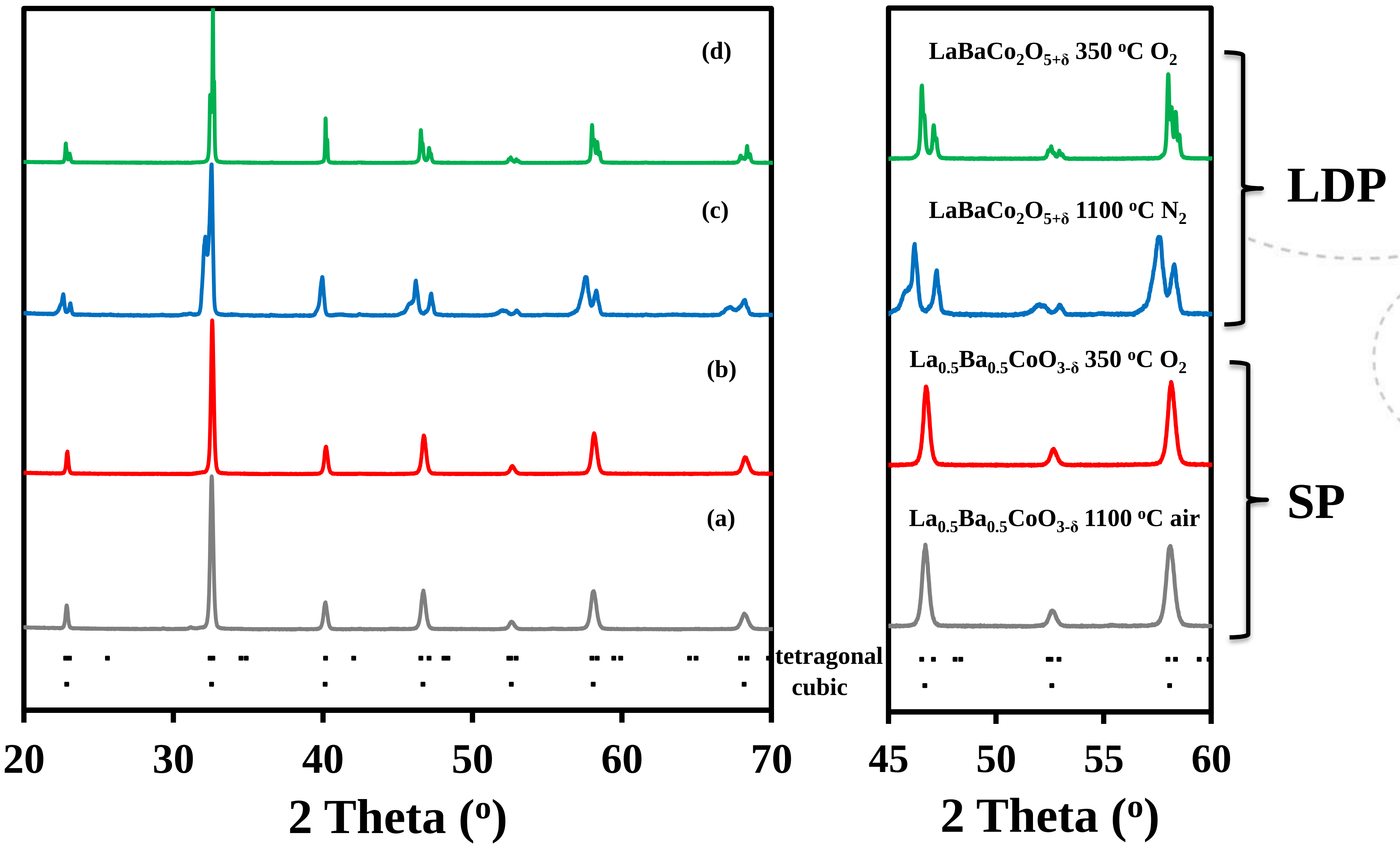
Synthesis


(d)
(c)
(b)
(a)
tetragonal
cubic
20
30
40
50
60
70
2 Theta (º)
LaBaCo$_2$O$_{5+\delta}$ 350 ºC O$_2$
LaBaCo$_2$O$_{5+\delta}$ 1100 ºC N$_2$
La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$ 350 ºC O$_2$
La$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$ 1100 ºC air
45
50
55
60
2 Theta (º)
LDP
SP