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National Institute of Metrology (Thailand)
NIMT

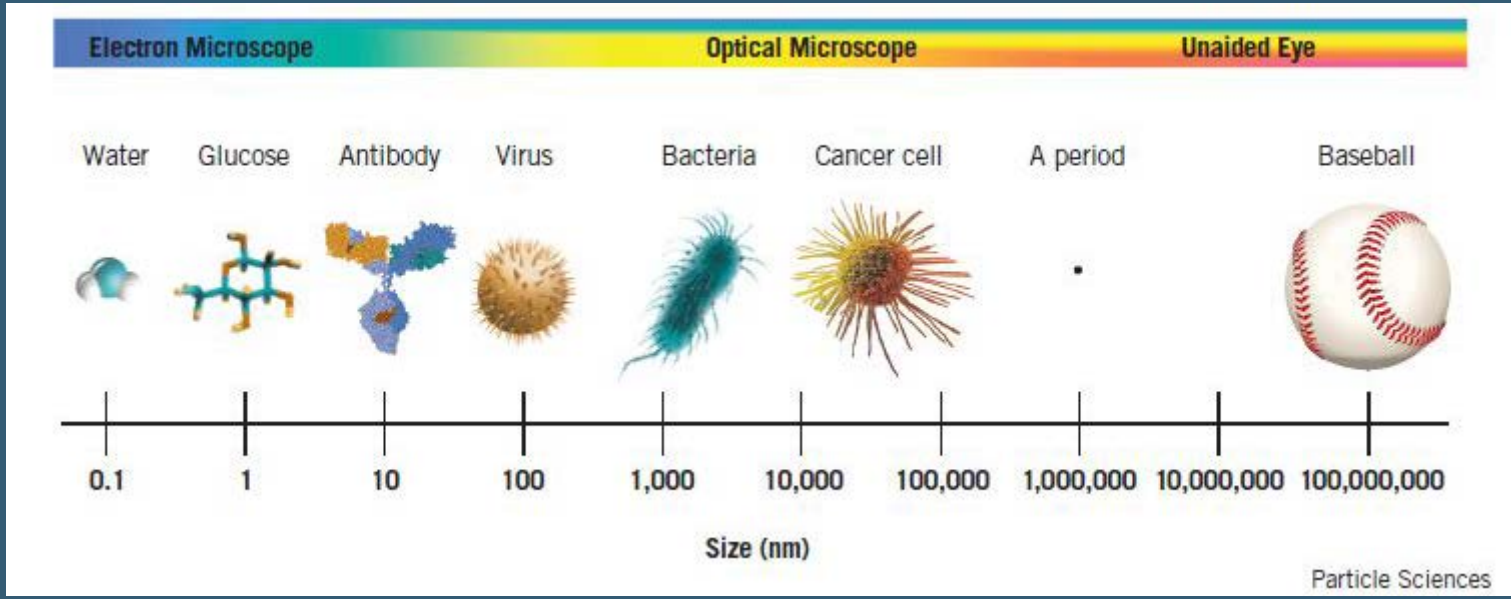
20 ปี แห่งการสถาปนา สถาบันมาตรวิทยาแห่งชาติ

MATERIAL CHARACTERIZATION TECHNIQUE FOR NANO-SCALE MEASUREMENT

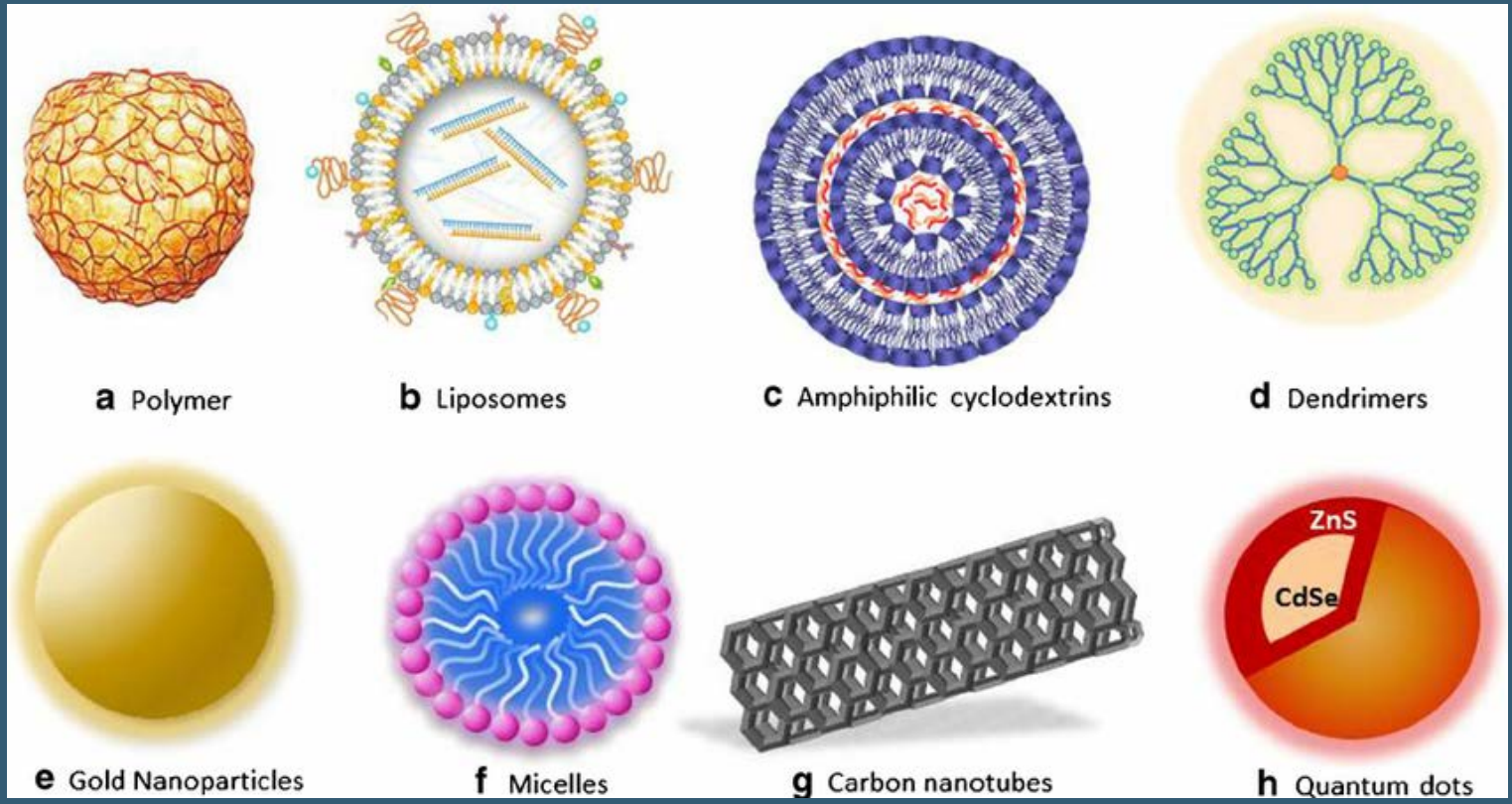
Dr Jariya Buajarern

Nanometrology Group, Dimensional Metrology Department

NANOSCALE


Electron Microscope
Optical Microscope
Unaided Eye
Water
Glucose
Antibody
Virus
Bacteria
Cancer cell
A period
Baseball
0.1
1
10
100
1,000
10,000
100,000
1,000,000
10,000,000
100,000,000
Size (nm)
Particle Sciences

NANOPARTICLES



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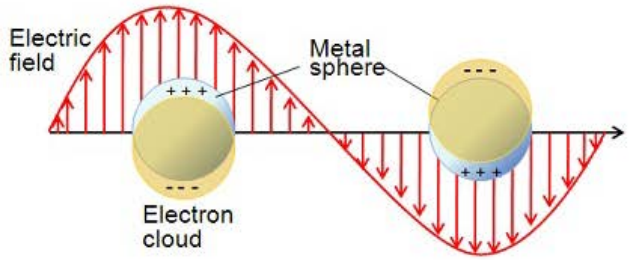
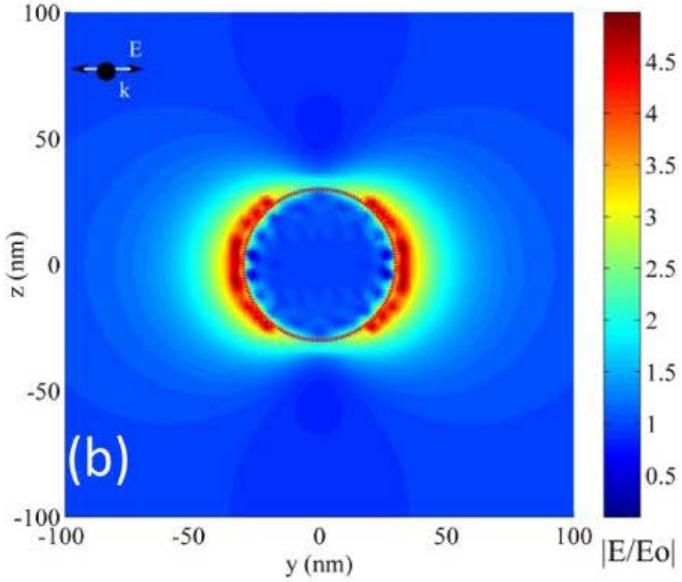
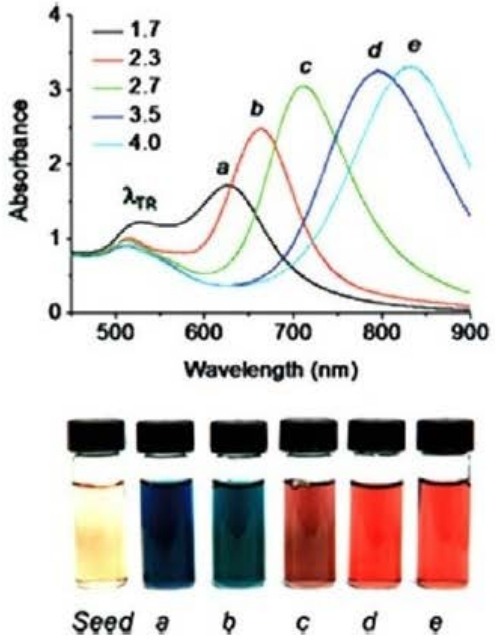
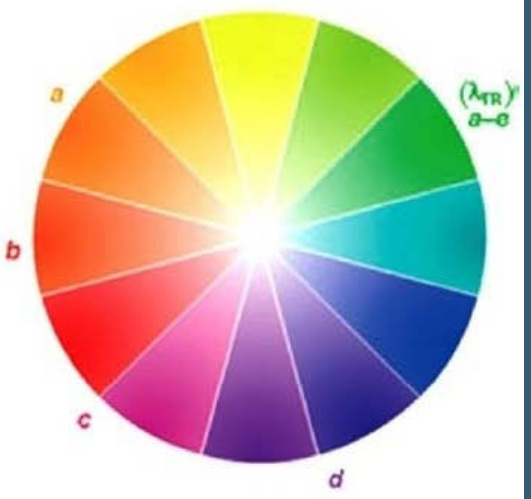
PROPERTIES





Simulation of the surface plasma resonance of a spherical particle





Different colors of gold nanoparticles and their respective light absorbance

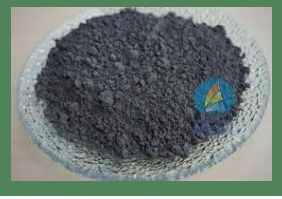
NANOTECHNOLOGY VALUE CHAIN

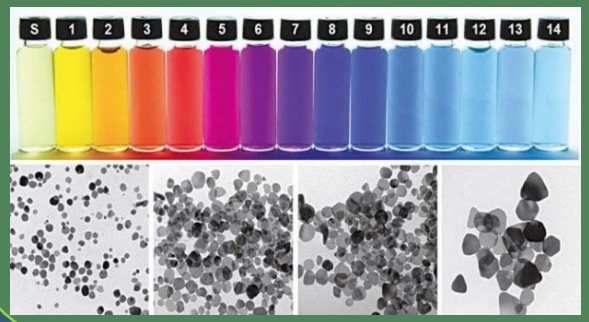
Nanomaterial → **Nanointermediates** → **Nano-enable products**

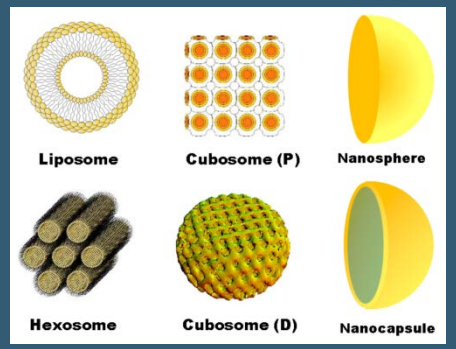
Nanoscale structures in unprocessed form

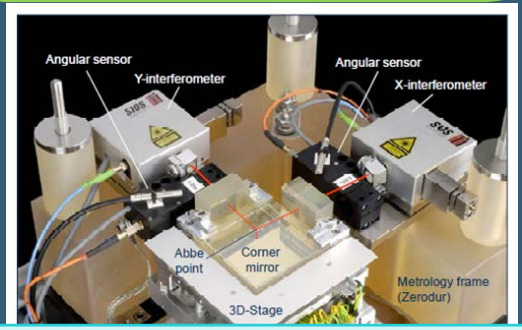
Intermediate products with nanoscale features

Finished goods incorporating nanotechnology









Needs!!!

Measurement methods, Instruments, Standards, Safety

ผลิตภัณฑ์ที่มีส่วนประกอบของวัสดุนาโน หรือใช้นาโนเทคโนโลยีเพื่อสร้างคุณลักษณะใหม่ ทั้งนี้ลักษณะของวัสดุนาโนที่เติมลงไปในผลิตภัณฑ์อาจมีโครงสร้างที่ซับซ้อน และแตกต่างจากวัสดุนาโนในรูปของวัตถุดิบ ดังนั้นการพิสูจน์ว่าผลิตภัณฑ์มีวัสดุนาโนอยู่จริง และปลอดภัย จึงเรื่องท้าทาย

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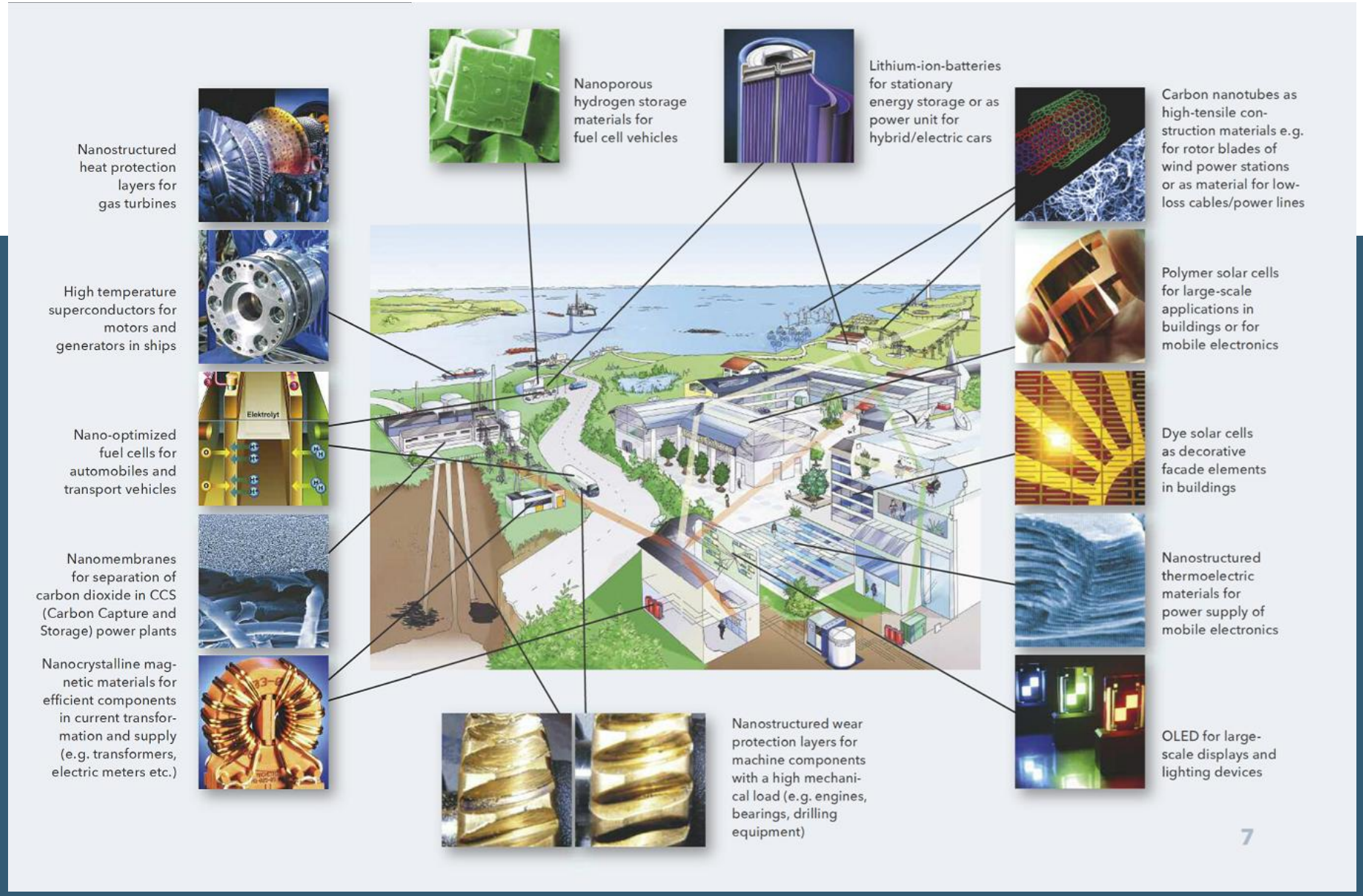
มว. สถาปนาระบบการสอบกลับได้ในการวัดวัสดุนาโนตั้งแต่ ปีพ.ศ.2558 และเปิดให้บริการสอบเทียบมาตรฐานสำหรับเครื่องทดสอบขนาดวัสดุนาโน



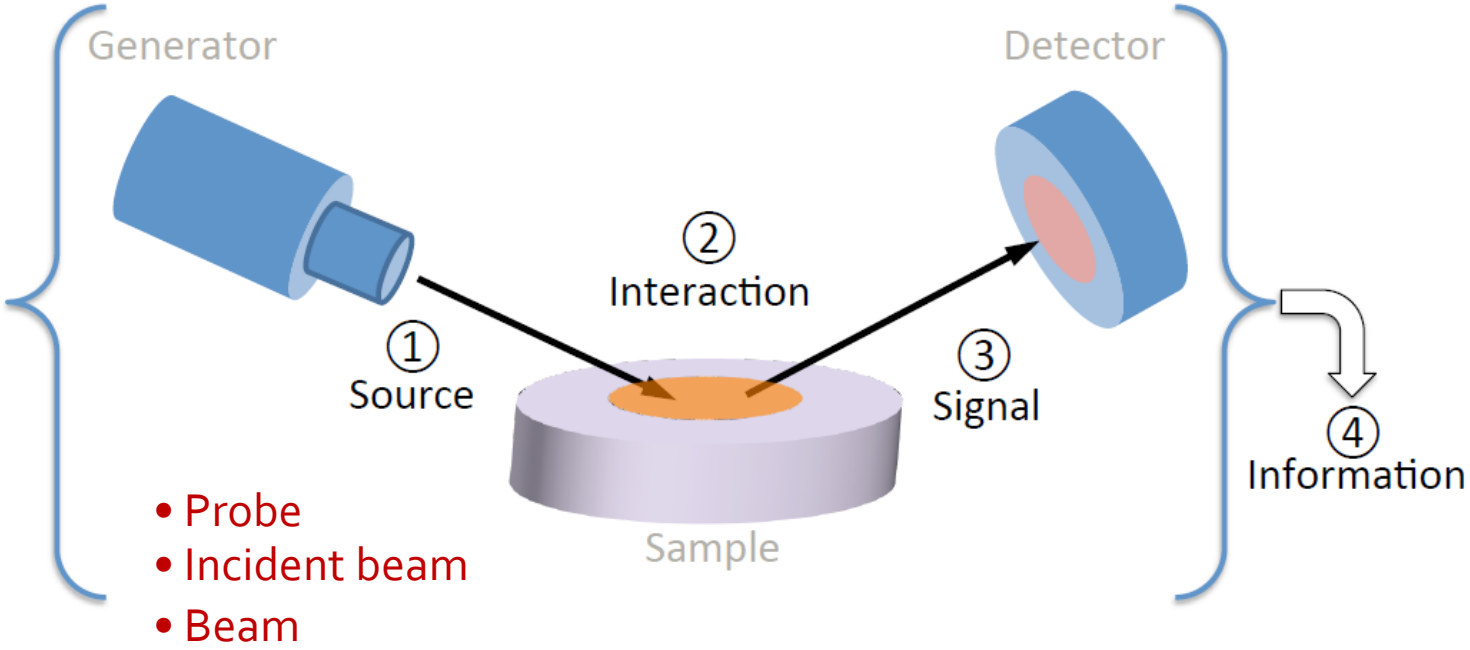
https://www.utwente.nl/mesaplus/nme/Introduction/

CHARACTERIZATION TECHNIQUES

Properties	Common Techniques
Size (primary particle)	TEM, SEM, AFM, XRD
Size (primary/aggregate/agglomerate)	TEM, SEM, AFM, DLS, FFF, AUC, CHDF, XDC, HPLC, DMA(1)
Size distribution	EM, SEM, AFM, DLS, AUC, FFF, HPLC, SMA
Molecular weight	SLS, AUC, GPC
Structure/Shape	TEM, SEM, AFM, NMR
Stability (3D structure)	DLS, AUC, FFF, SEM, TEM

Ref: Prof. Supapan Seraphin

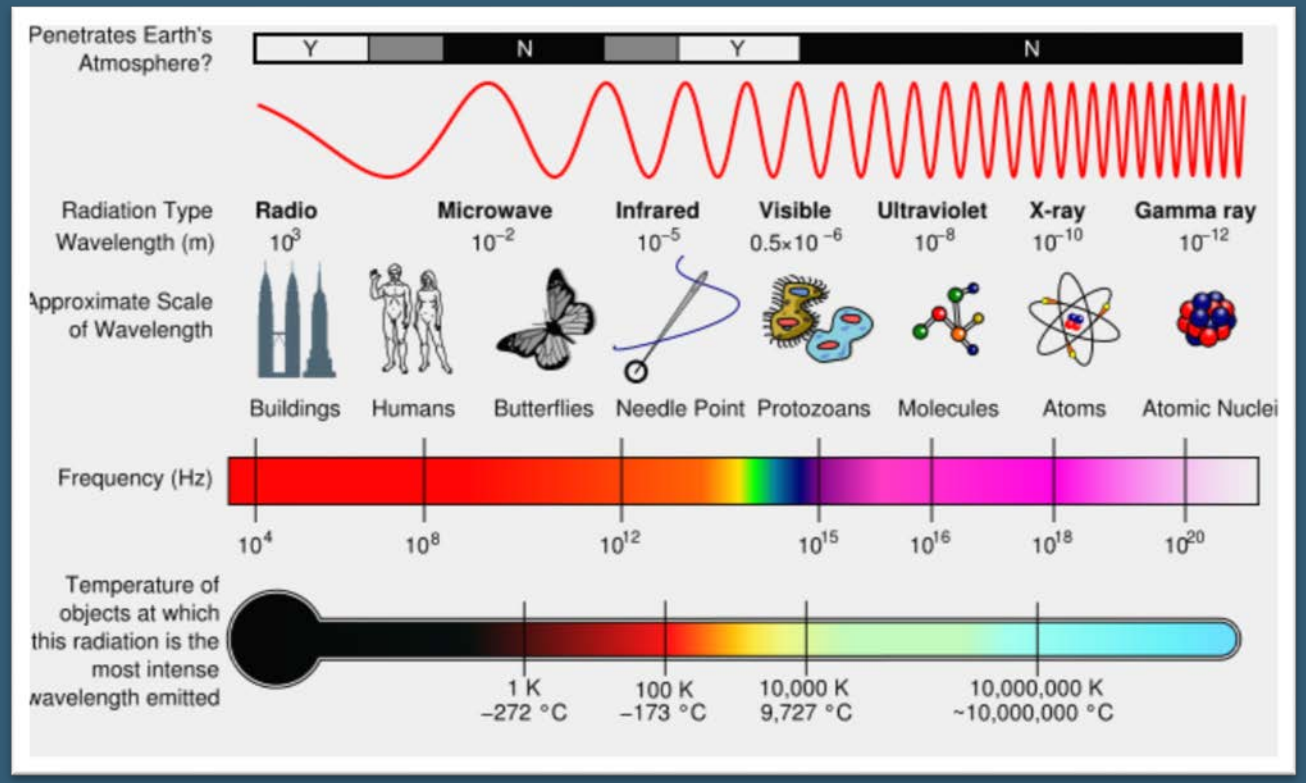
BASIC PRINCIPLE



① A source radiation is aimed at the sample
② It interacts with the sample in some way
③ As a result of the interaction, a signal is produced
④ Analysis of the signal reveals information about the sample

Ref: Prof. Supapan Seraphin

ELECTRO-MAGNETIC RADIATION (PHOTONS)



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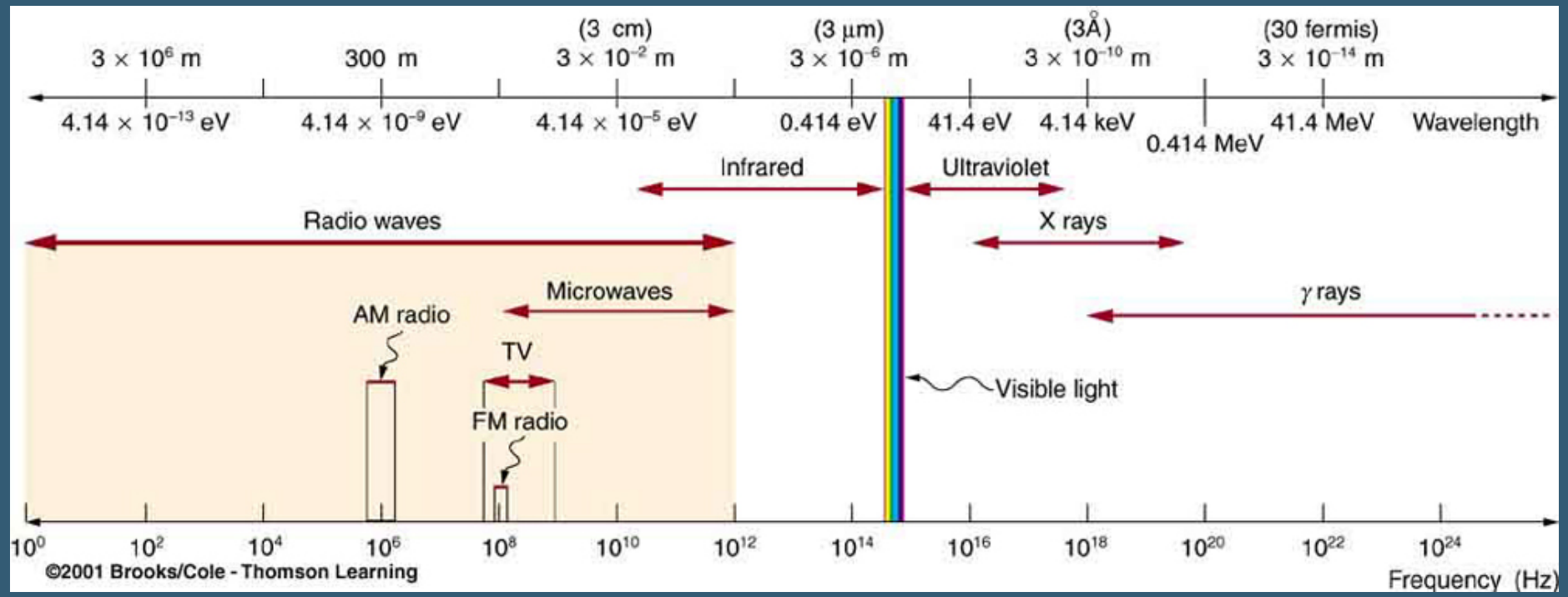
Ref: Prof. Supapan Seraphin

PHOTON ENERGY IN EV

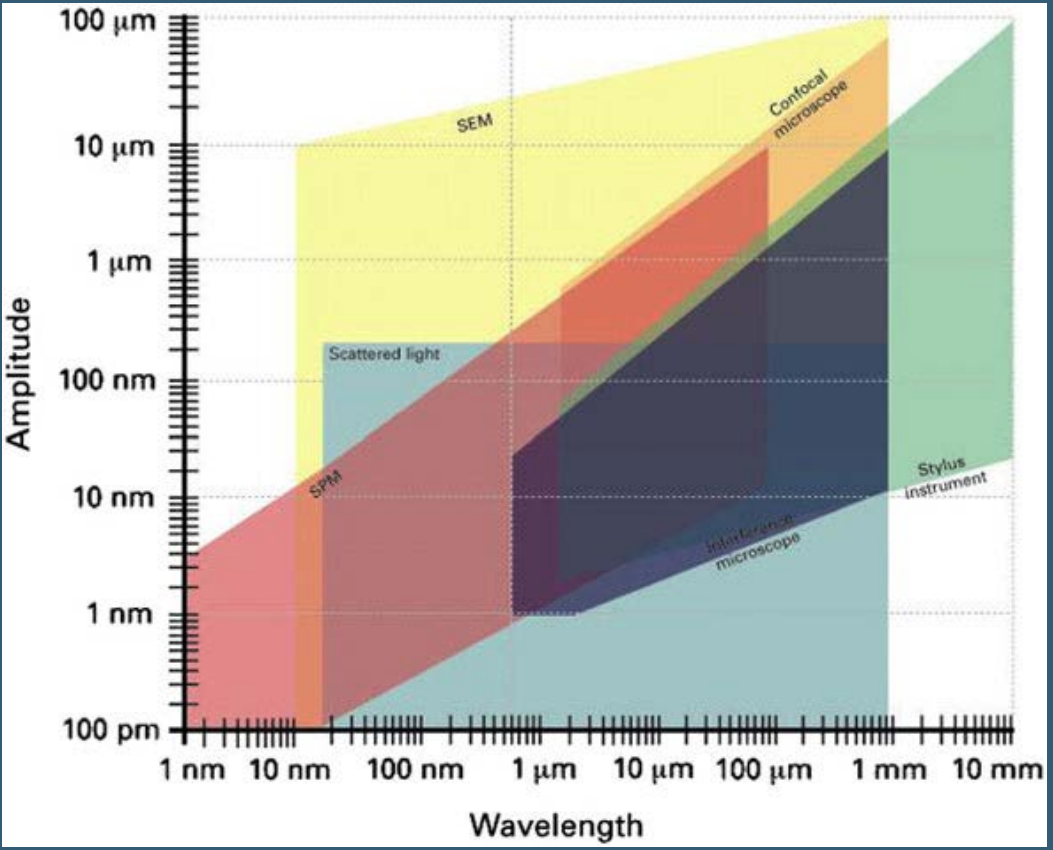


CATEGORIES OF TECHNIQUES

- Microscopy (imaging)
- Diffraction (crystal structure)
- Spectroscopy (chemical composition/elemental analysis)

CHARACTERIZATION TECHNIQUES: DIMENSIONAL NANOMETROLOGY

- Spatial resolution = $\frac{0.611 \cdot \lambda}{NA}$



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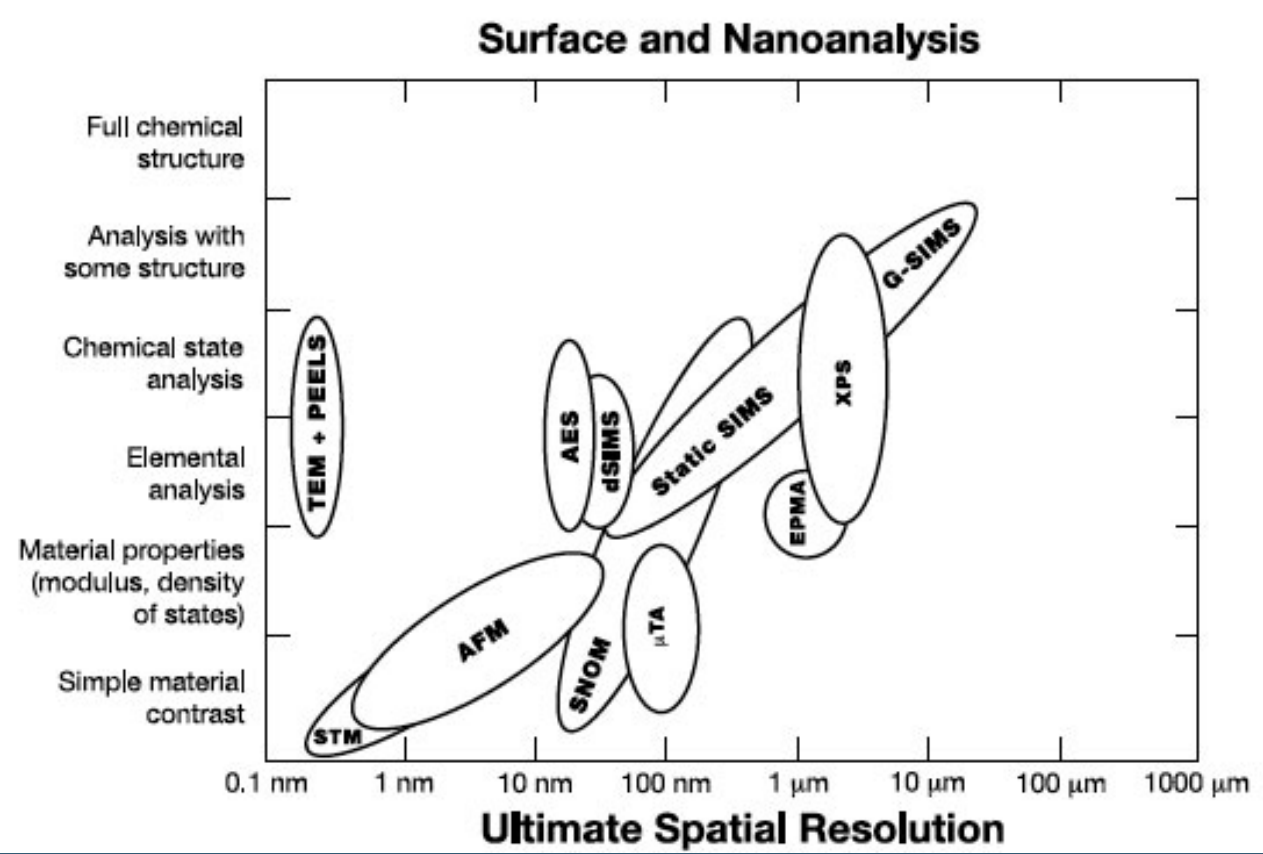
CHARACTERIZATION TECHNIQUES: CHEMICAL NANOMETROLOGY



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TRANSMISSION ELECTRON MICROSCOPE (TEM)

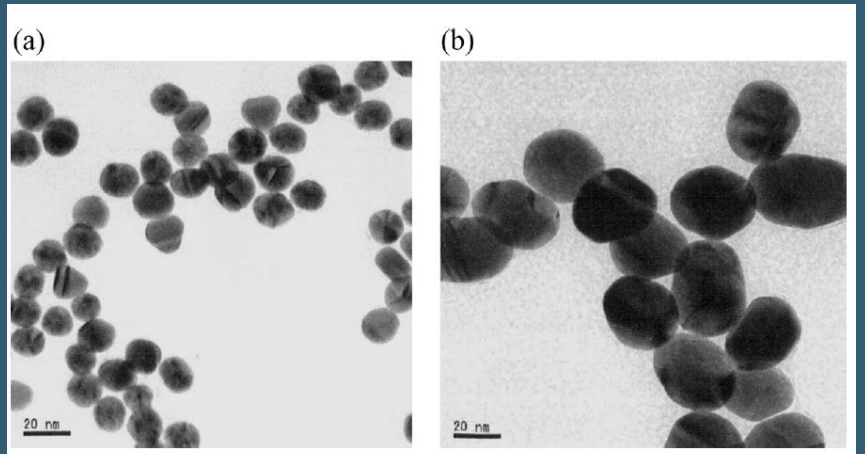
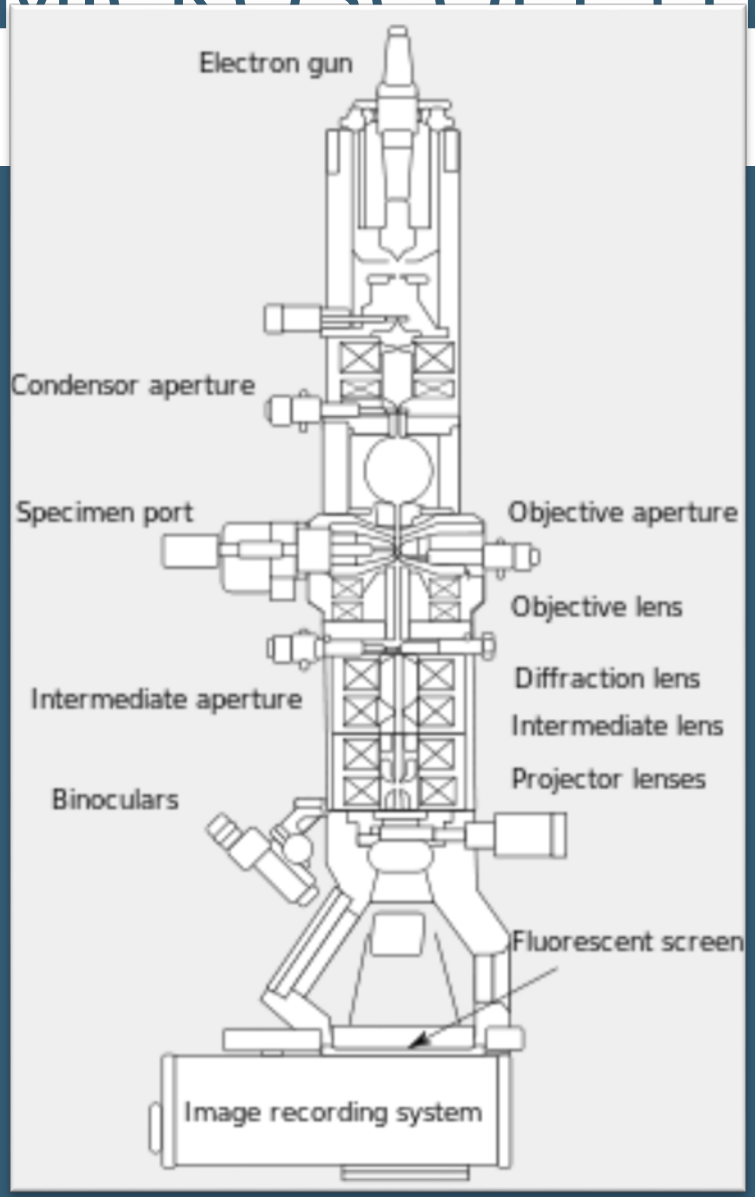
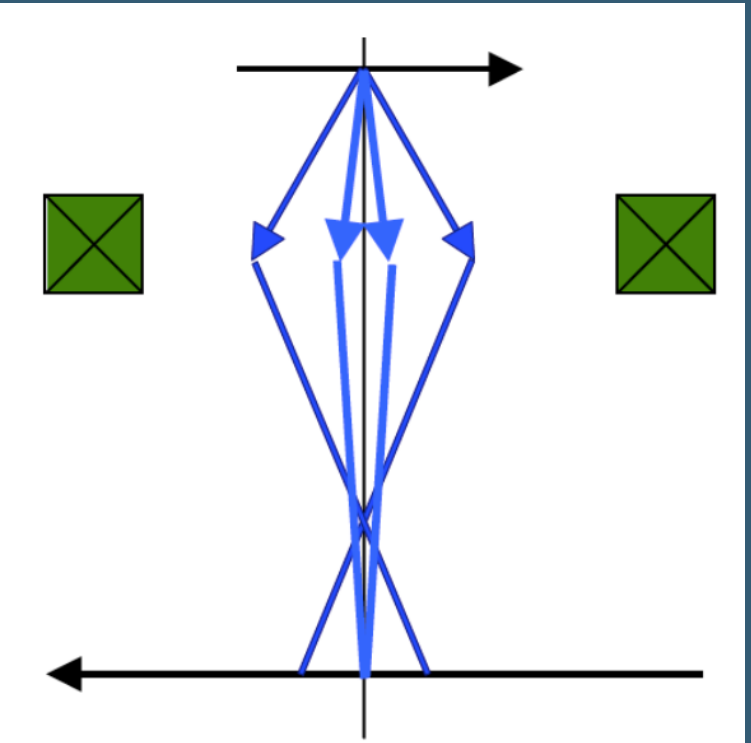


Fig. 1. TEM images of gold nanoparticles.
(a) Au 15 nm, (b) Au 35 nm.



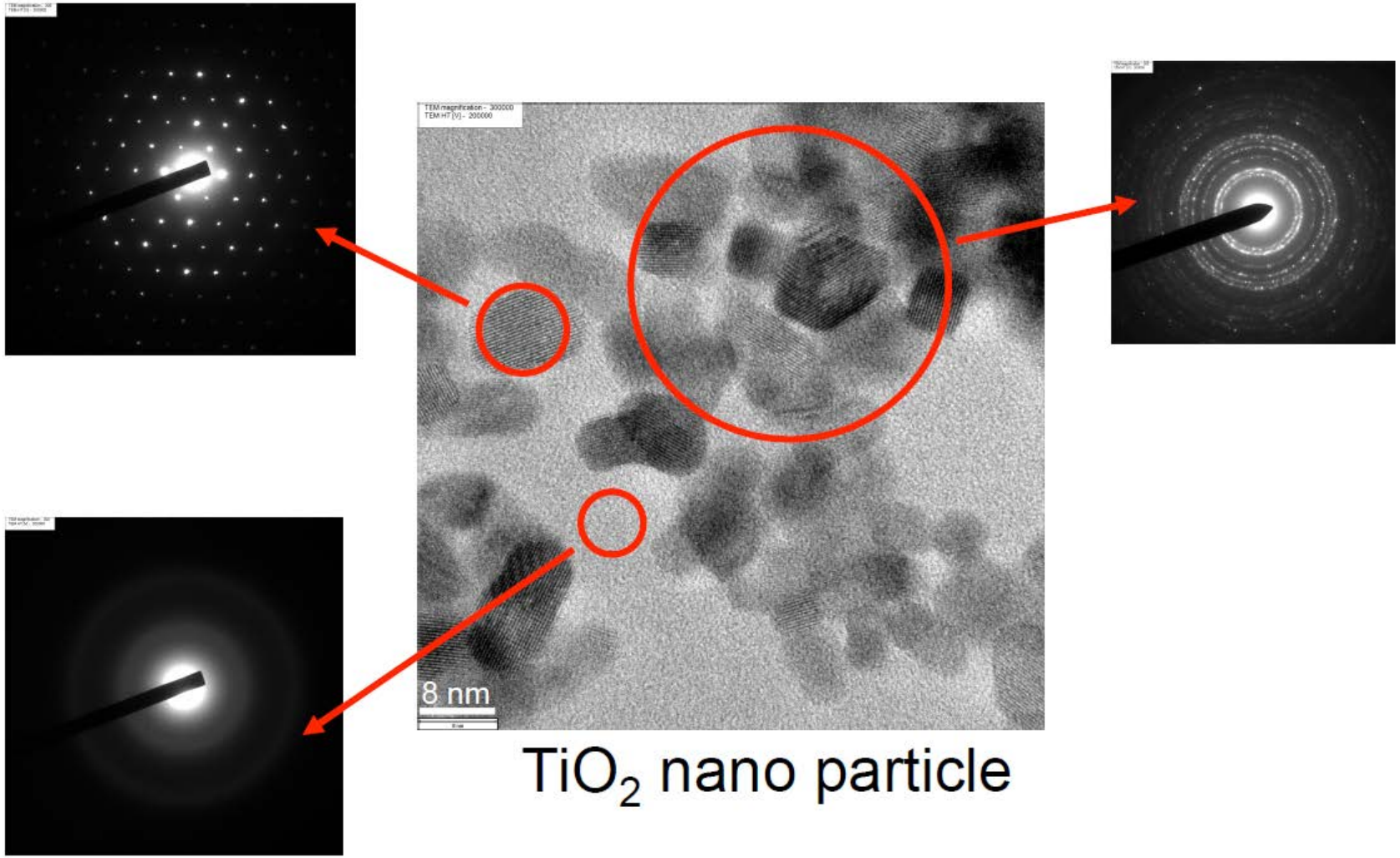
PARAMETERS THAT AFFECT IMAGE RESOLUTION

- Wavelength
- Spherical aberration
- Diffraction vector
- Defocus



Spherical aberration

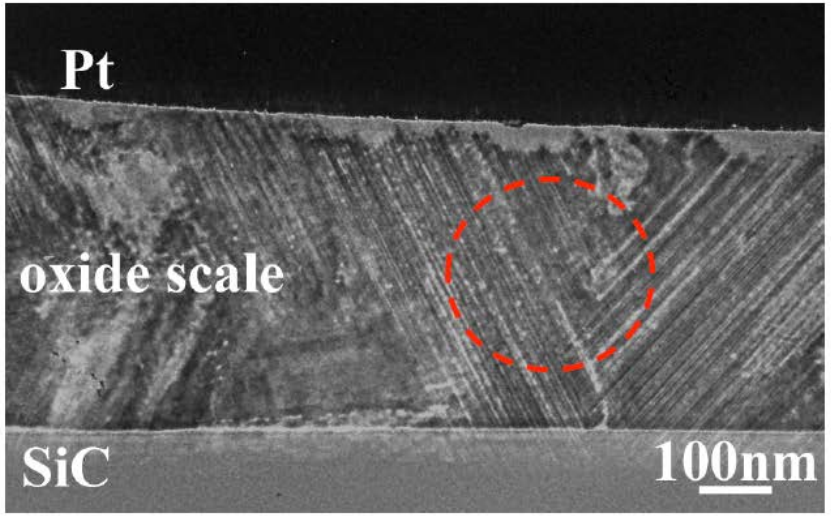
Electron Diffraction Pattern

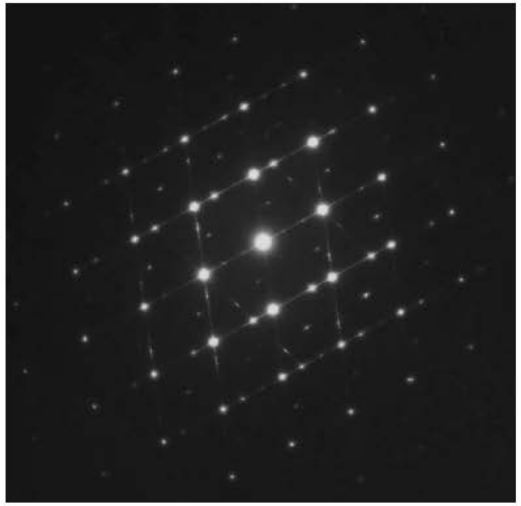


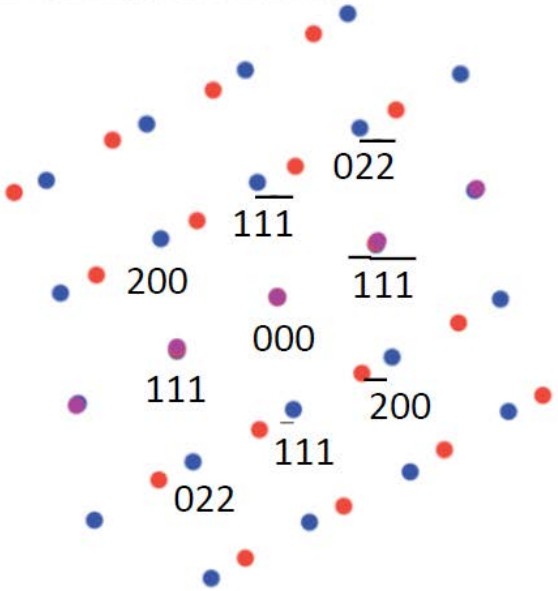
TiO_2 nano particle

Ref: Prof. Supapan Seraphin

Electron Diffraction Pattern of Twin Crystal



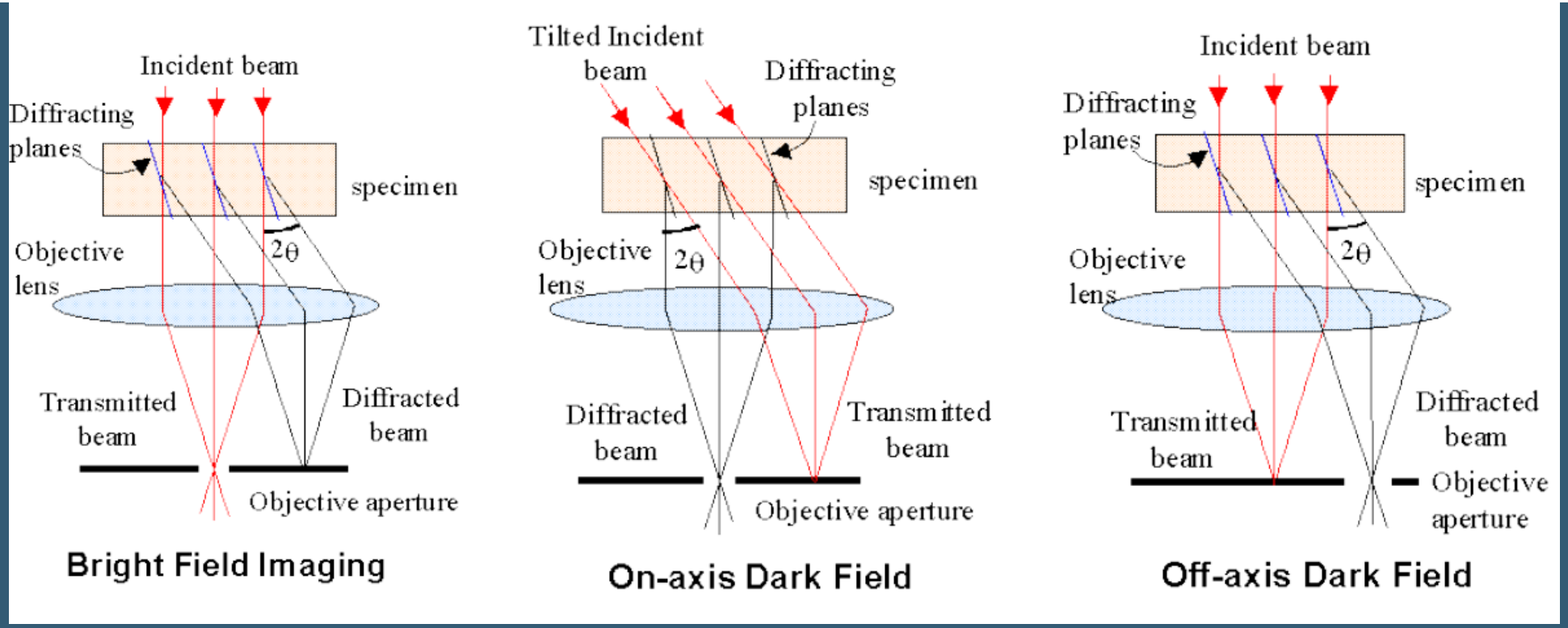




Cristobalite (high)

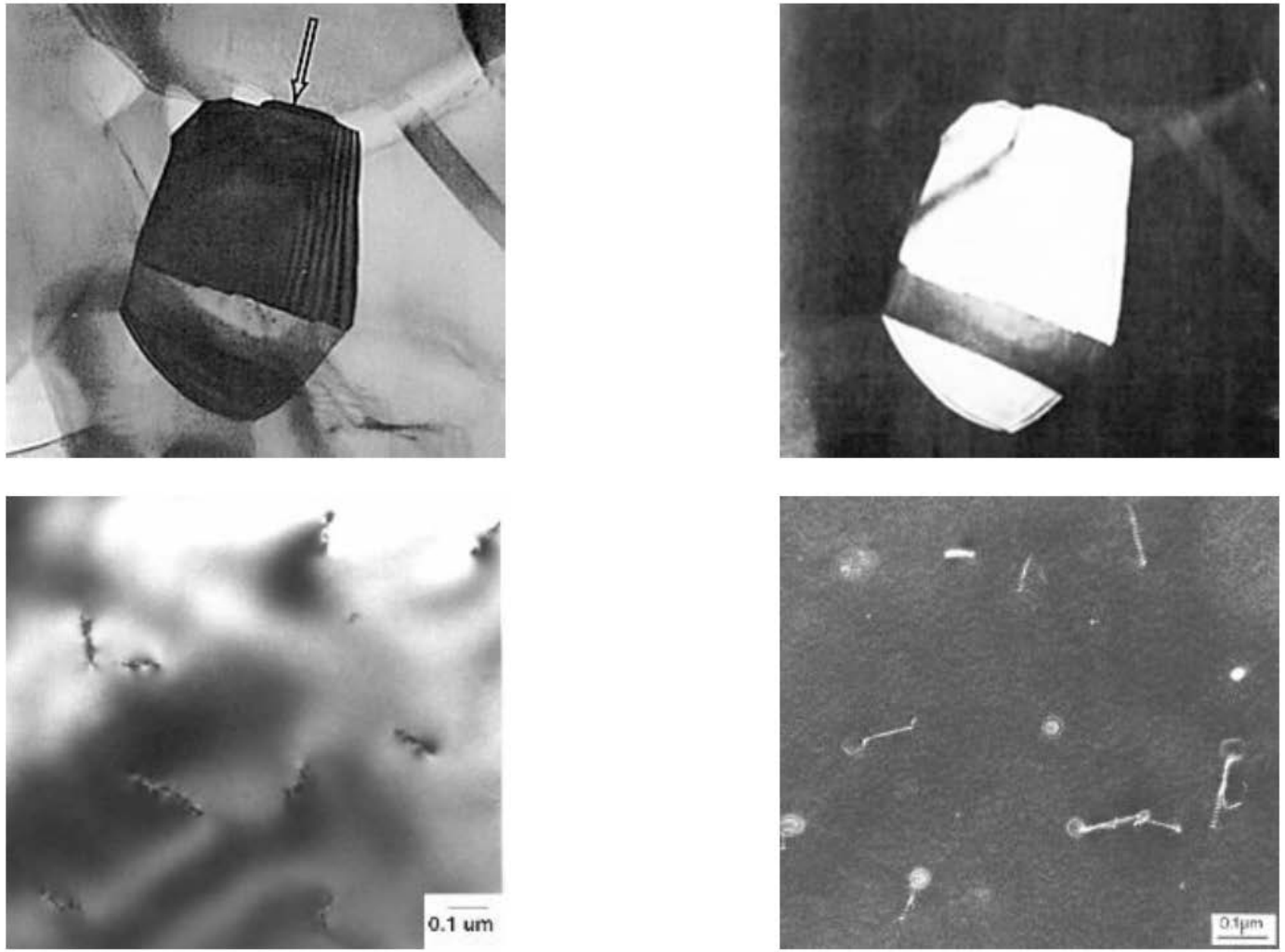
Ref: Prof. Supapan Seraphin

Bright-field and Dark-field Imaging



Ref: Prof. Supapan Seraphin

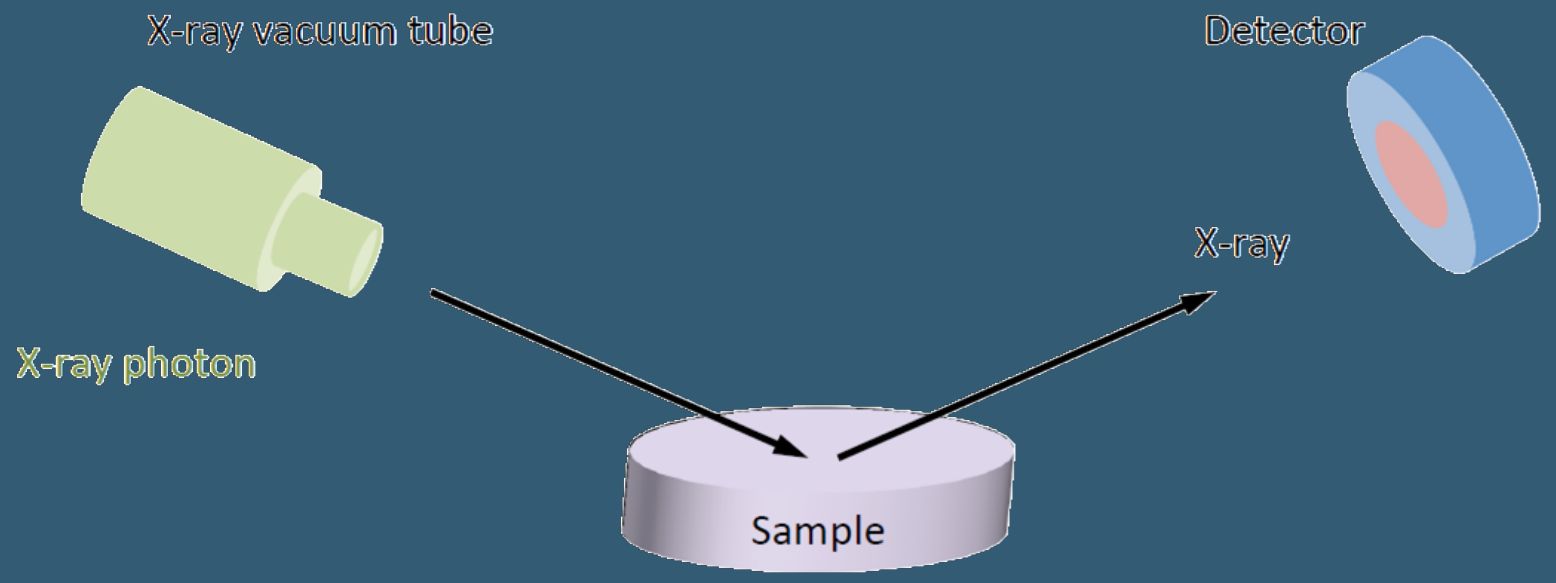
Advantages of dark field imaging



Ref: Prof. Supapan Seraphin

X-RAY DIFFRACTION (XRD)

- Incident beam X-ray
- Diffraction
- Detected beam X-ray

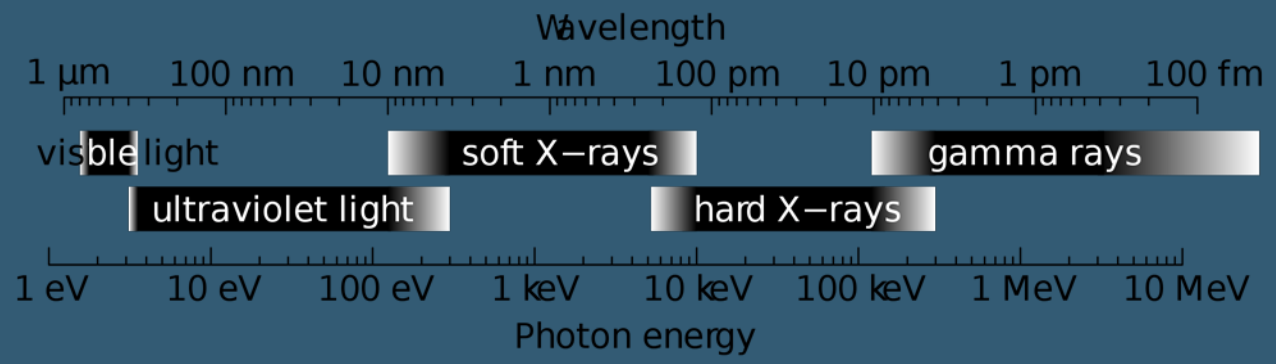


PRINCIPLES

- Diffraction = scattering from regular spacing
- This gives interference (Diffraction pattern) or peaks
- Crystal structure is regular arrangement
- Crystal structure + lattice parameter = finger print of the material
- Diffraction pattern = finger print

WHAT WE CAN GET FROM XRD

- Crystal structure (FCC, BCC, ….)
- D-spacing (0.1-0.3 nm) and lattice parameters
- Orientation
- Phase information (FeO or Fe_2O_3)
- Internal stresses



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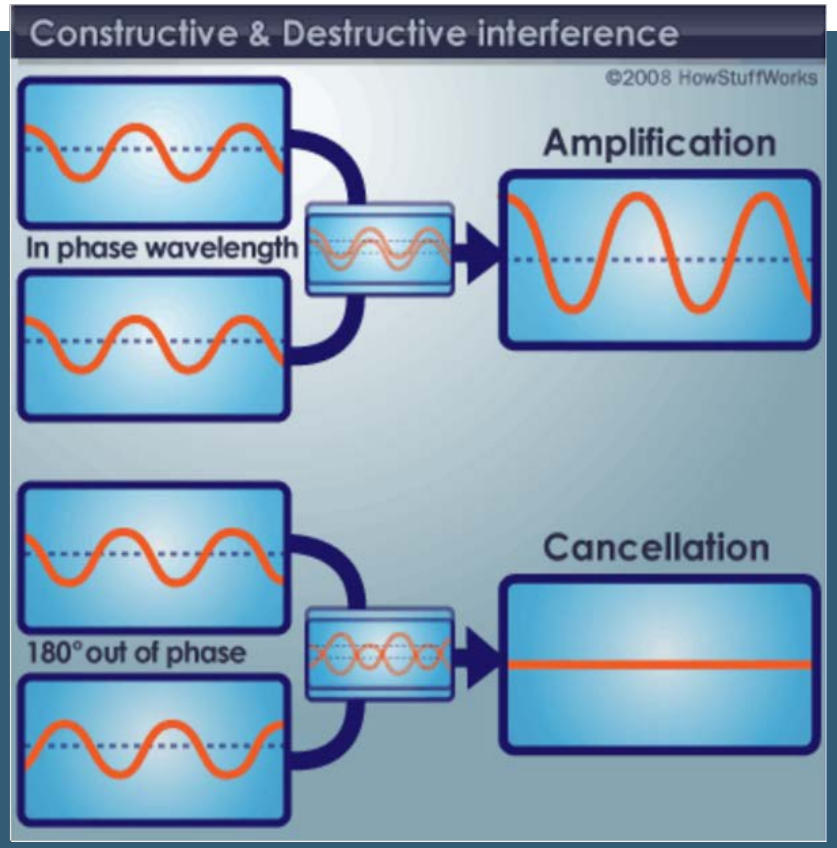
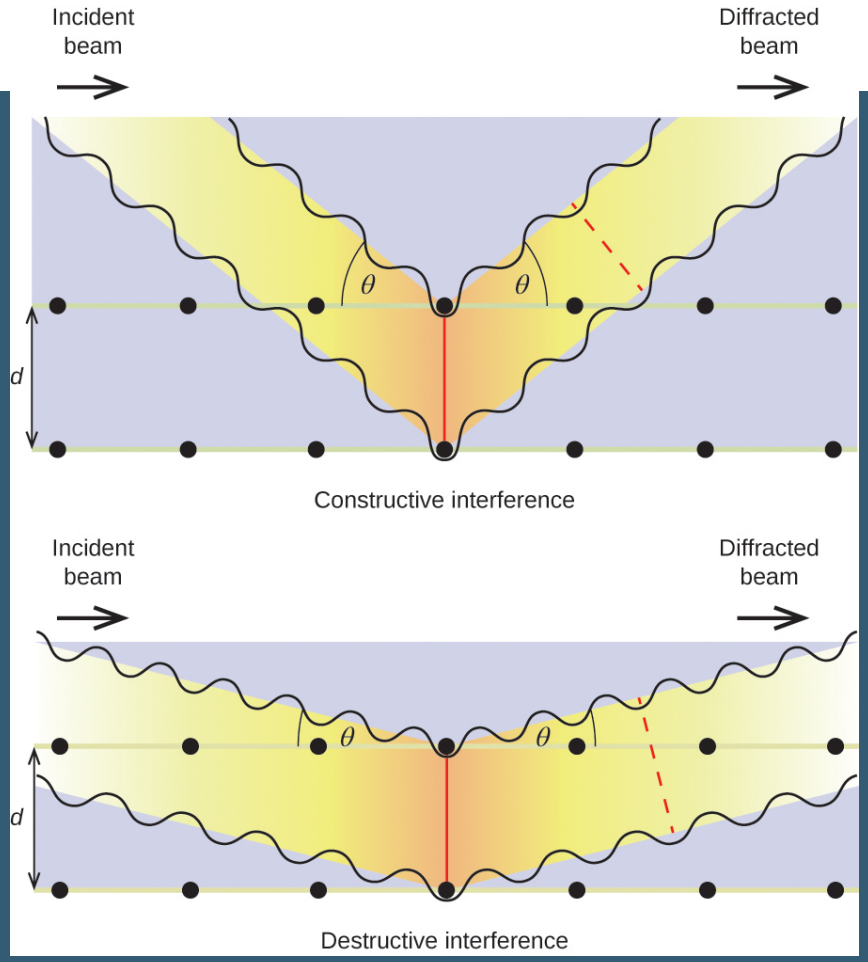
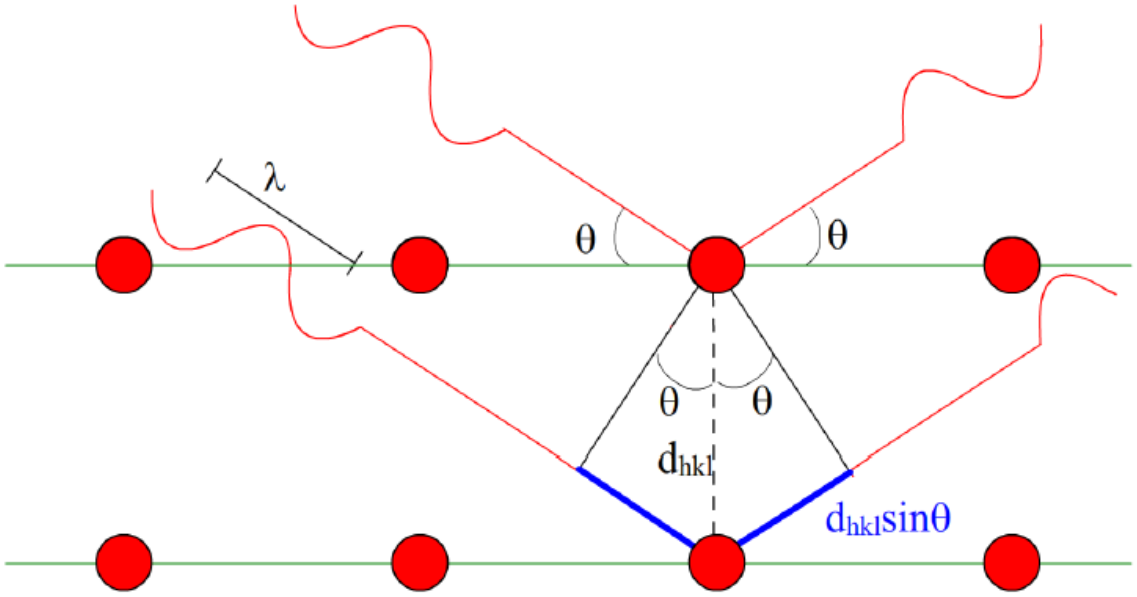
INTERACTION (DIFFRACTION)

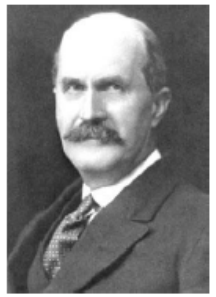




BRAGG'S LAW



Jointly awarded the 1915
Nobel Prize in Physics



William Henry Bragg

William Lawrence Bragg

Total path difference = $2d_{hkl}\sin\theta$

Constructive Interference when $n\lambda = 2d_{hkl}\sin\theta$

http://www.doitpoms.ac.uk/tlplib/xray-diffraction/flash/bragg.swf

$$d_{hkl} = n\lambda / 2 \cdot \sin\theta$$

DETECTION

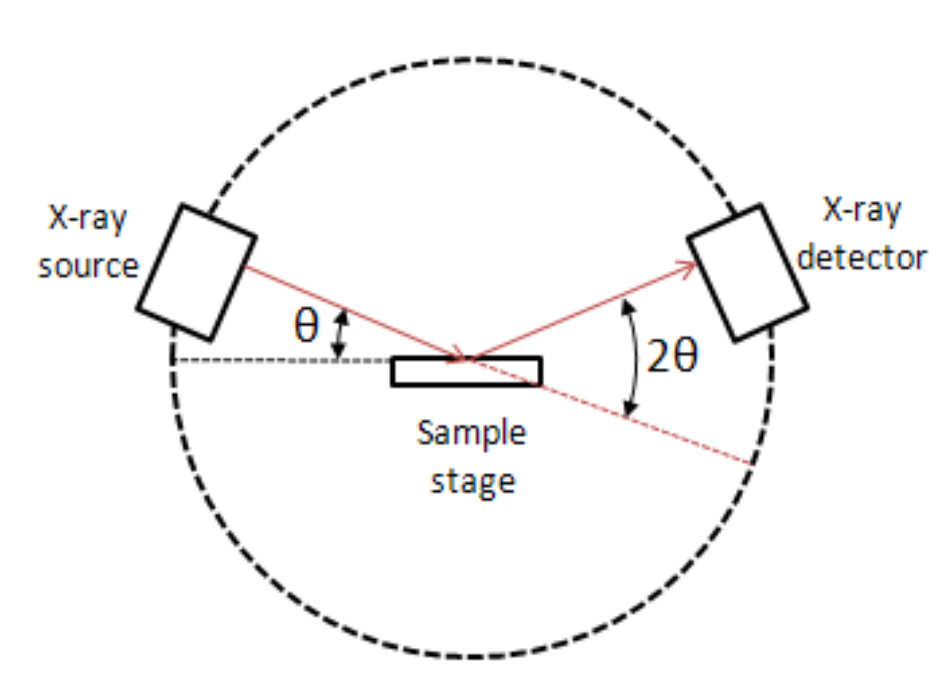
X-Ray can be detected in 2 main ways:

1) Measuring blackening produced in photographic film. Converts amount of blackening into x-ray intensity

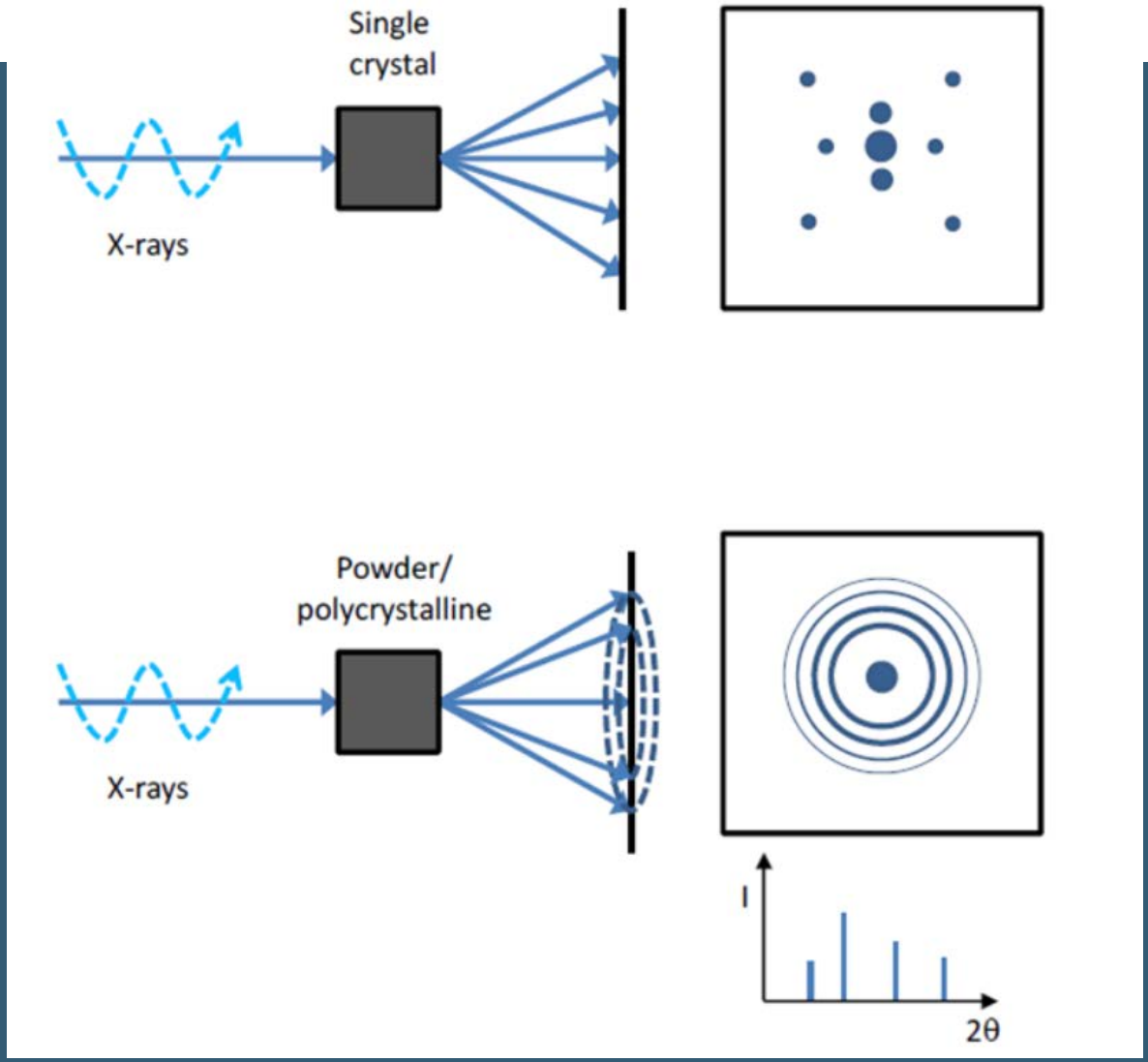
2) Measuring pulses of electric current. Convert pulses into x-ray intensity

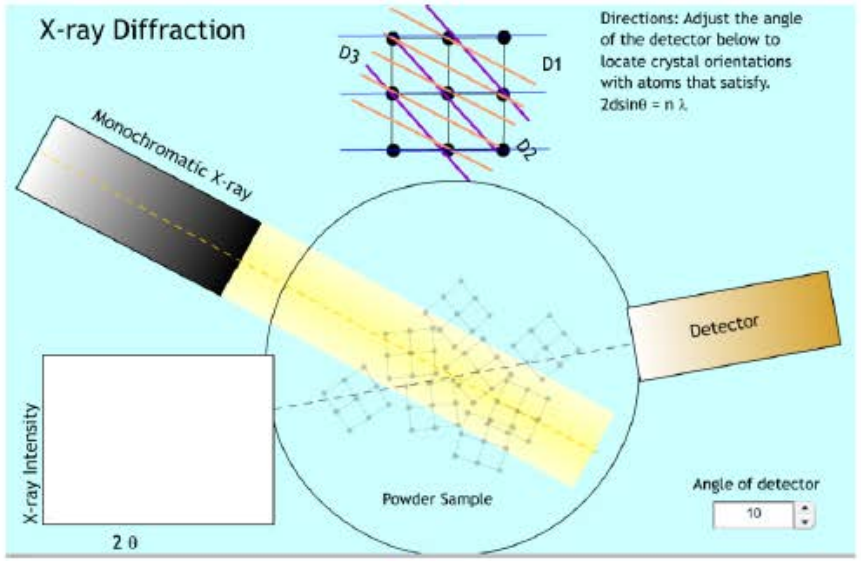
X-RAY DIFFRACTOMETER

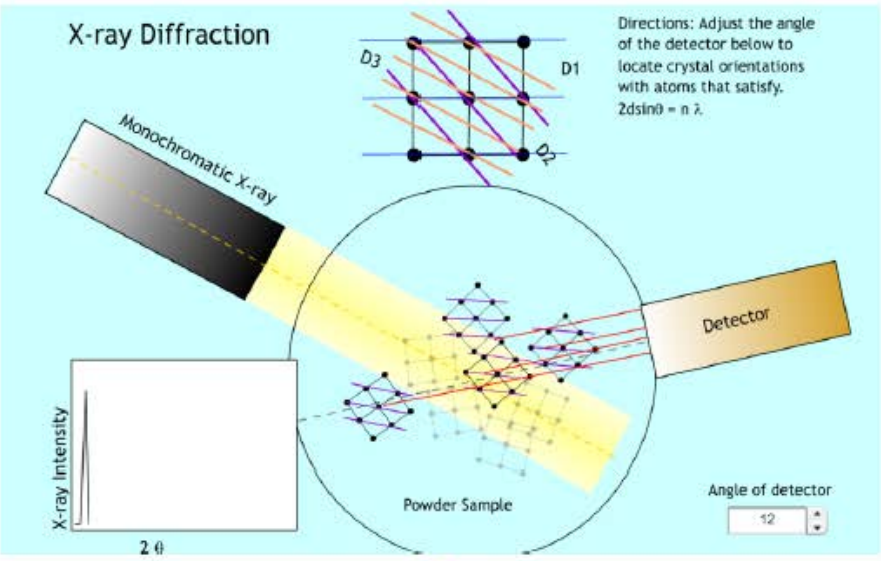
1) X-ray source
2) Interaction
3) X-ray detector
4) Analysis

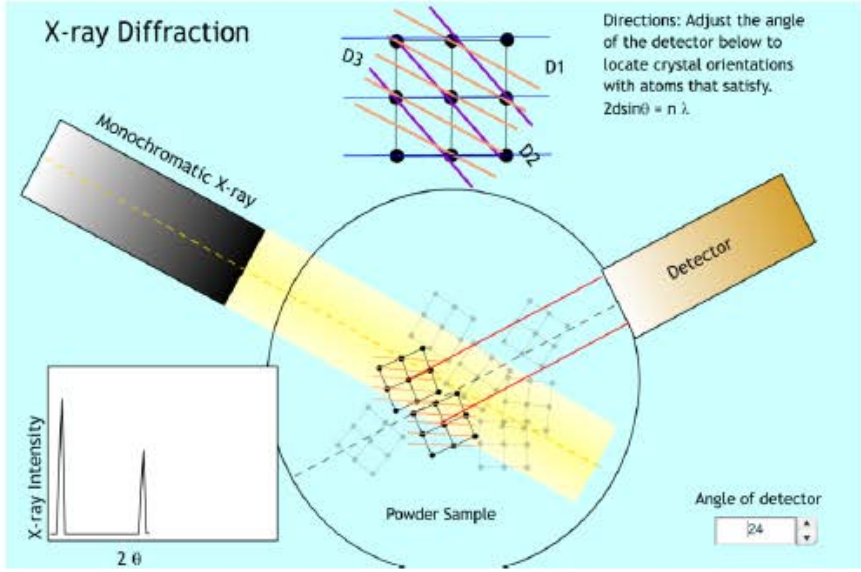


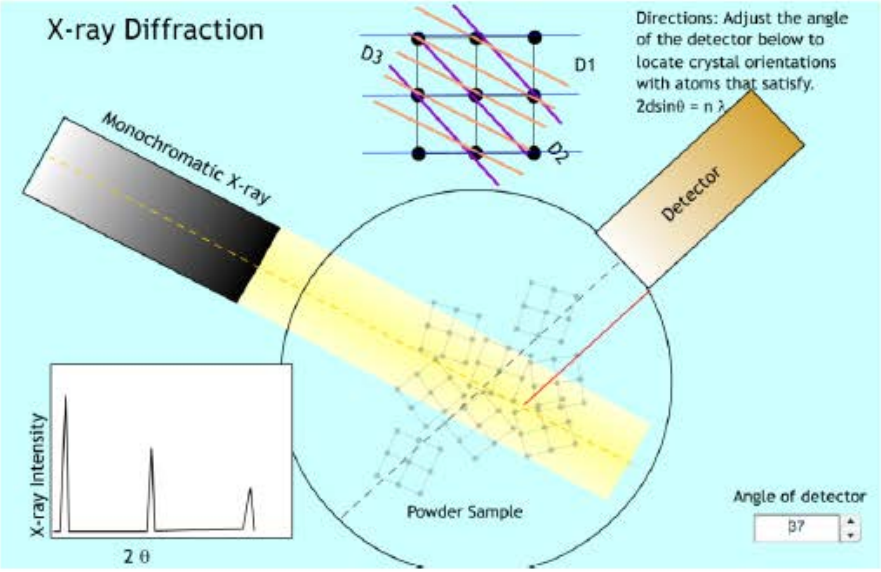
DIFFRACTION PATTERN







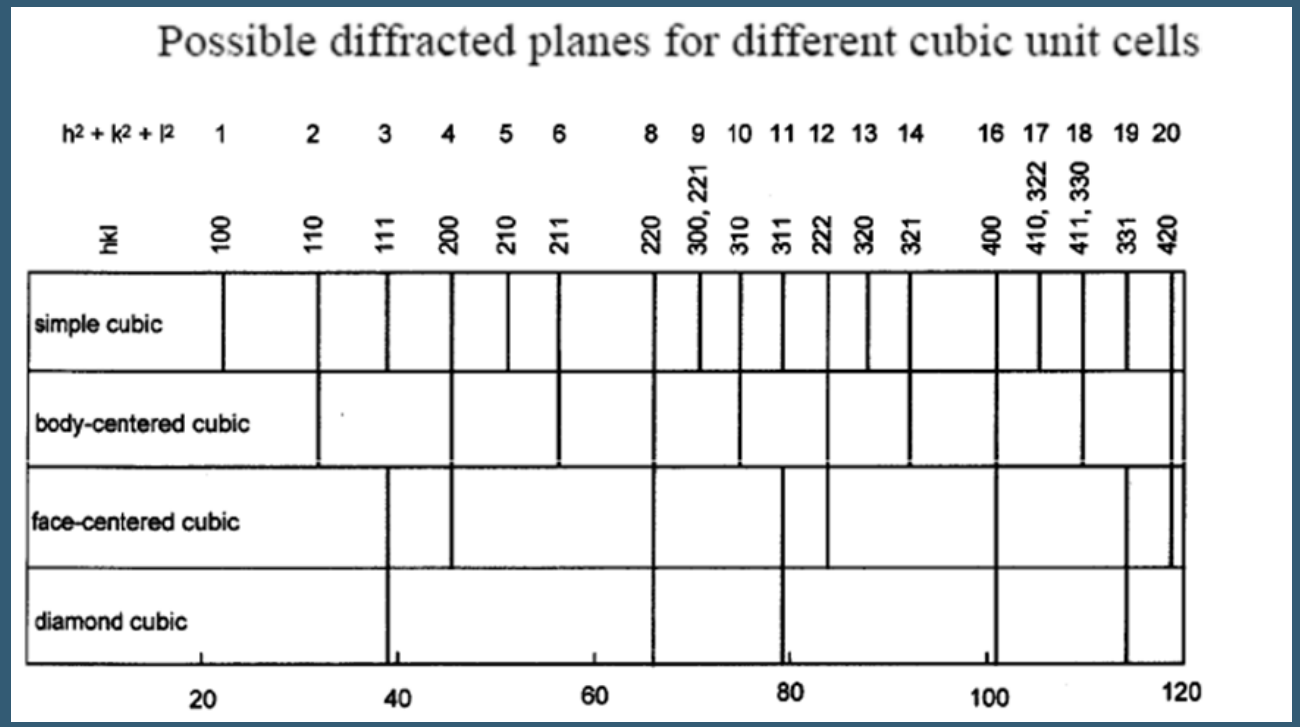




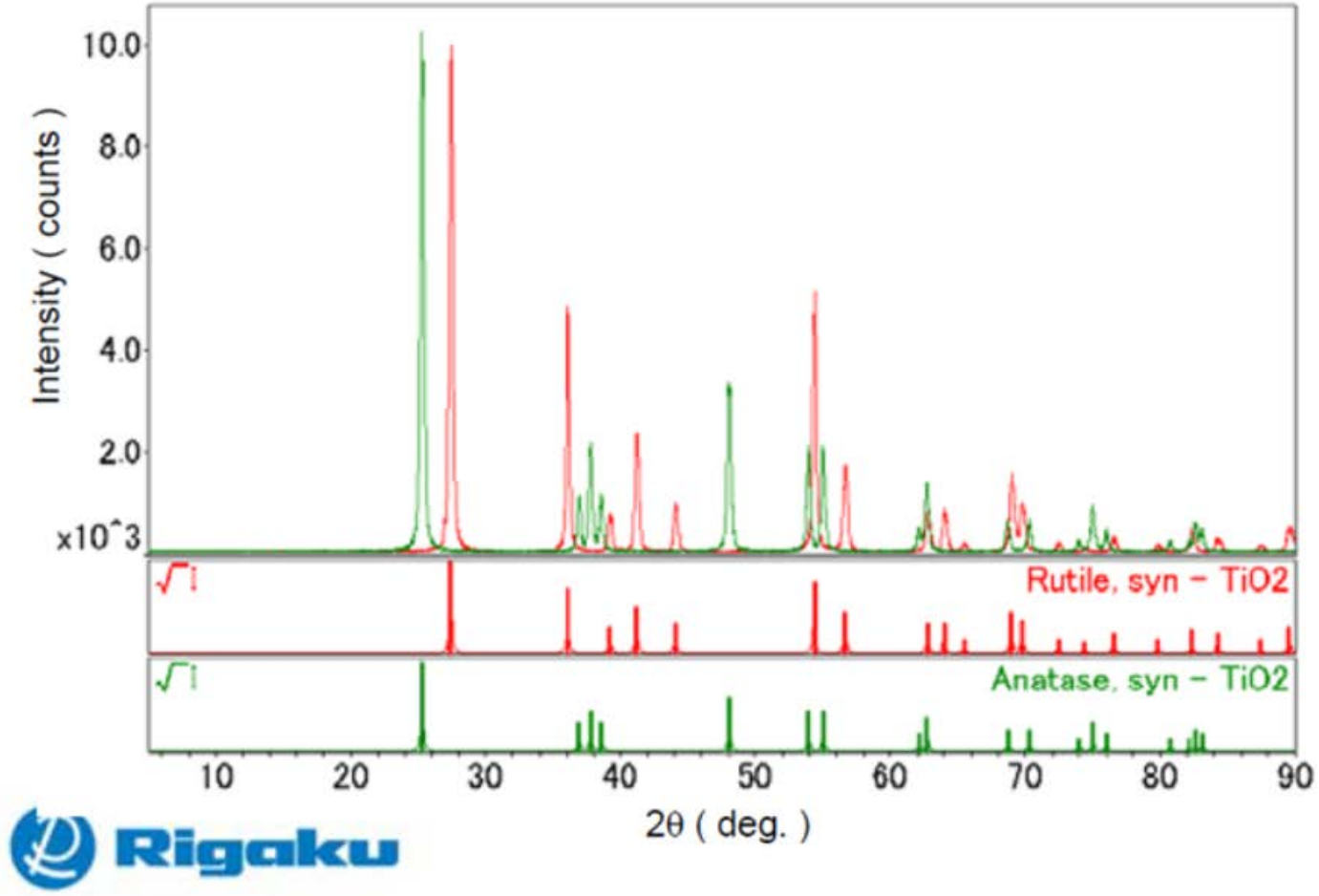
http://photonicswiki.org/images/4/46/Xrd.swf

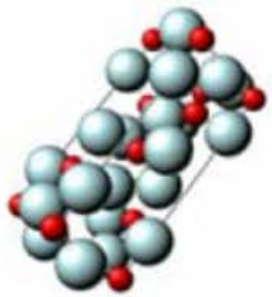
ANALYSIS

- We get from XRD: peaks at 2θ
- We analyze:
  - Peak position (Planes of atoms = Crystal structure)
  - Width
  - Intensity



EXAMPLE 1

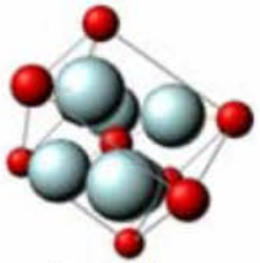




Anatase

Used For Photocatalyst

TiO2



Rutile

Used For Cosmetic

http://homepage.ntu.edu.tw/~kcyuan/form/For_Rigaku-Upload_powder.pdf

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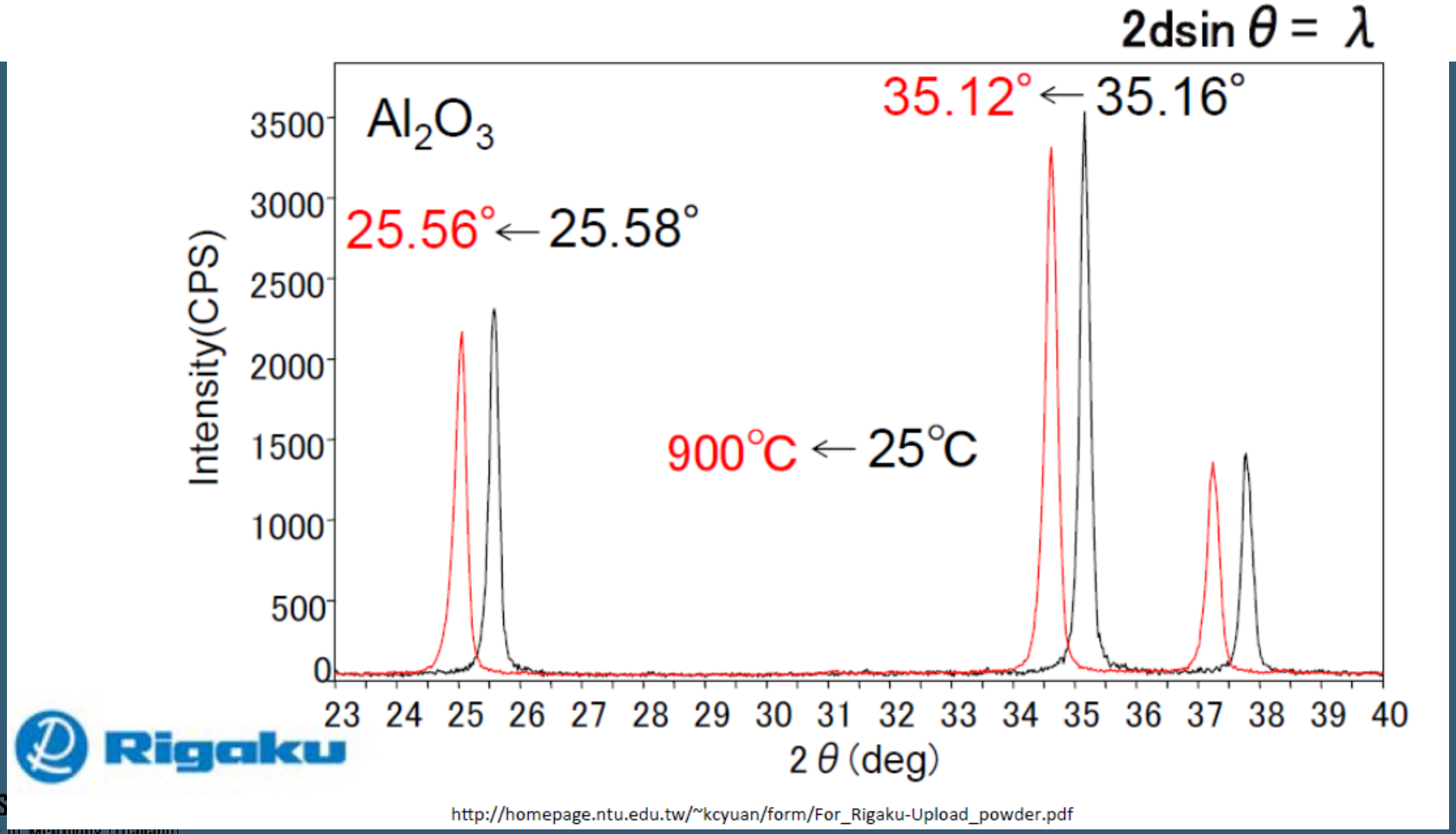
EXAMPLE 2



http://homepage.ntu.edu.tw/~kcyuan/form/For_Rigaku-Upload_powder.pdf

Peak width

- Grain size
- Internal Strains

- Grain size

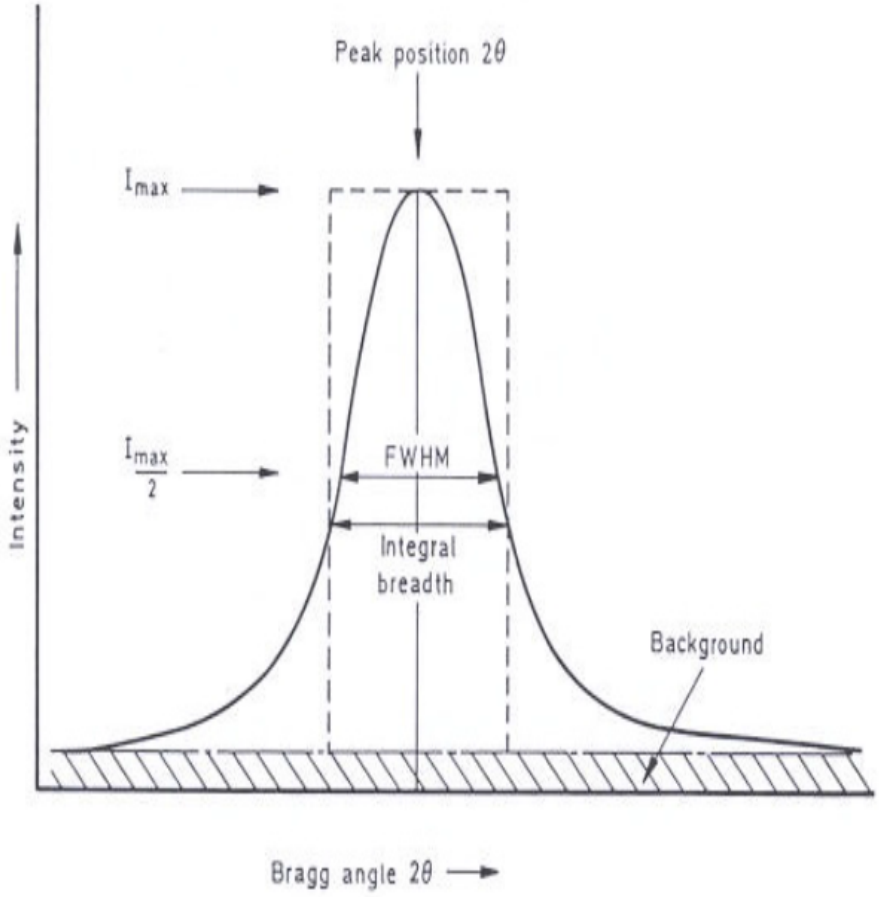
Scherrer Equation

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

Smaller grains wider peak

B: width K: constant

L: grain size

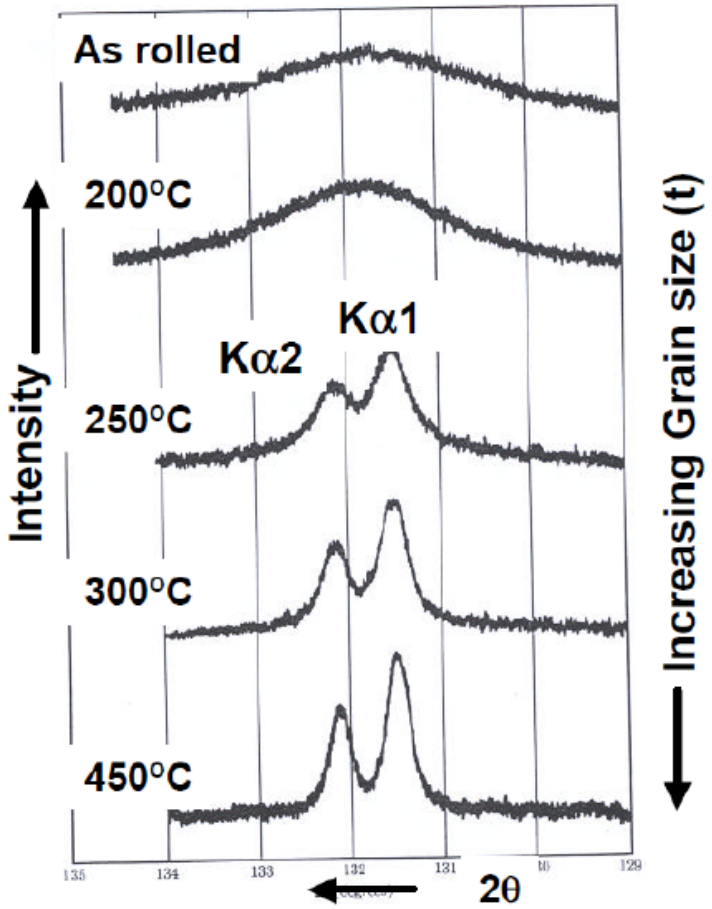


Elements of X-RAY Diffraction By B.D.Cullity and S.R.Stock

EXAMPLE 3

- Rolled material has very small grains ⟶ broader peak

- As the material annealed grains start to grow and peak becomes sharper



(331) Peak of cold-rolled and Annealed 70Cu-30Zn (brass)

Elements of X-RAY Diffraction By B.D.Cullity and S.R.Stock

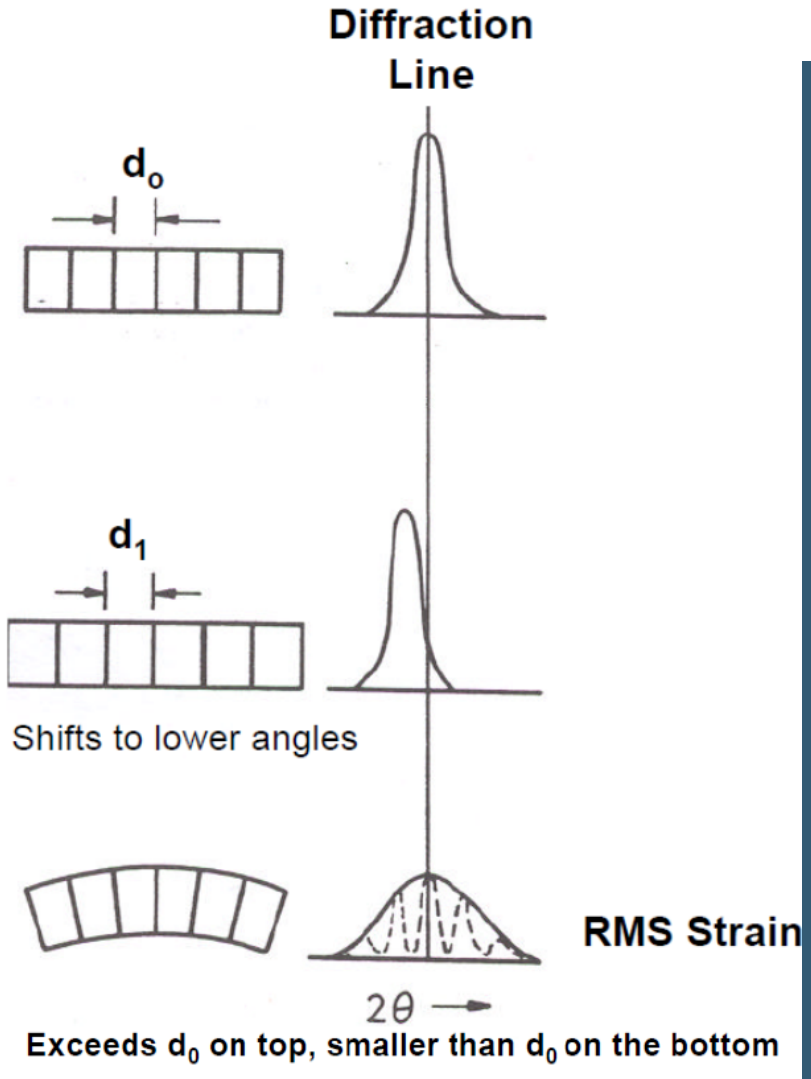
EXAMPLE 4

- Internal strain

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

- Tensile stress increase d
- As d increase peak shifts to the right
- Compressive stress decrease d

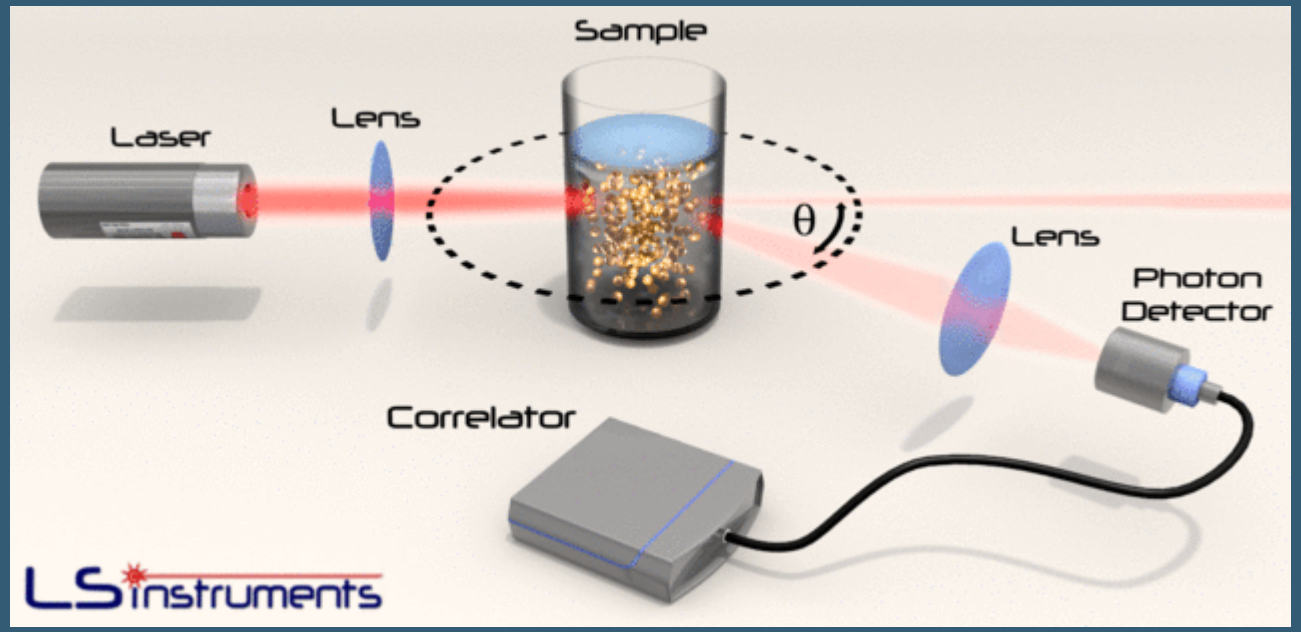
  - shift peak to the left



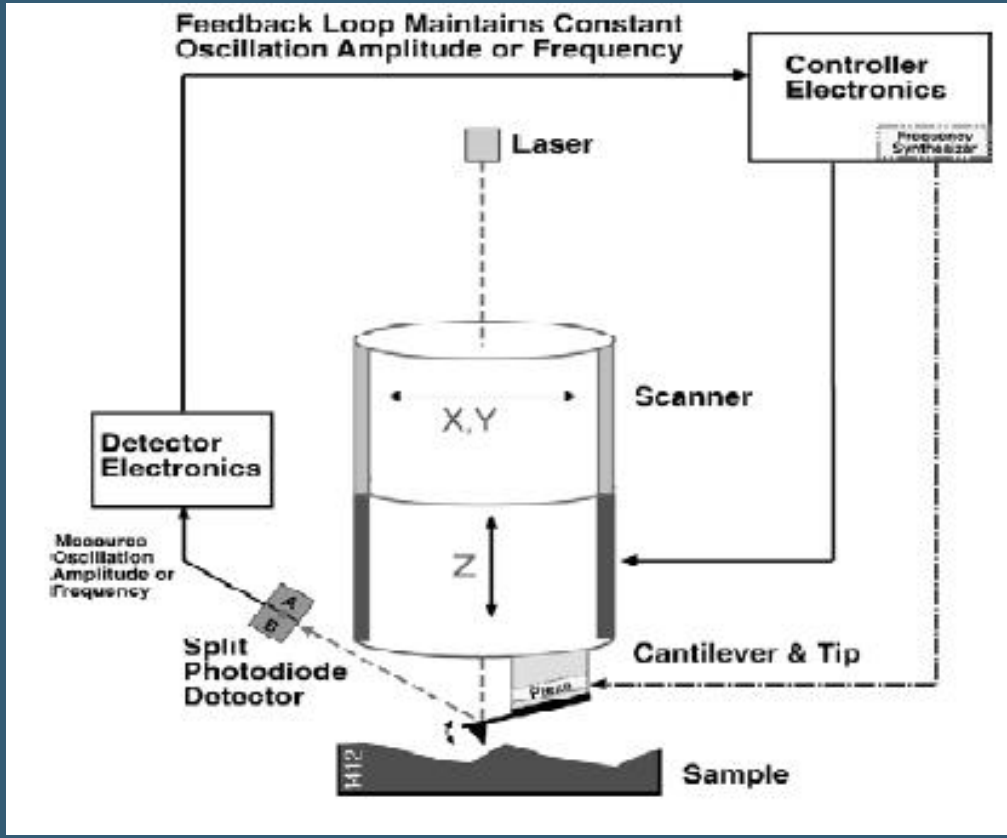
Elements of X-RAY Diffraction By B.D.Cullity and S.R.Stock

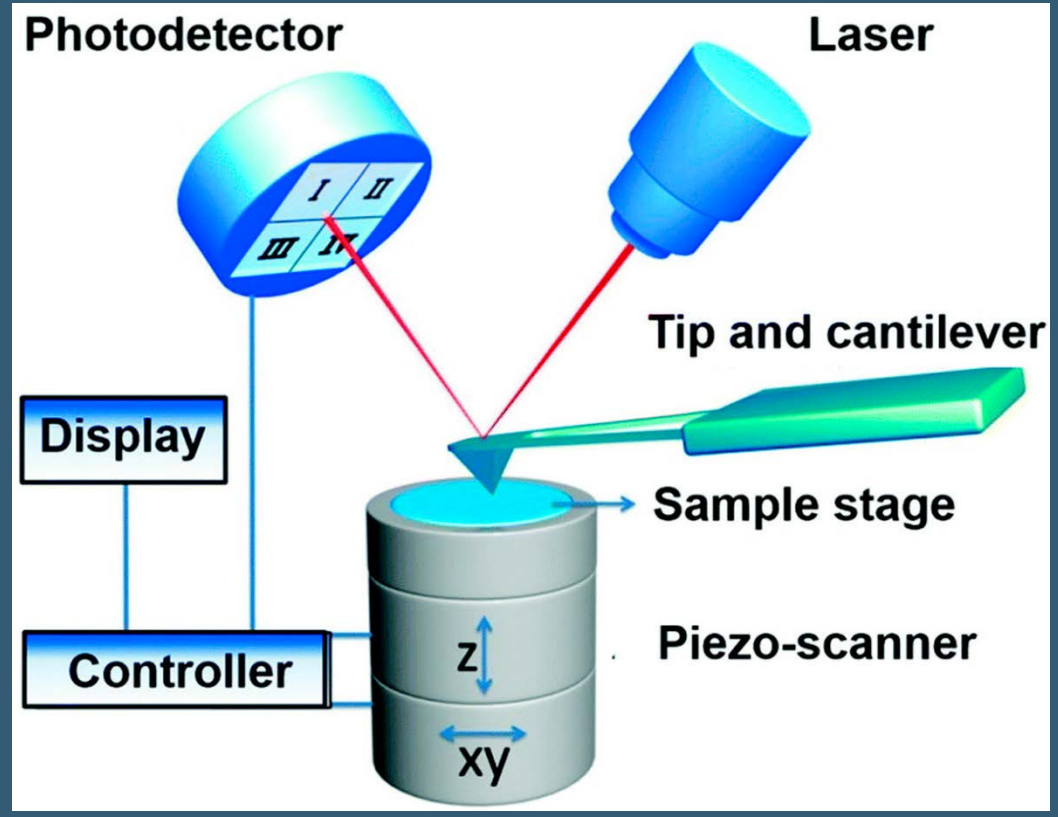
DYNAMIC LIGHT SCATTERING (DLS)

$$R = \frac{k_B T}{6\pi\eta} \cdot \frac{16\pi^2 n^2 \cdot \sin^2(\theta/2)}{\Gamma \cdot \lambda^2}$$



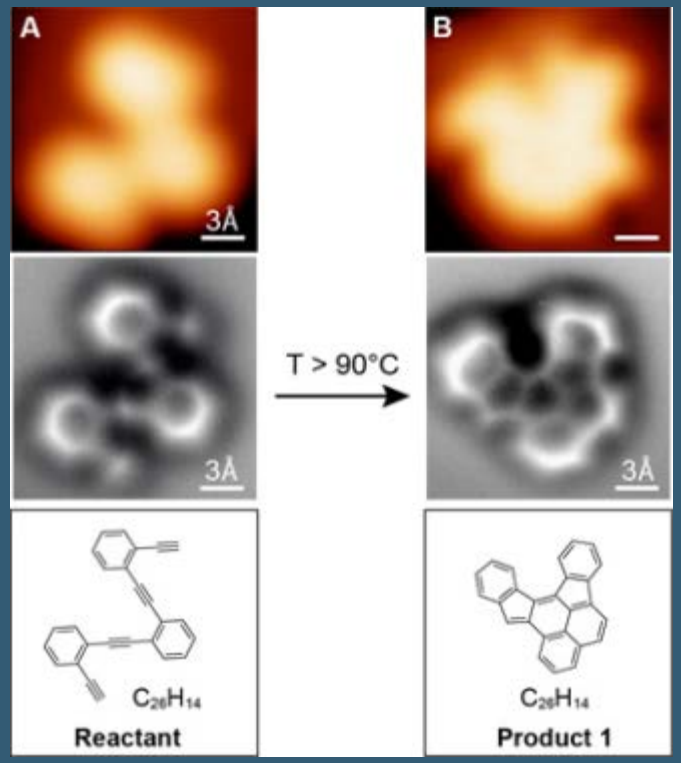
ATOMIC FORCE MICROSCOPE





APPLICATIONS OF AFM

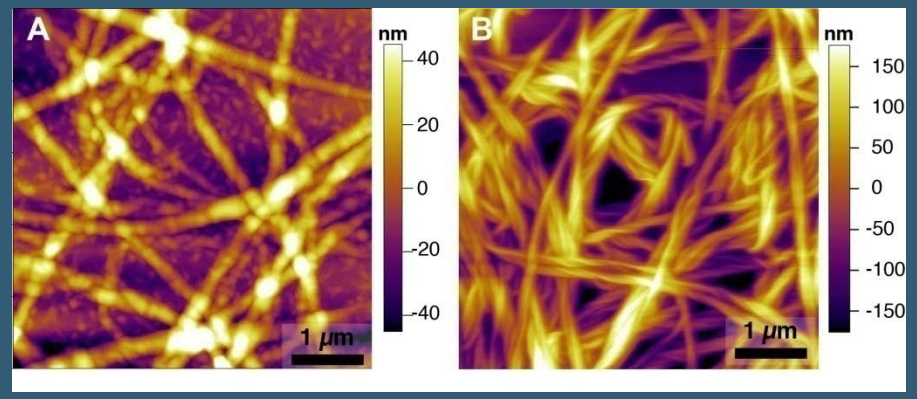
- Take Atomic-Scale Picture of Chemical Bonds
- Bond length and molecular structure

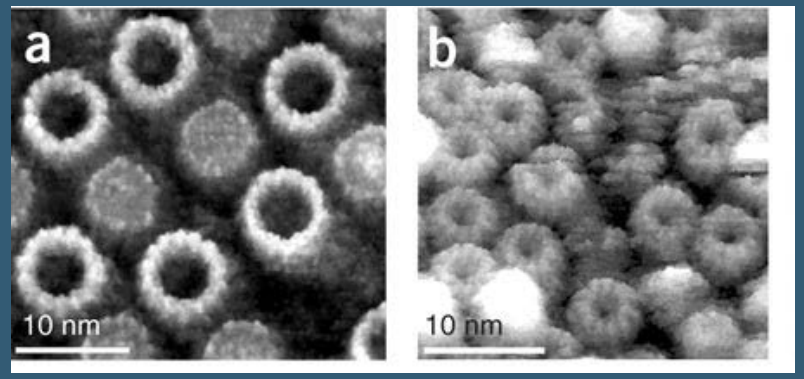


APPLICATIONS OF AFM

- Take Atomic-Scale Picture of biological specimen
  - Collagen fibril matrices
  - Native membrane proteins

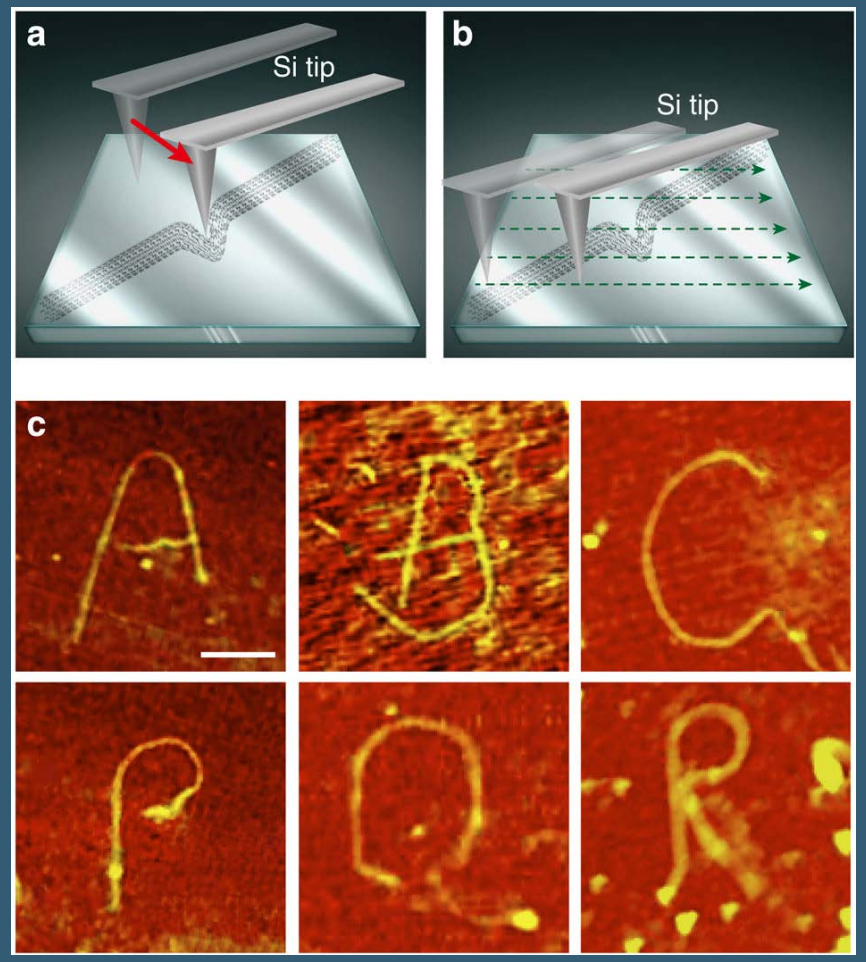
- Size, Diameter, Physical and chemical properties





APPLICATIONS OF AFM

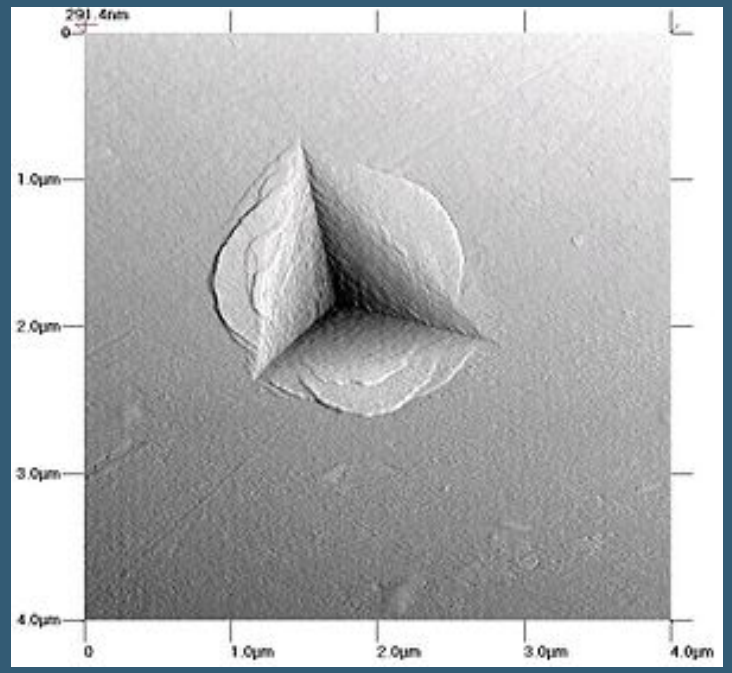
- Manipulation
- Lithography



APPLICATIONS OF AFM

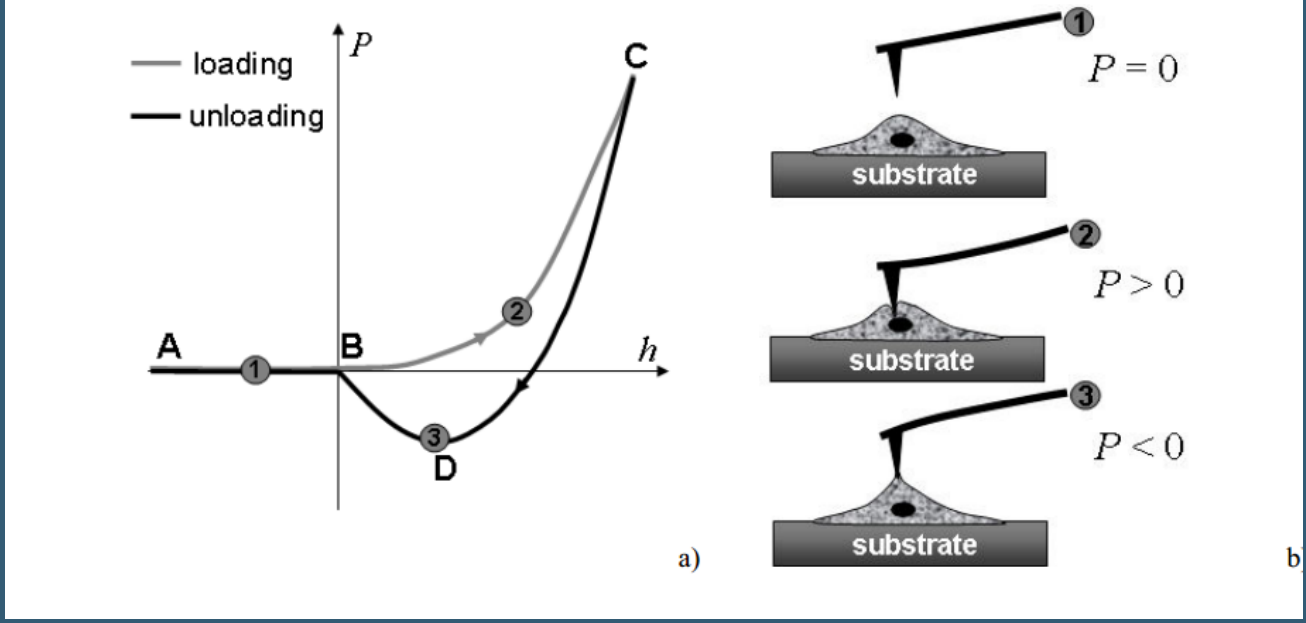
- Material properties of substrates
  - Indentation

- Size, depth → Hardness



APPLICATIONS OF AFM

- Nano-force measurement



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THANK YOU

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