MATERIAL CHARACTERIZATION TECHNIQUE FOR NANO-SCALE MEASUREMENT

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NANOSCALE

NANOPARTICLES

a Polymer   b Liposomes   c Amphiphilic cyclodextrins   d Dendrimers

e Gold Nanoparticles   f Micelles   g Carbon nanotubes   h Quantum dots

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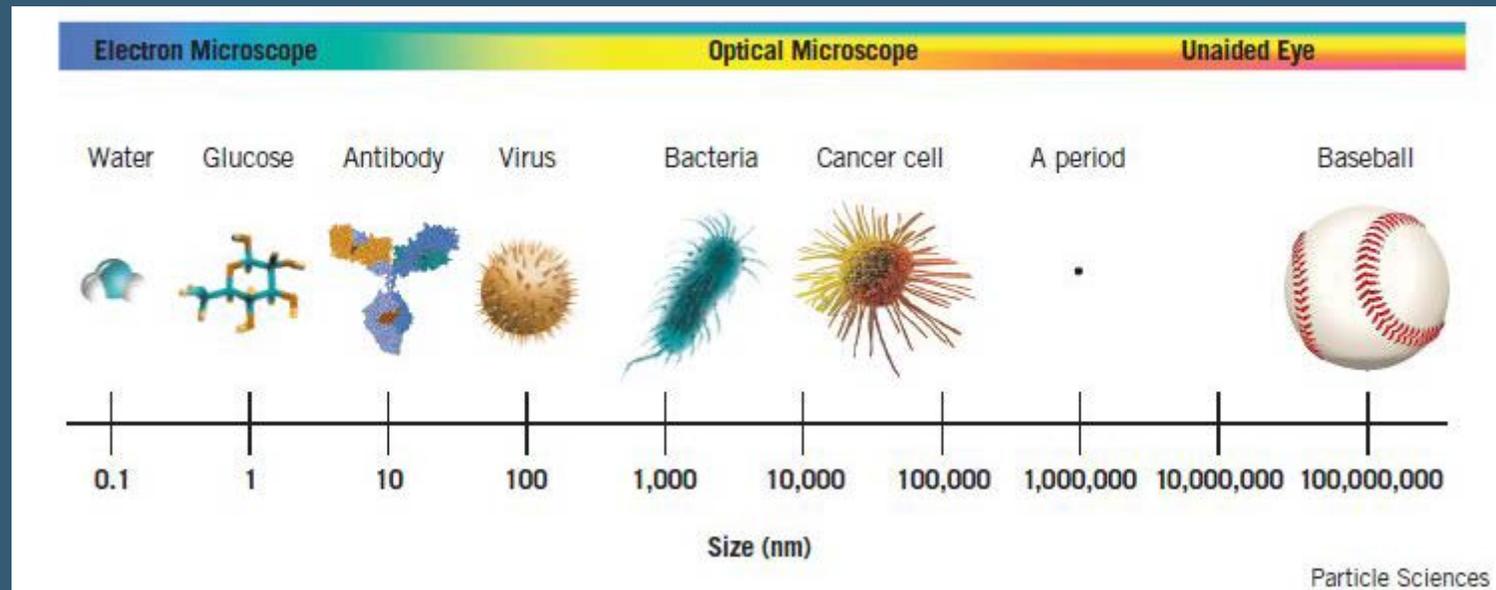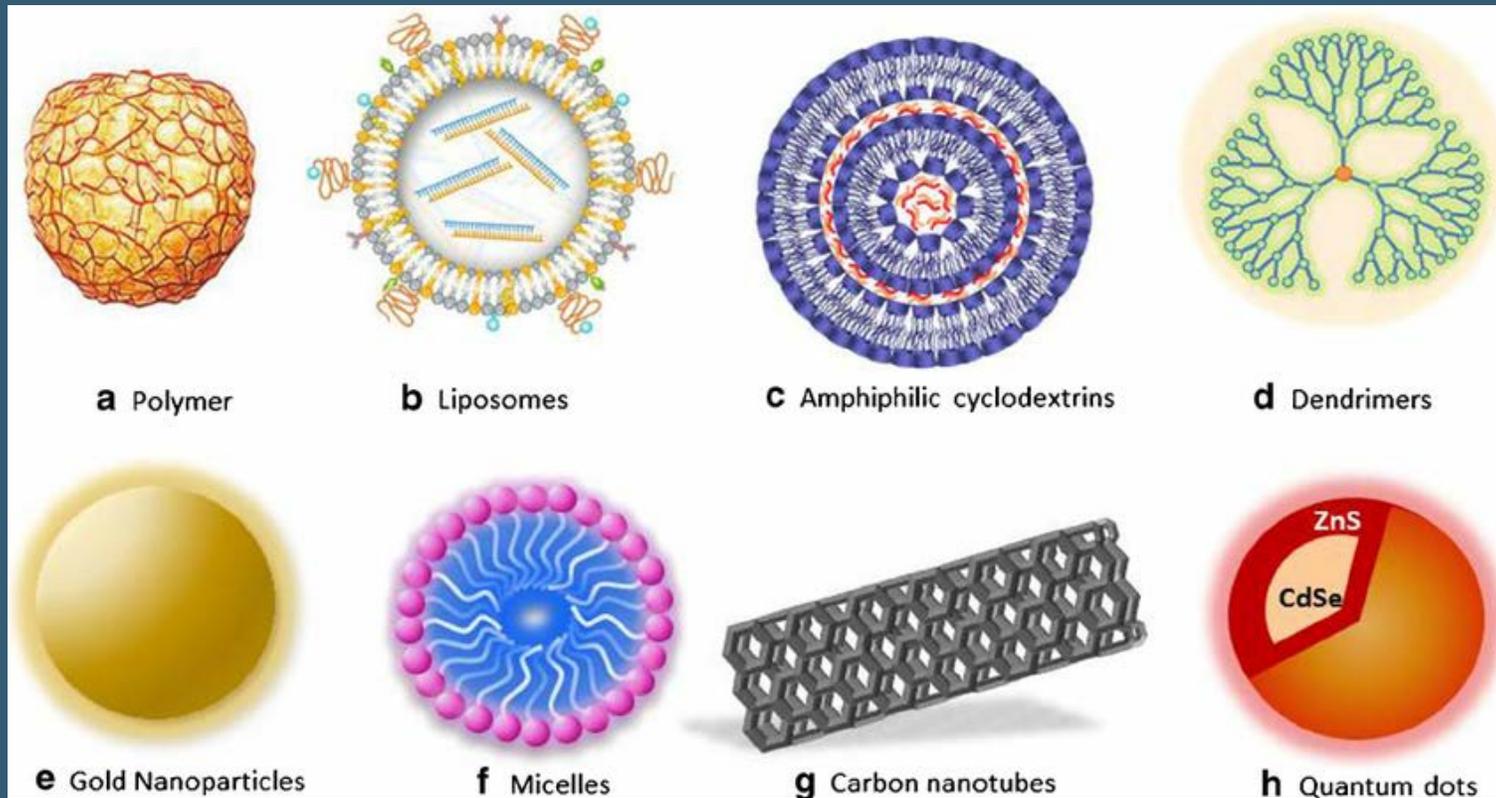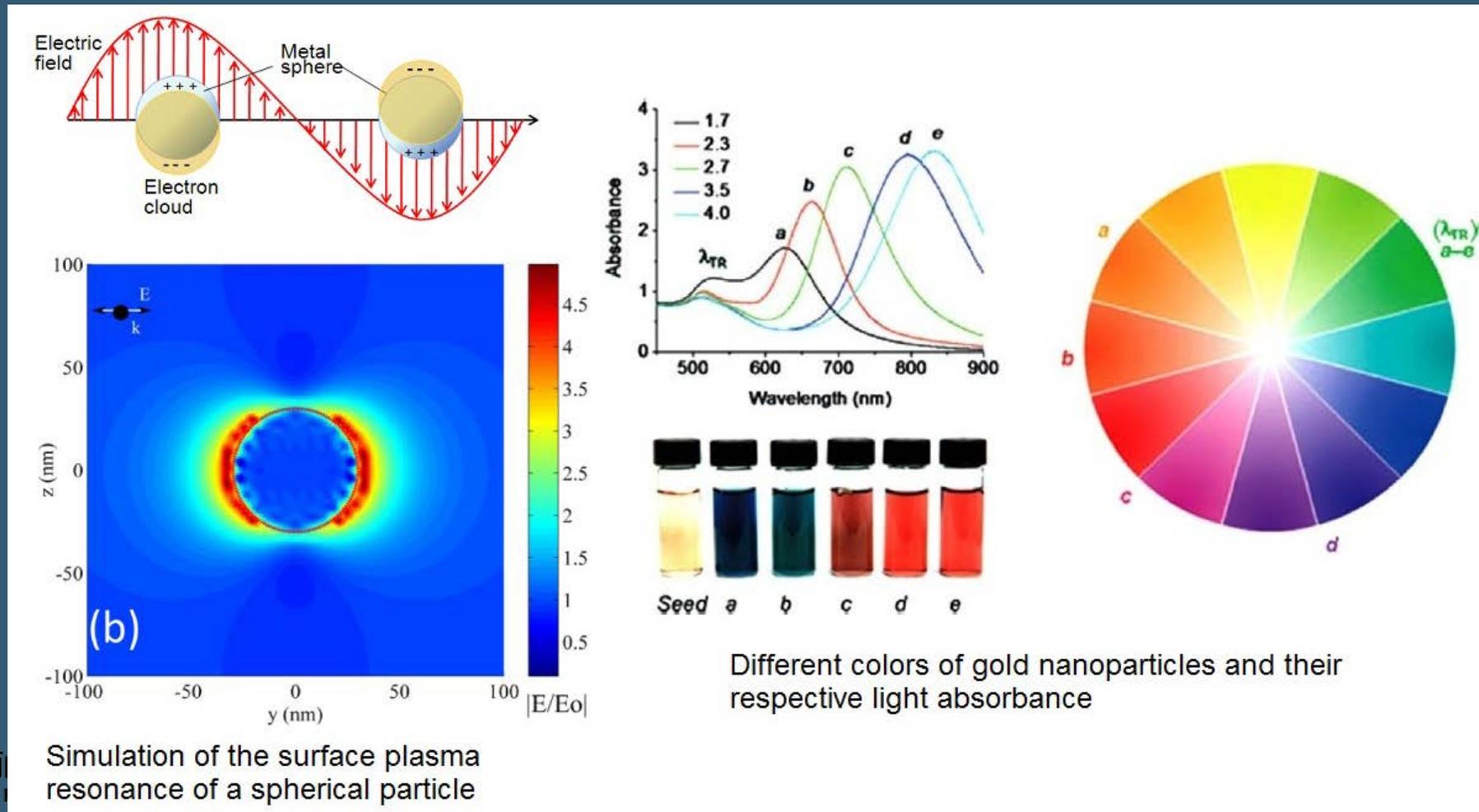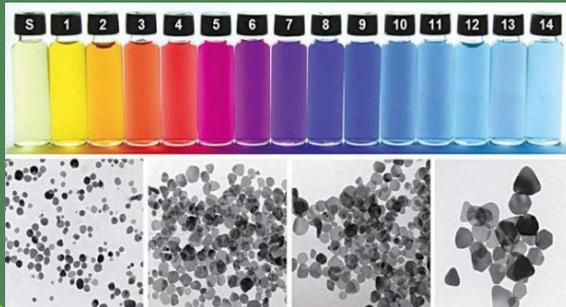National Institute of Metrology (Thailand)

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**
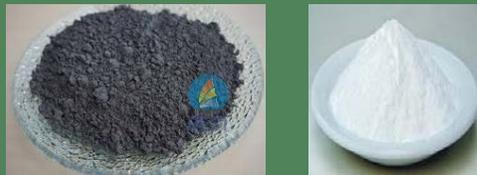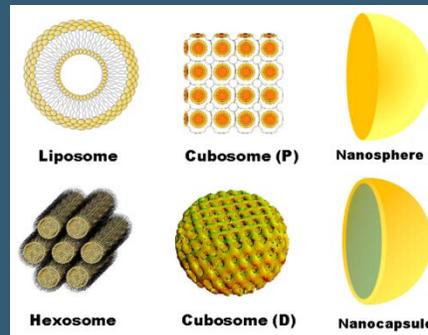
Liposome   Cubosome (P)   Nanosphere

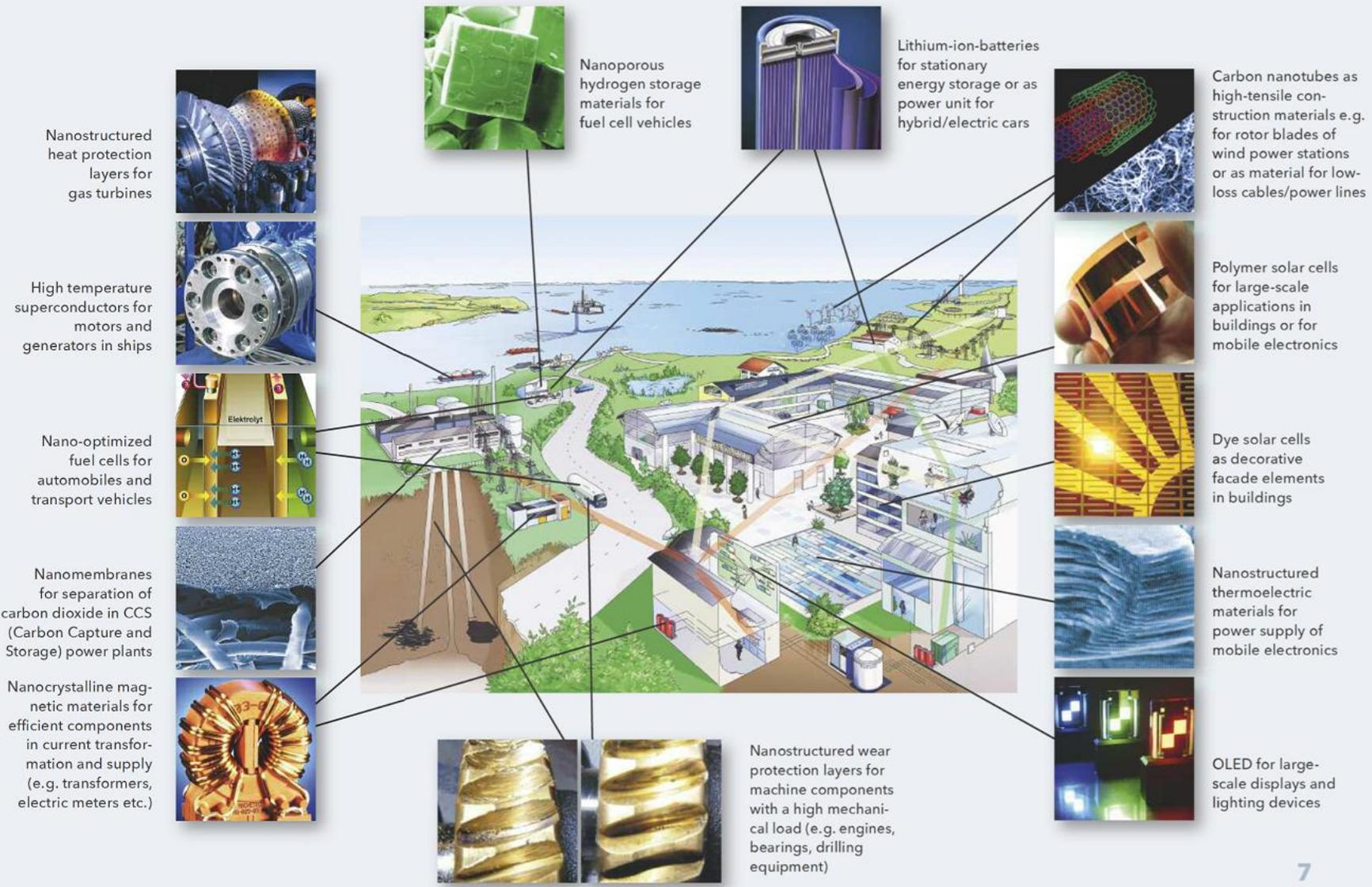Hexosome   Cubosome (D)   Nanocapsule
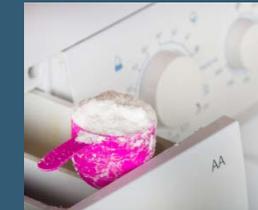
Needs!!!

Measurement methods, Instruments, Standards, Safety

ผลิตภัณฑ์ที่มีส่วนประกอบของวัสดุนาโน หรือใช้นาโนเทคโนโลยีเพื่อสร้างคุณลักษณะใหม่ ทั้งนี้ลักษณะของวัสดุนาโนที่เติมลงไปในผลิตภัณฑ์อาจมีโครงสร้างที่ซับซ้อน และแตกต่างจากวัสดุนาโนในรูปของวัตถุดิบ ดังนั้นการพิสูจน์ว่าผลิตภัณฑ์มีวัสดุนาโนอยู่จริง และปลอดภัย จึงเรื่องท้าทาย
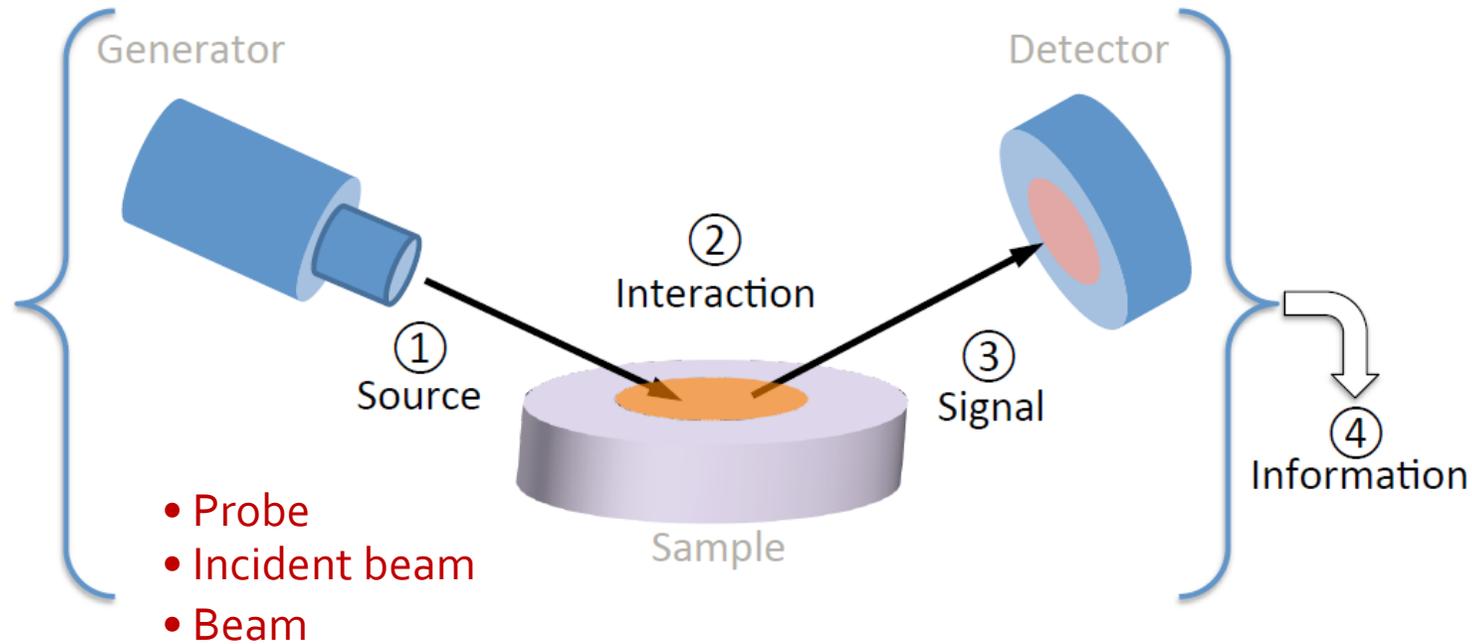
Angular sensor   Angular sensor
Y-interferometer   X-interferometer
Abbe point   Corner mirror   Metrology frame (Zerodur)
3D-Stage
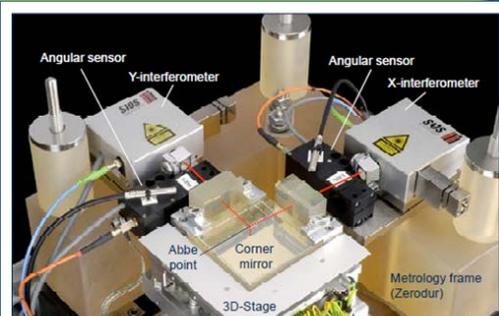
มว. สถาปนาระบบการสอบกลับได้ในการวัดวัสดุนาโนตั้งแต่ ปีพ.ศ.2558
และเปิดให้บริการสอบเทียบมาตรฐานสำหรับเครื่องทดสอบขนาดวัสดุนาโน

Nanostructured heat protection layers for gas turbines

High temperature superconductors for motors and generators in ships

Nano-optimized fuel cells for automobiles and transport vehicles

Nanomembranes for separation of carbon dioxide in CCS (Carbon Capture and Storage) power plants

Nanocrystalline magnetic materials for efficient components in current transformation and supply (e.g. transformers, electric meters etc.)

Nanoporous hydrogen storage materials for fuel cell vehicles

Lithium-ion-batteries for stationary energy storage or as power unit for hybrid/electric cars

Carbon nanotubes as high-tensile construction materials e.g. for rotor blades of wind power stations or as material for low-loss cables/power lines

Polymer solar cells for large-scale applications in buildings or for mobile electronics

Dye solar cells as decorative facade elements in buildings

Nanostructured thermoelectric materials for power supply of mobile electronics

Nanostructured wear protection layers for machine components with a high mechanical load (e.g. engines, bearings, drilling equipment)

OLED for large-scale displays and lighting devices

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

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Ref: Prof. Supapan Seraphin

BASIC PRINCIPLE

- Probe
- Incident beam
- Beam

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

ELECTRO-MAGNETIC RADIATION (PHOTONS)

PHOTON ENERGY IN EV

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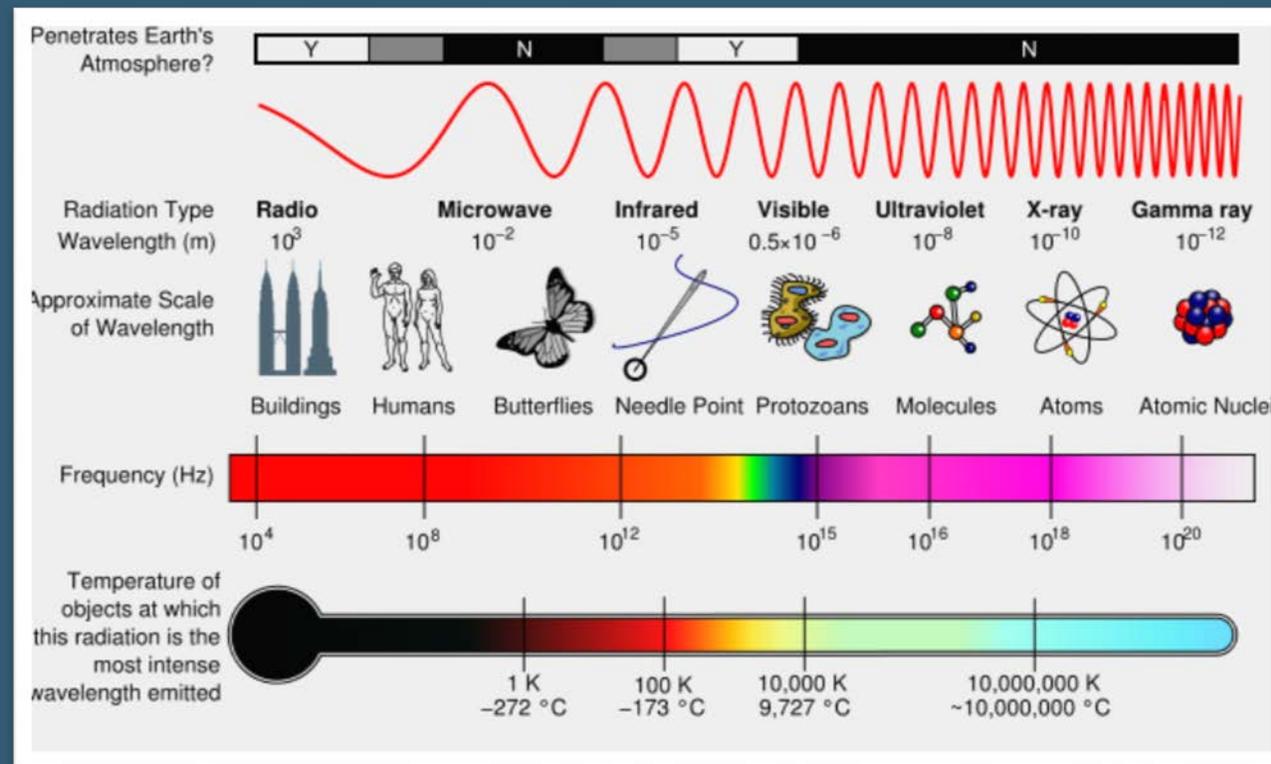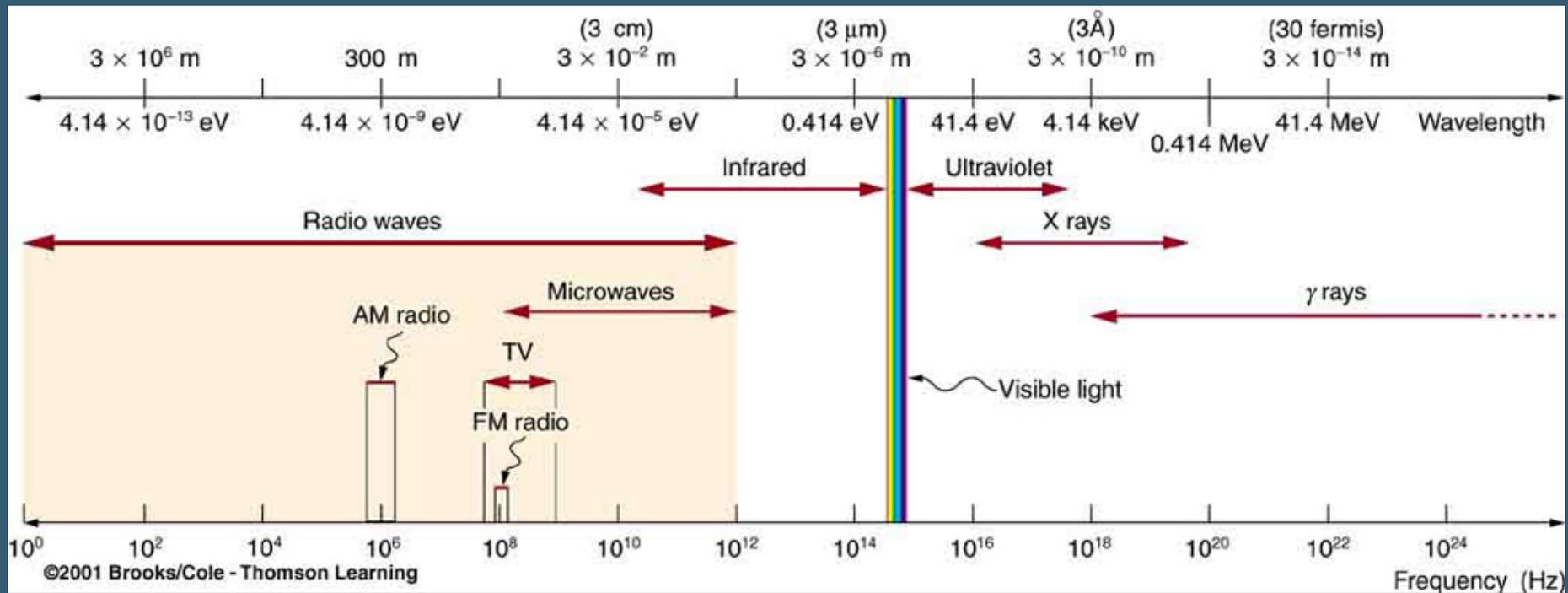
CATEGORIES OF TECHNIQUES

- Microscopy (imaging)

- Diffraction (crystal structure)

- Spectroscopy (chemical composition/elemental analysis)

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CHARACTERIZATION TECHNIQUES: DIMENSIONAL NANOMETROLOGY

- Spatial resolution = $\dfrac{0.611 \cdot \lambda}{NA}$
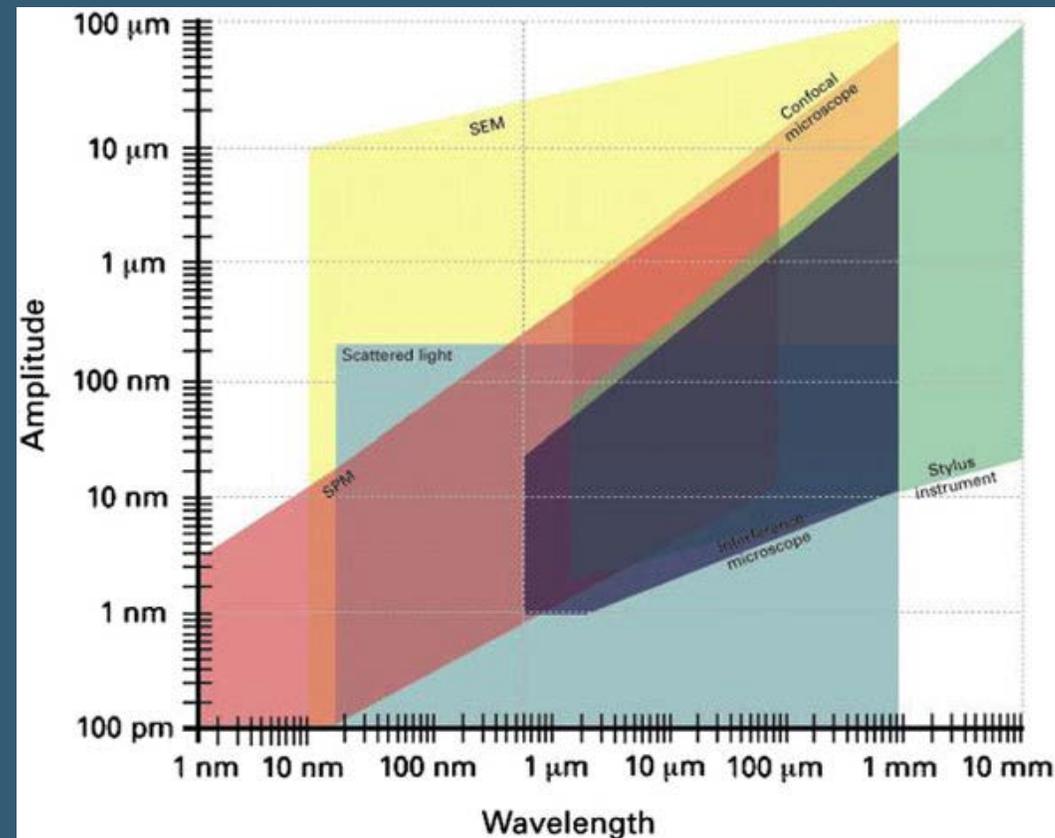
CHARACTERIZATION TECHNIQUES: CHEMICAL NANOMETROLOGY

Surface and Nanoanalysis
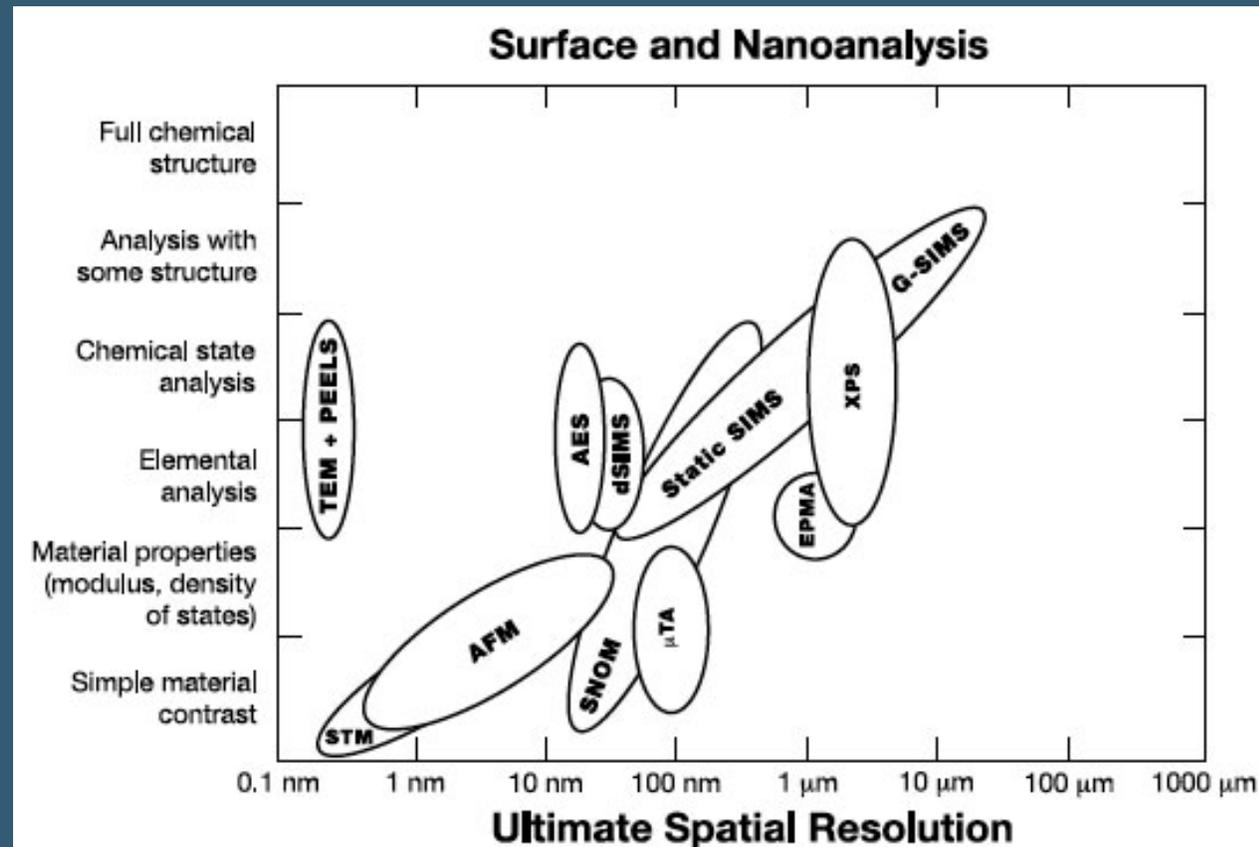
TRANSMISSION ELECTRON MICROSCOPE (TEM)
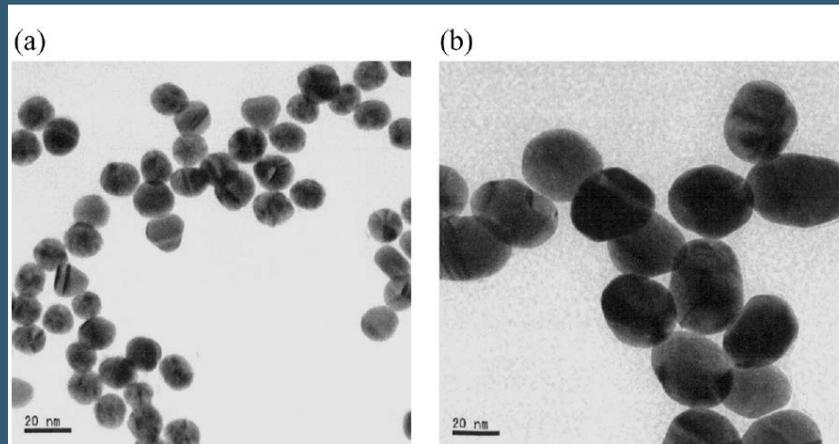
Fig. 1. TEM images of gold nanoparticles.
(a) Au 15 nm, (b) Au 35 nm.

Electron gun

Condensor aperture

Specimen port

Objective aperture

Objective lens

Diffraction lens

Intermediate aperture

Intermediate lens

Projector lenses

Binoculars

Fluorescent screen

Image recording system
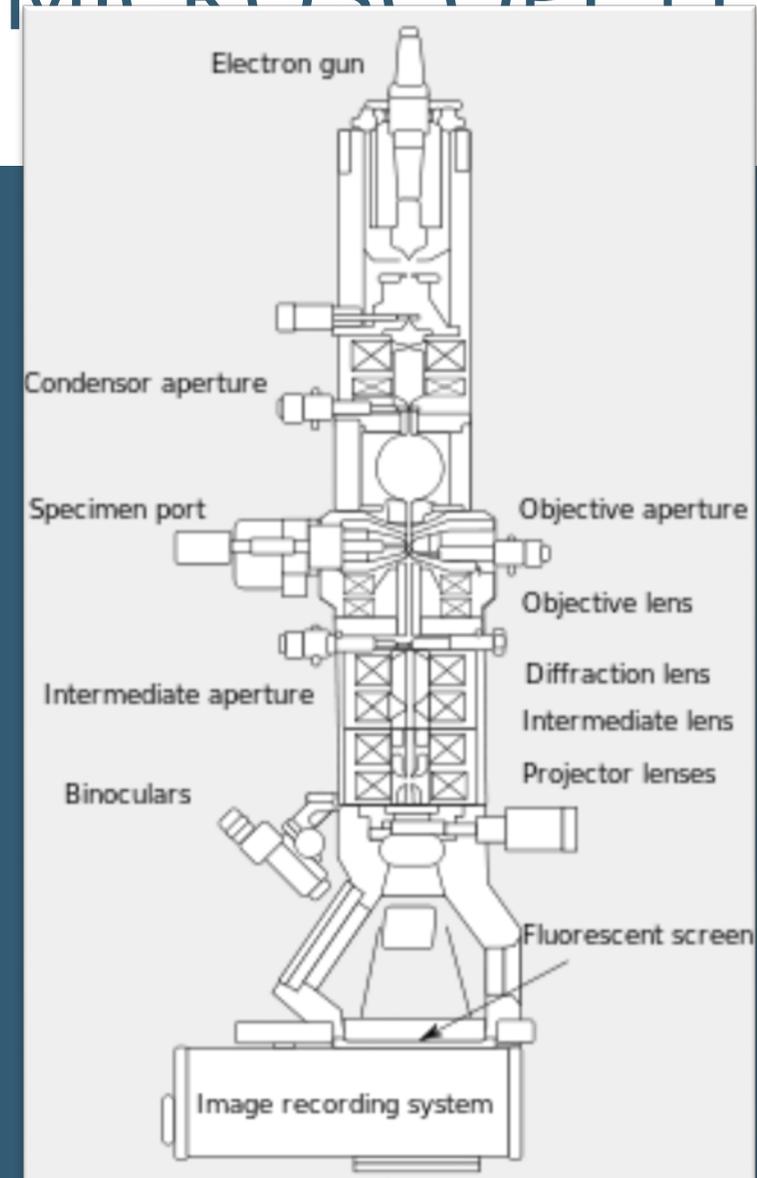
PARAMETERS THAT AFFECT IMAGE RESOLUTION

- Wavelength
- Spherical aberration
- Diffraction vector
- Defocus

Spherical aberration
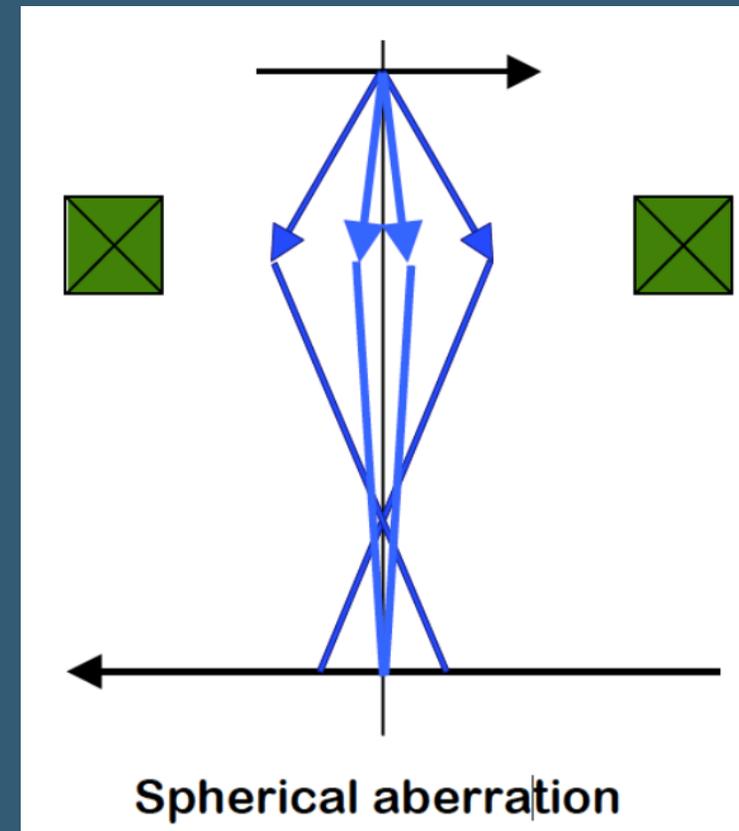
Electron Diffraction Pattern

TiO$_2$ nano particle

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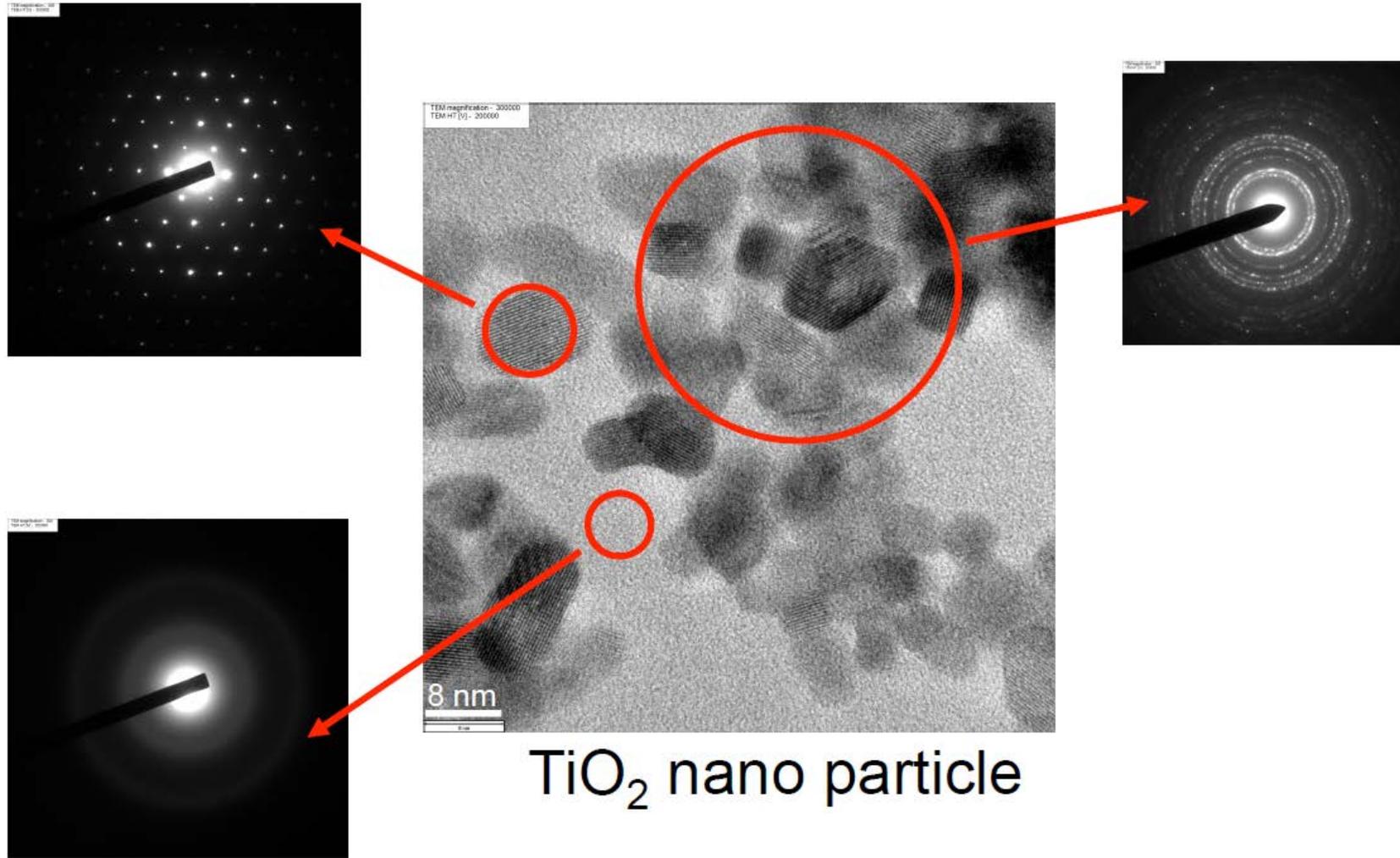
Electron Diffraction Pattern of Twin Crystal

Pt

oxide scale

SiC   100nm

Cristobalite（high）

$0\overline{2}\overline{2}$

$\overline{1}\overline{1}1$

200                $\overline{1}11$

000

111                $\overline{2}00$

$\overline{1}11$

$0\overline{2}2$

Ref: Prof. Supapan Seraphin
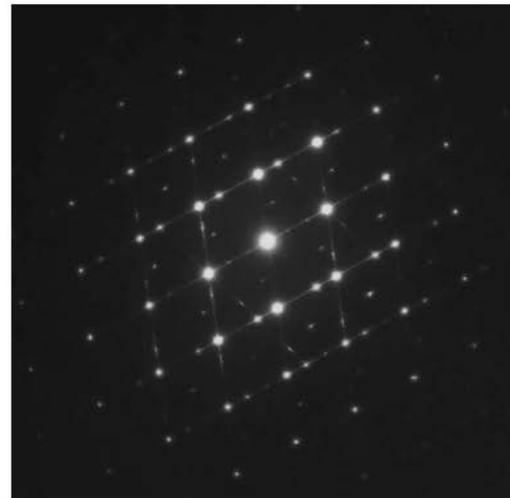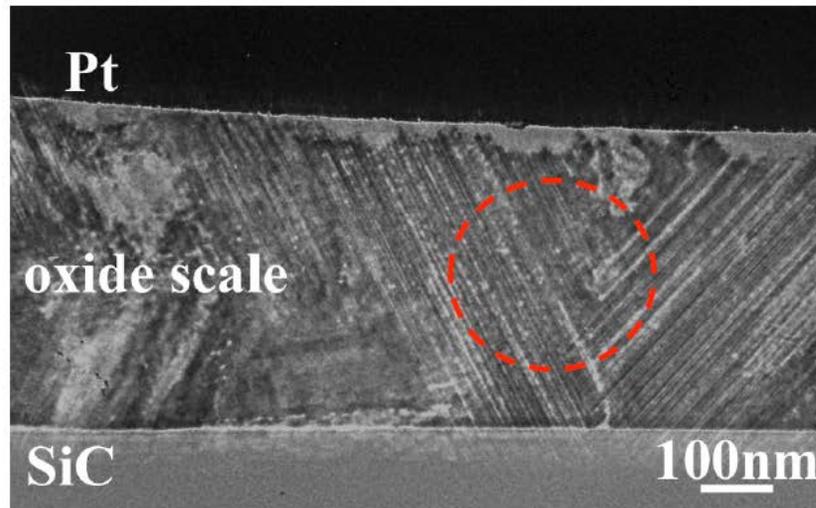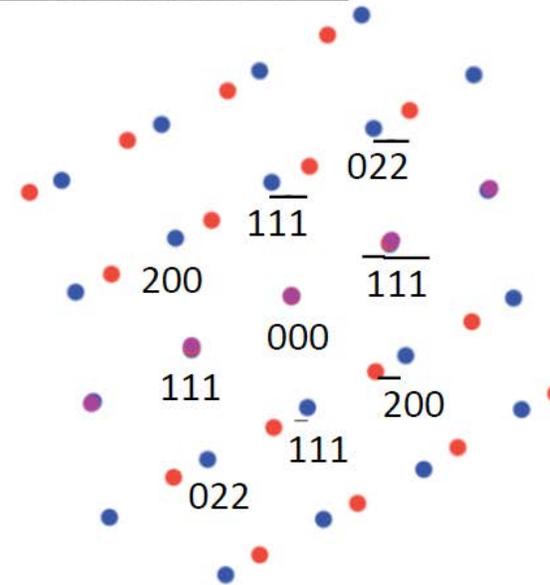
Bright-field and Dark-field Imaging

Bright Field Imaging

On-axis Dark Field

Off-axis Dark Field

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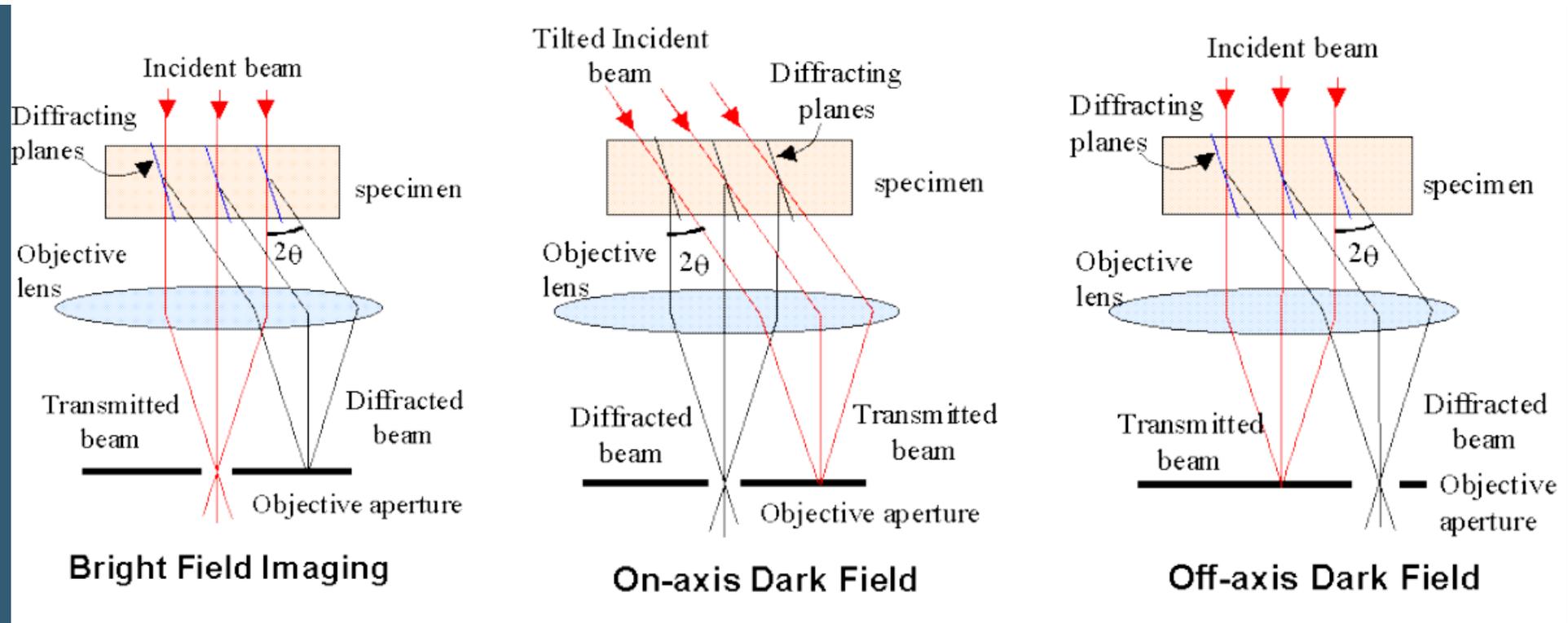
Advantages of dark field imaging
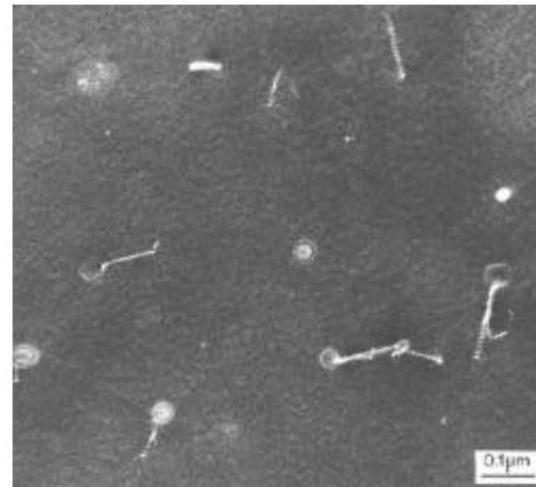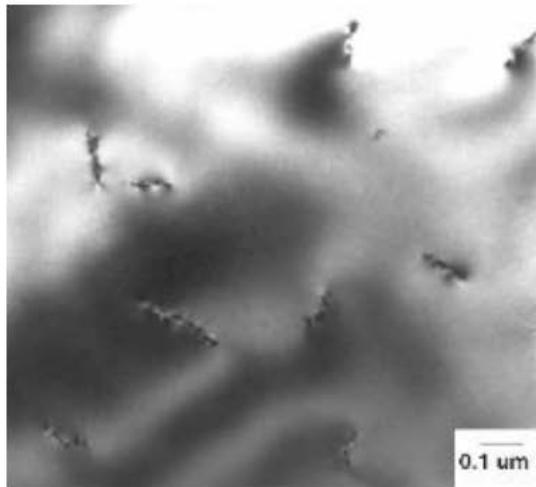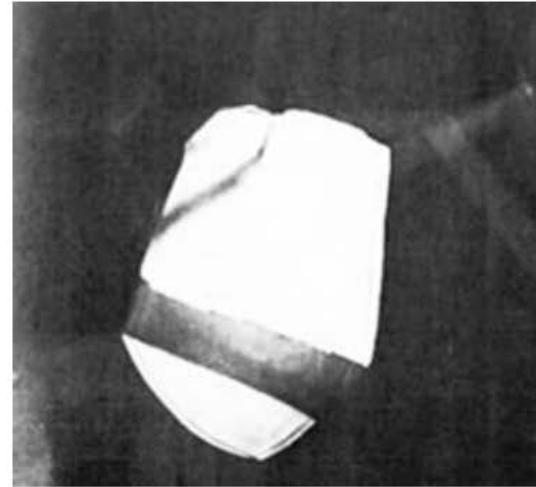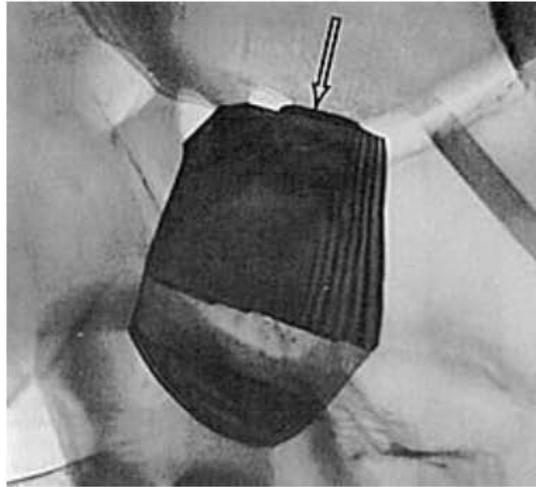
X-RAY DIFFRACTION (XRD)

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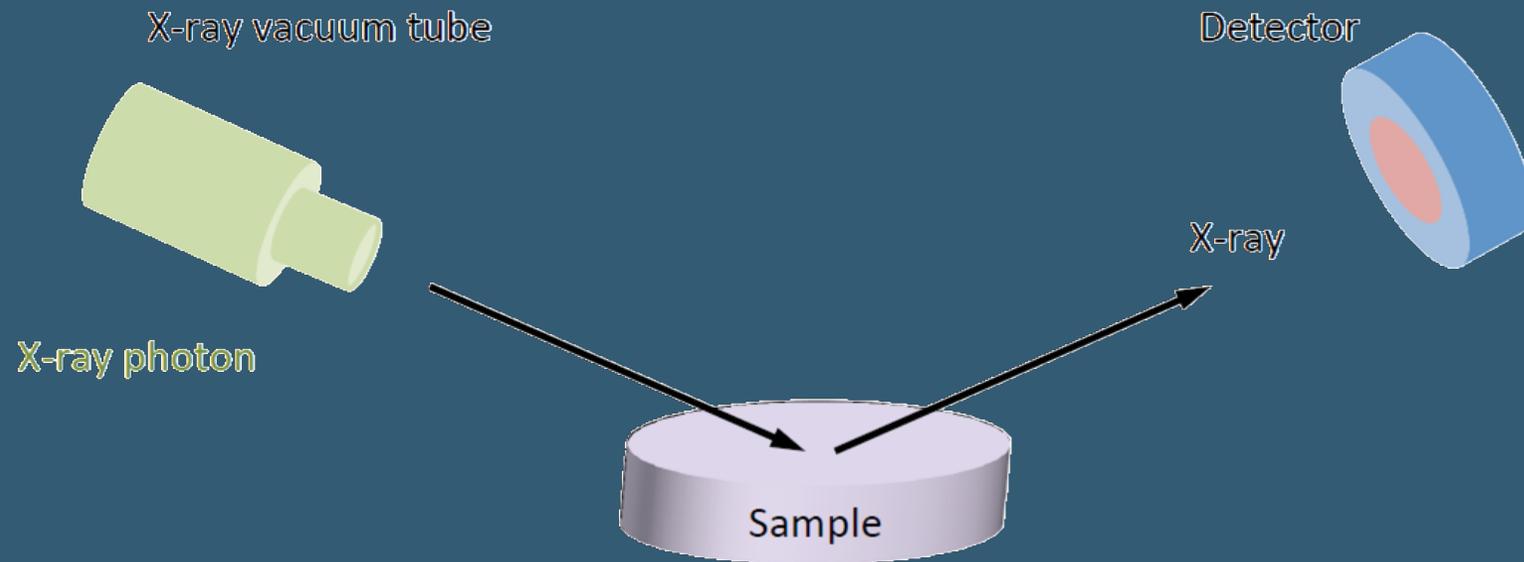
PRINCIPLES

- 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
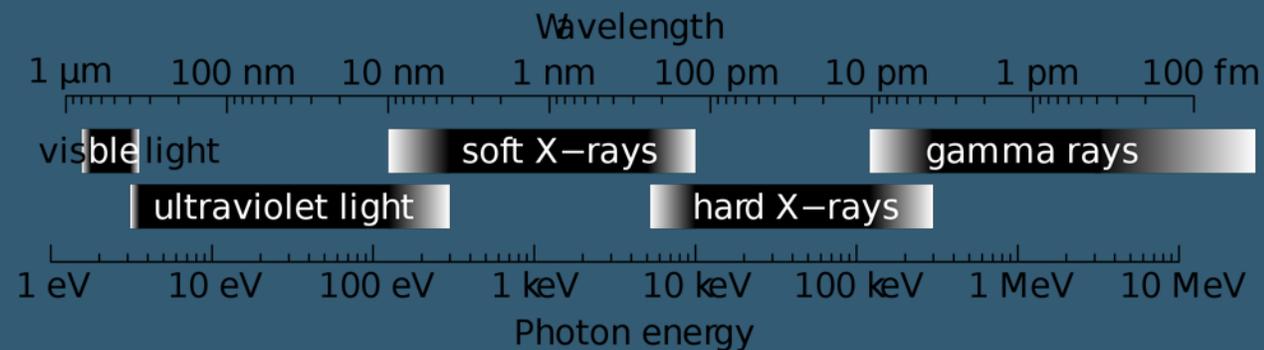
INTERACTION (DIFFRACTION)

BRAGG'S LAW

Jointly awarded the 1915
Nobel Prize in Physics

William Henry Bragg   William Lawrence Bragg
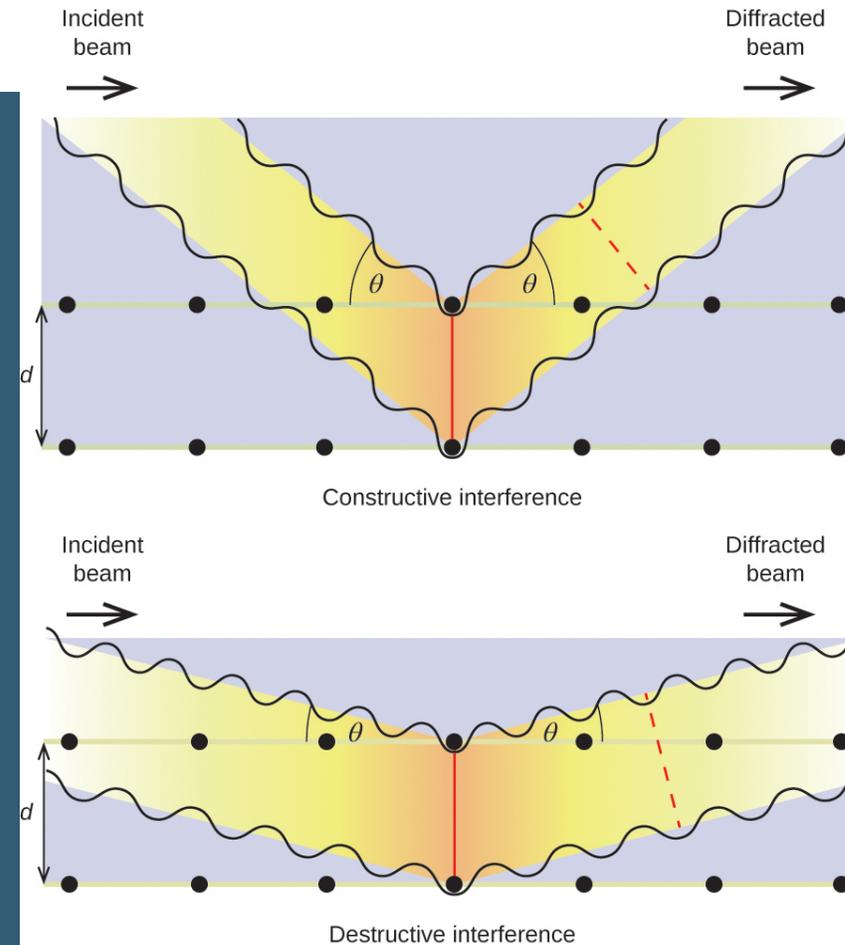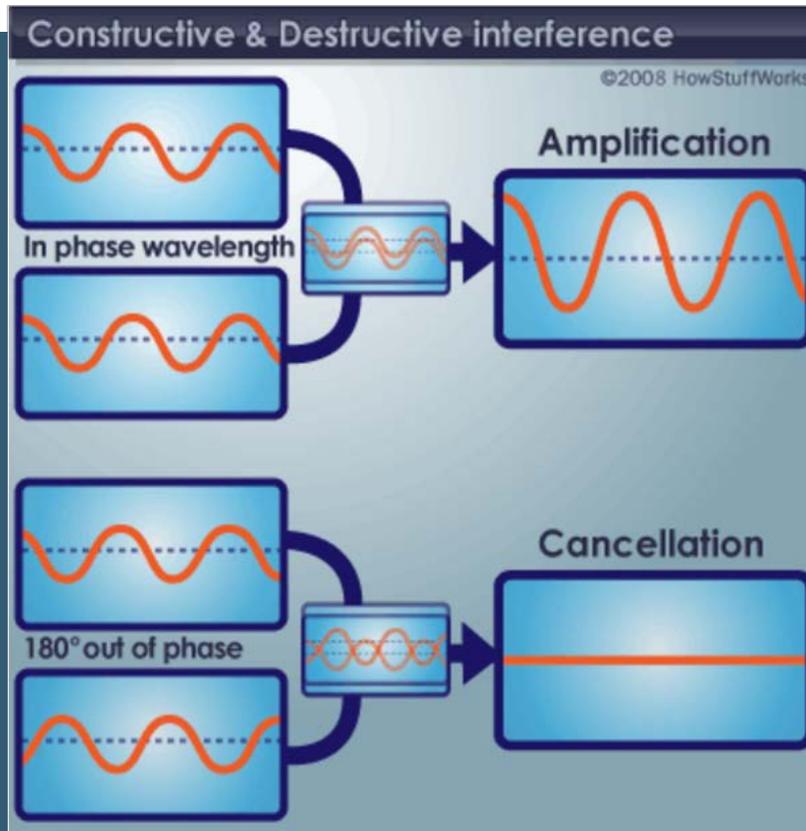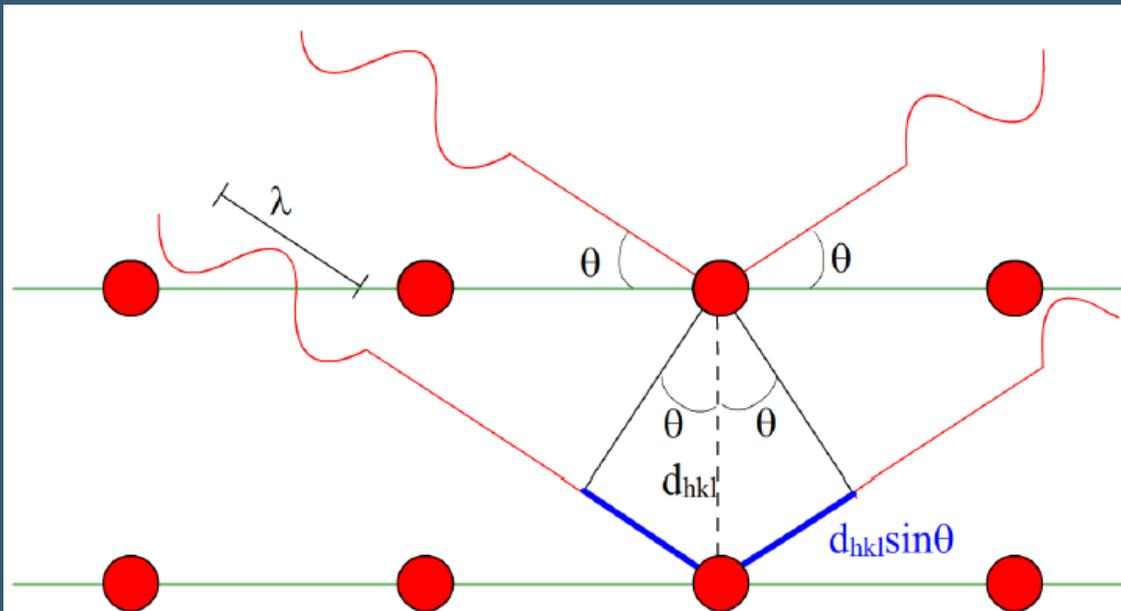
Total path difference = $2d_{hkl}\sin\theta$

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

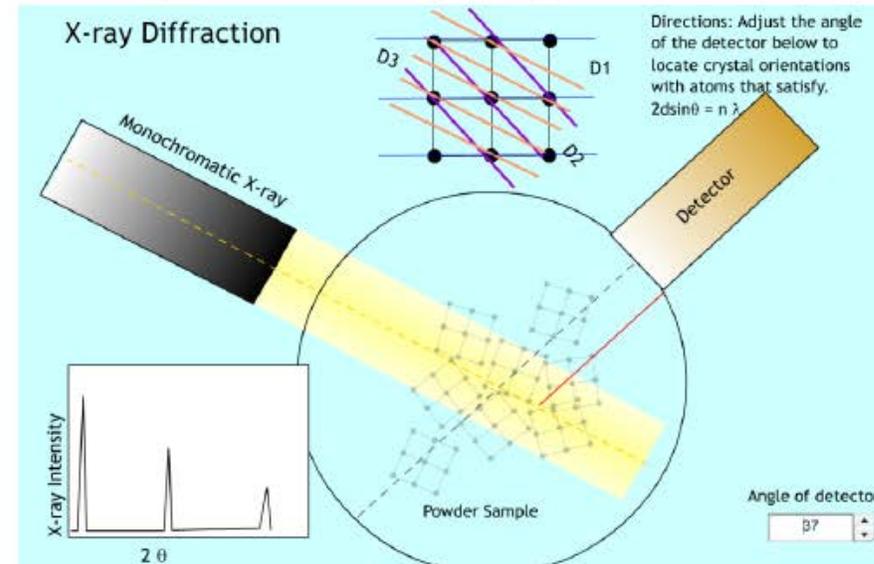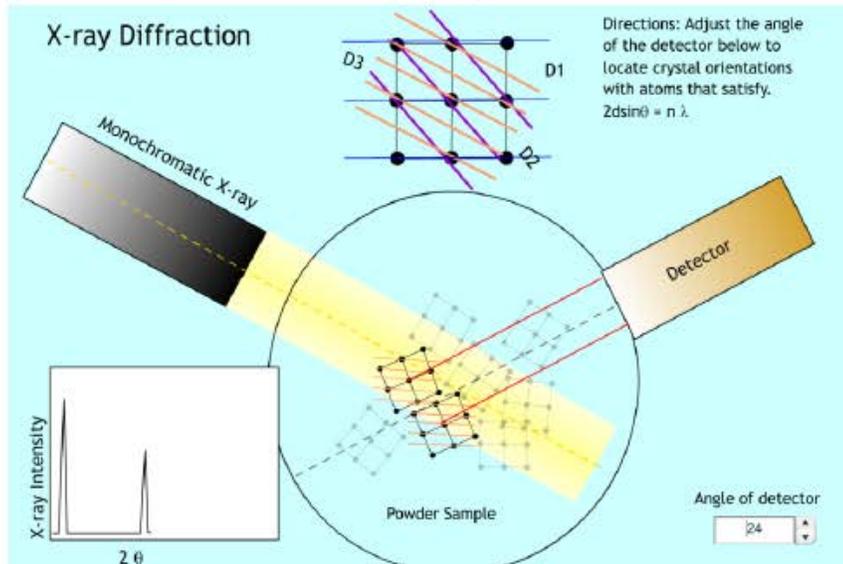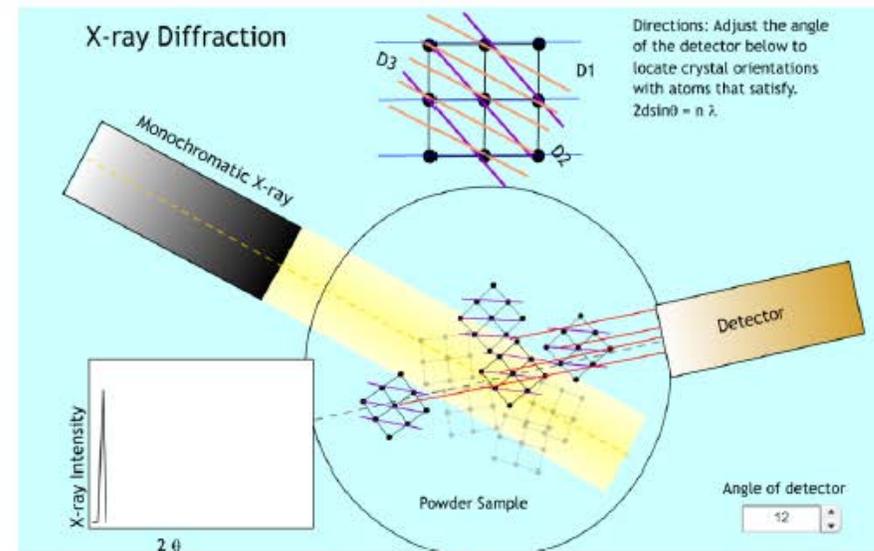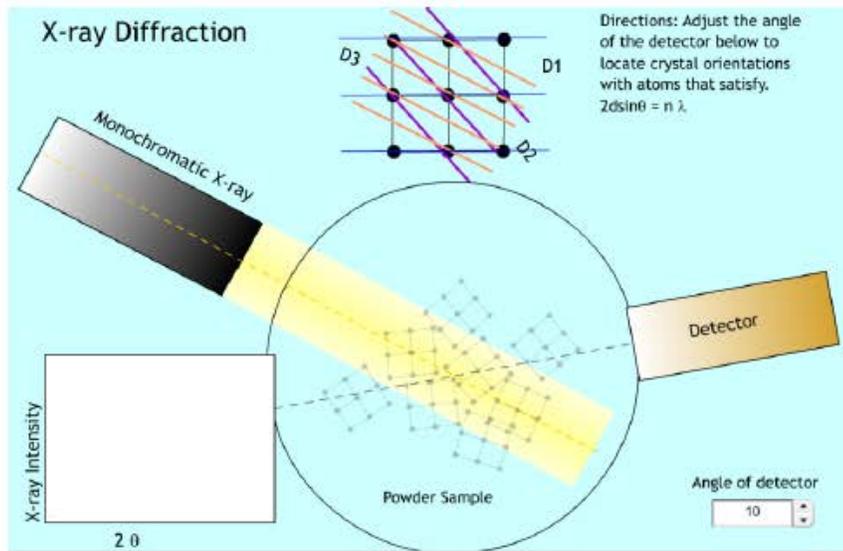2) Measuring pulses of electric current. Convert pulses into x-ray intensity

X-RAY DIFFRACTOMETER

1) X-ray source

2) Interaction

3) X-ray detector

4) Analysis

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DIFFRACTION PATTERN

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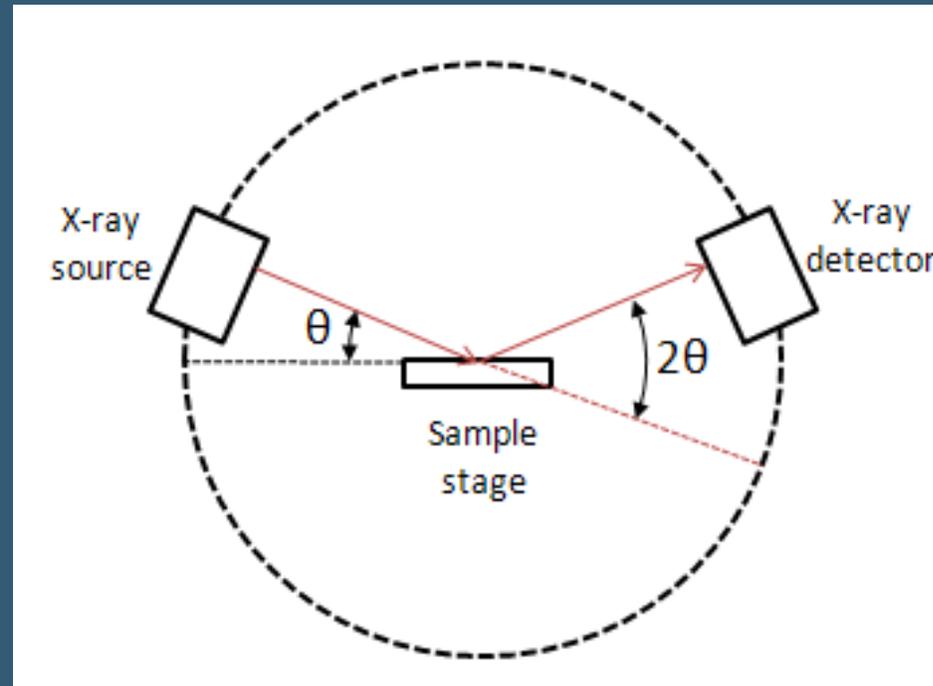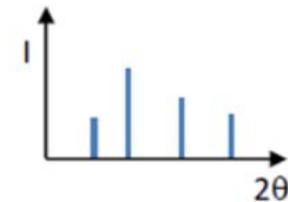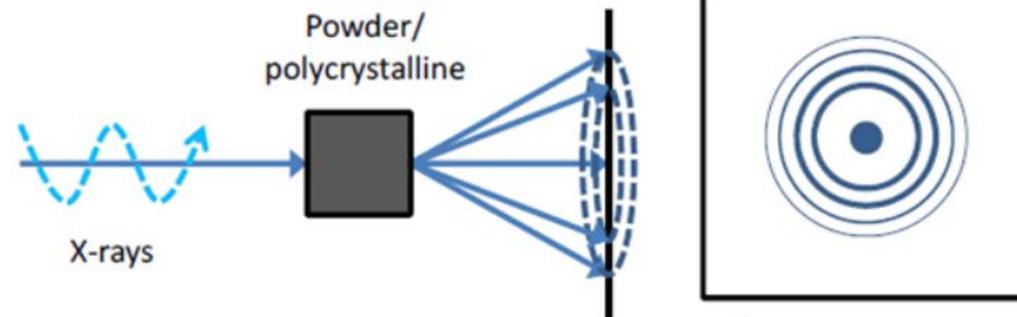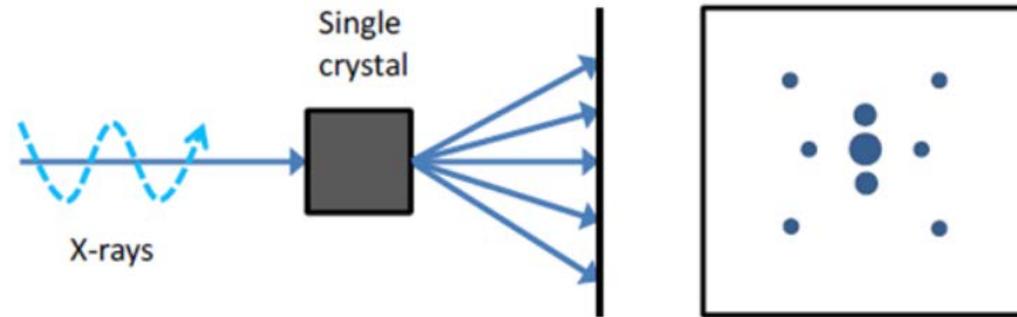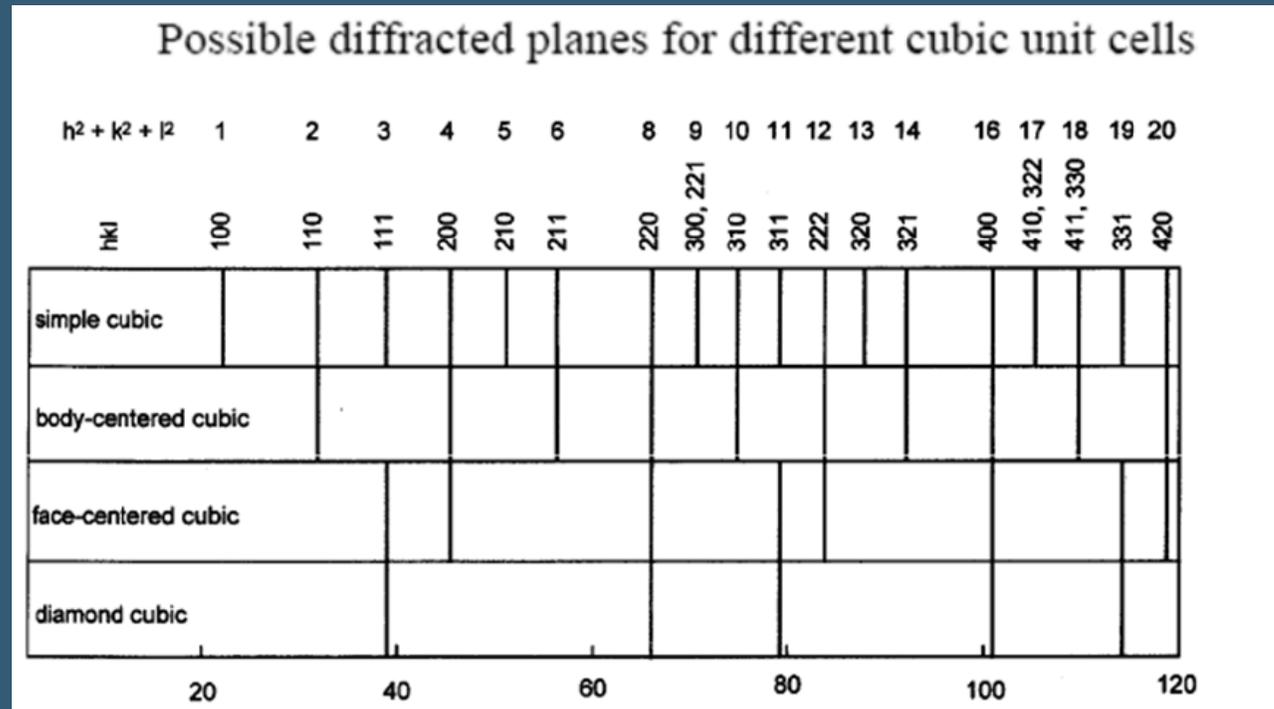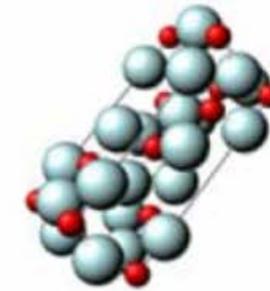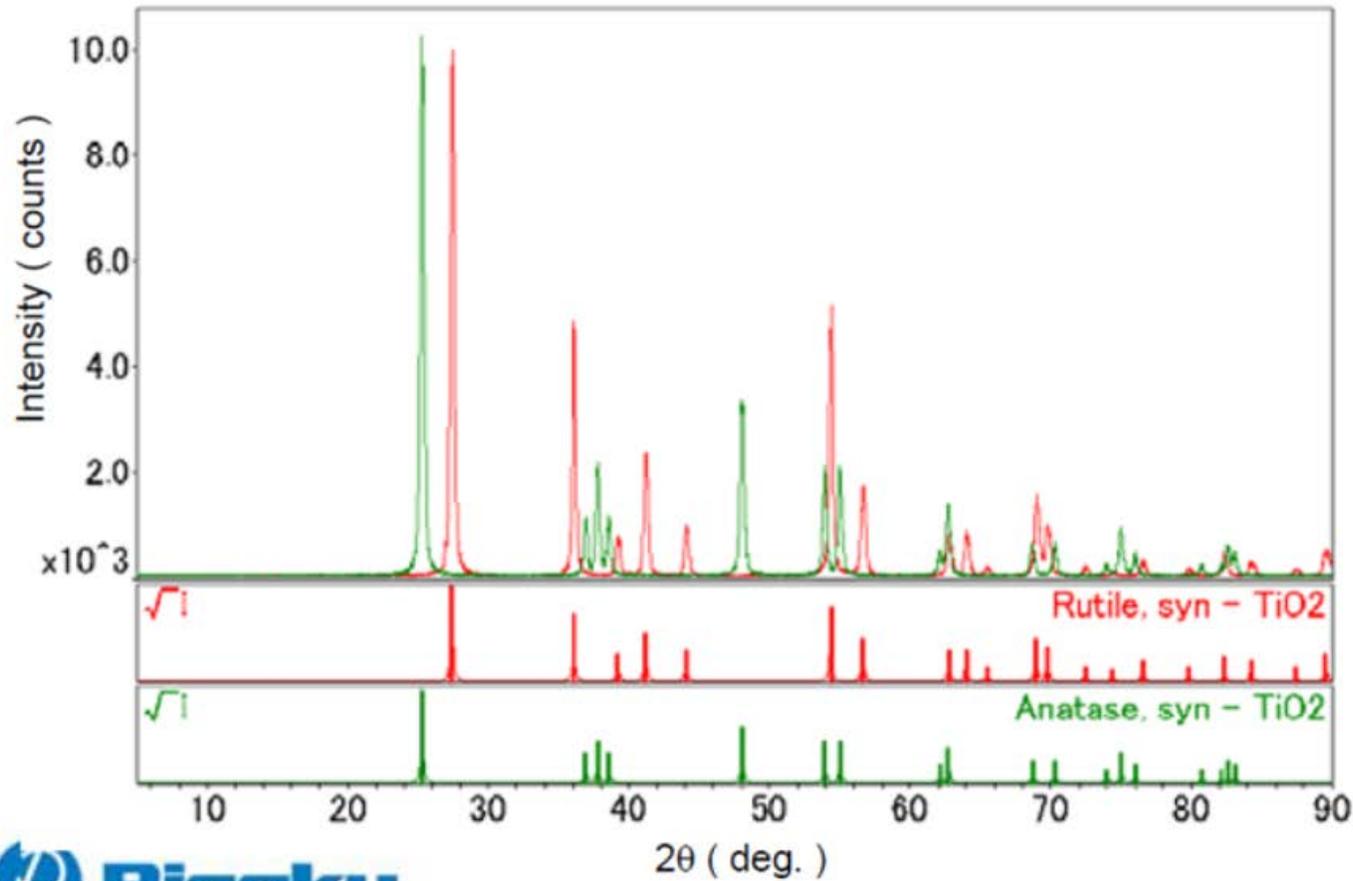
ANALYSIS

- We get from XRD: peaks at 2θ

- We analyze:
  - Peak position (Planes of atoms = Crystal structure)
  - Width
  - Intensity

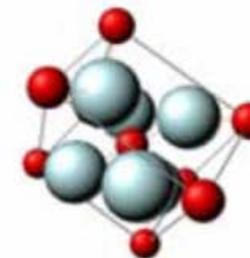Possible diffracted planes for different cubic unit cells

EXAMPLE 1

Anatase
Used For Photocatalyst

TiO2

Rutile
Used For Cosmetic

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

EXAMPLE 2

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

Al_2O_3

$25.56° \leftarrow 25.58°$

$35.12° \leftarrow 35.16°$

$900°C \leftarrow 25°C$

Intensity(CPS)

2θ (deg)

http://homepage.ntu.edu.tw/~kcyuan/form/For_Rigaku-Upload_powder.pdf
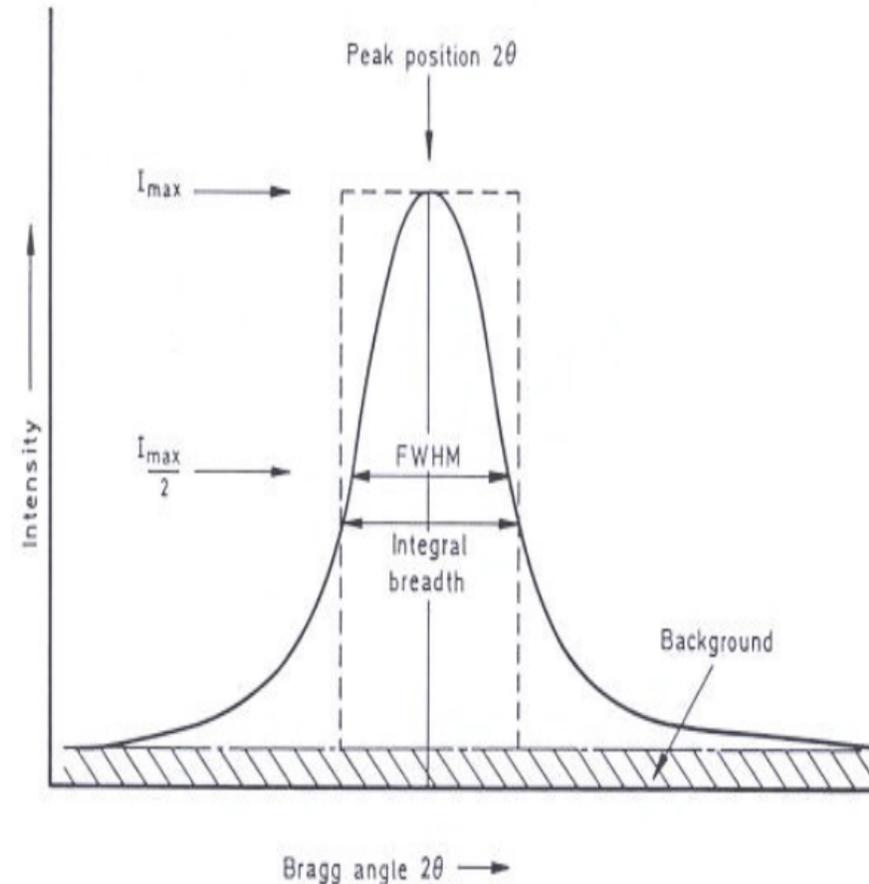
31
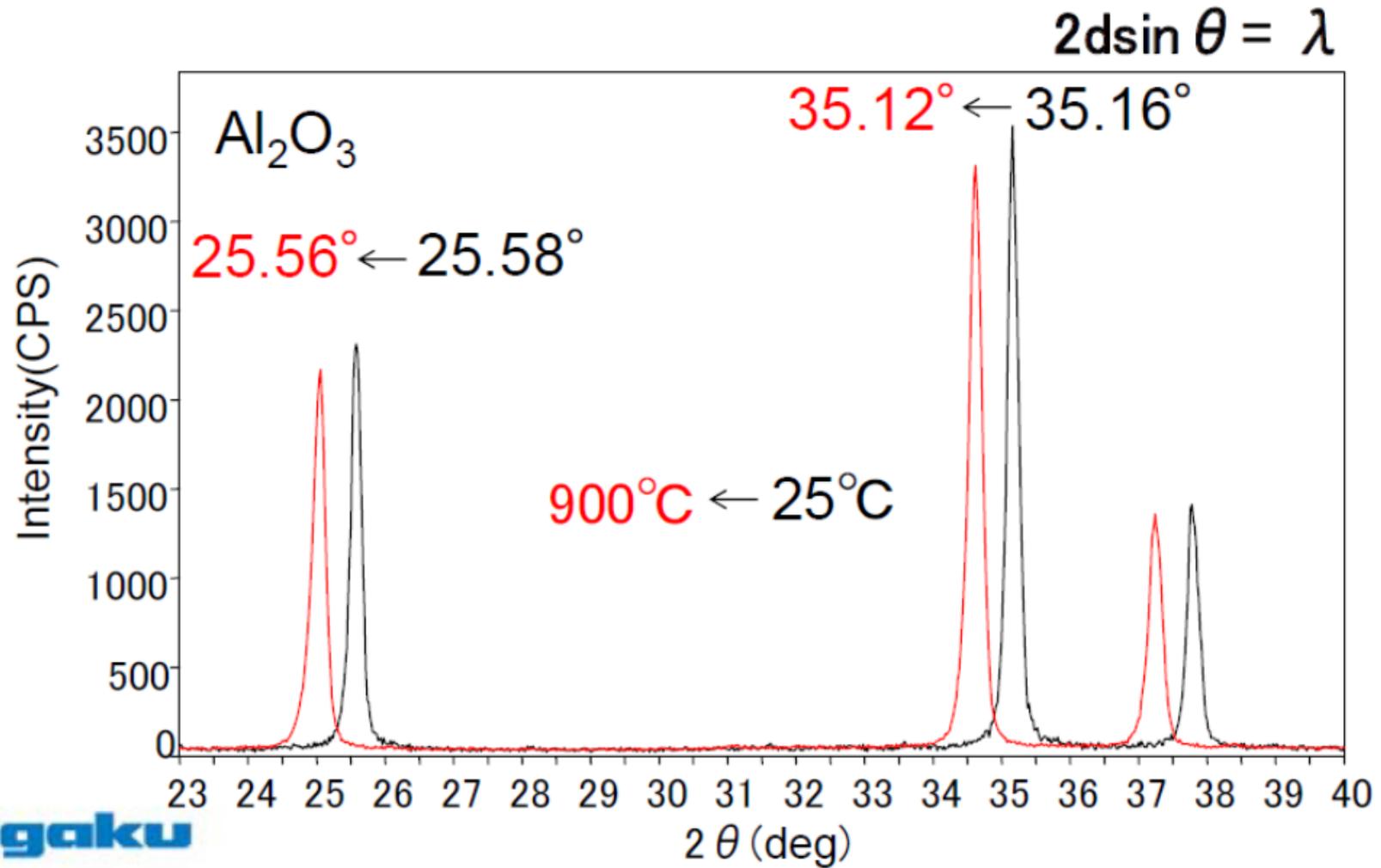
Peak width

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

Peak position 2θ

I_{max}

$\frac{I_{max}}{2}$

FWHM

Integral breadth

Background

Intensity

Bragg angle 2θ

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

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EXAMPLE 3

- Rolled material has very small grains ⟶ broader peak

- As the material annealed grains start to grow and peak becomes sharper
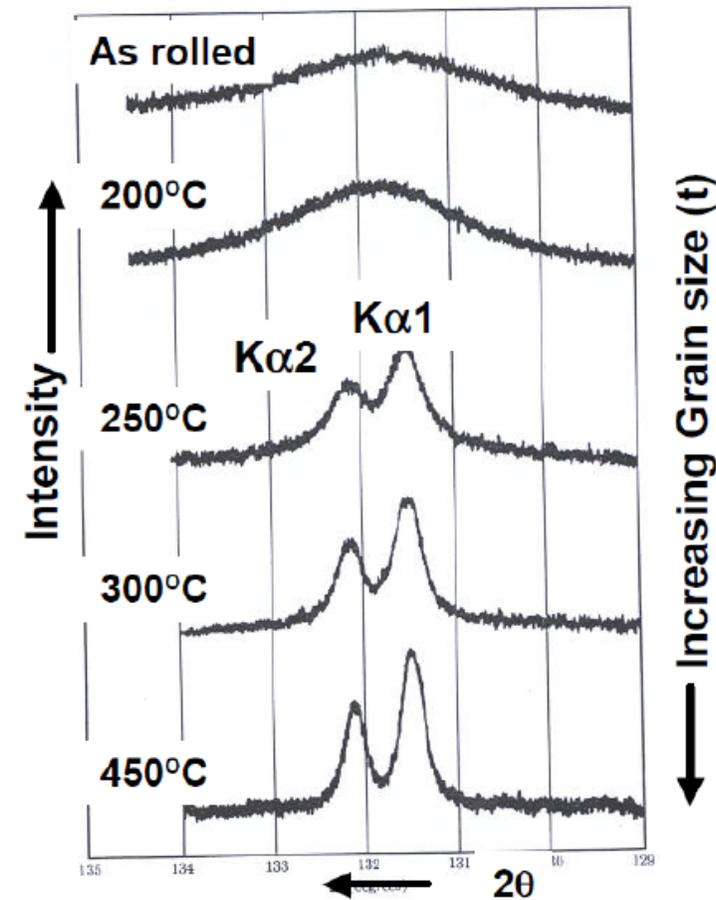
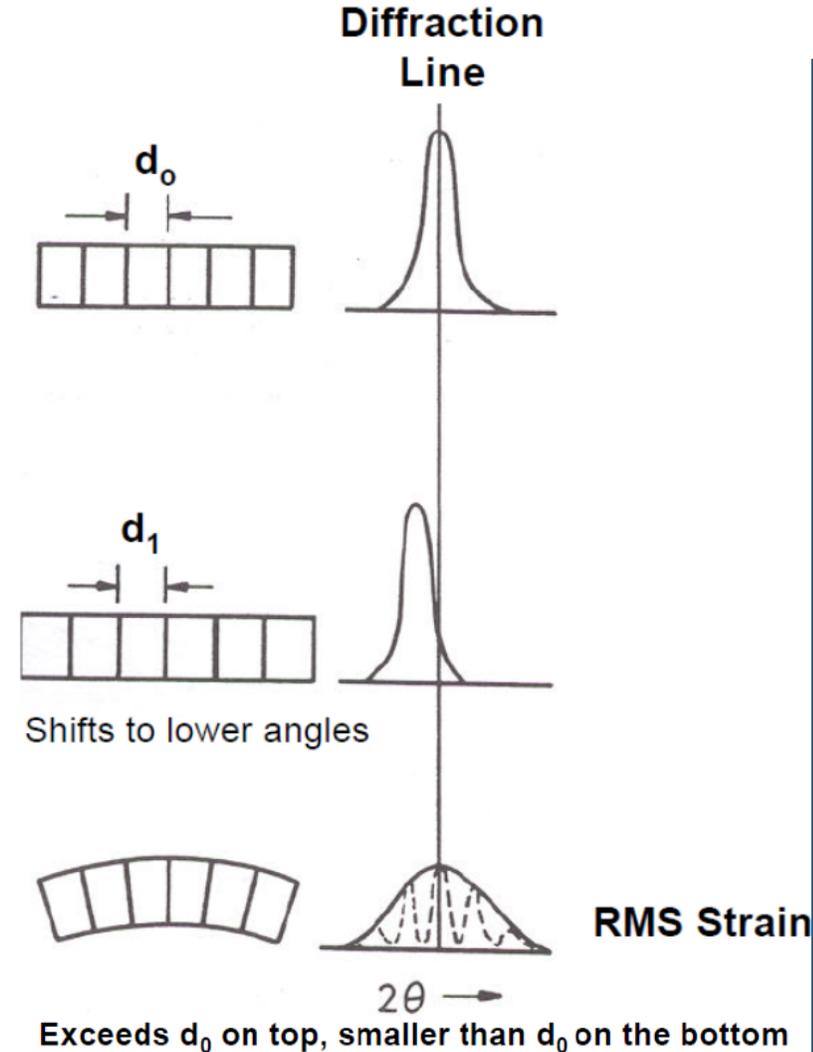(331) Peak of cold-rolled and Annealed 70Cu-30Zn (brass)

Elements of X-RAY Diffraction By B.D.Cullity and S.R.Stock
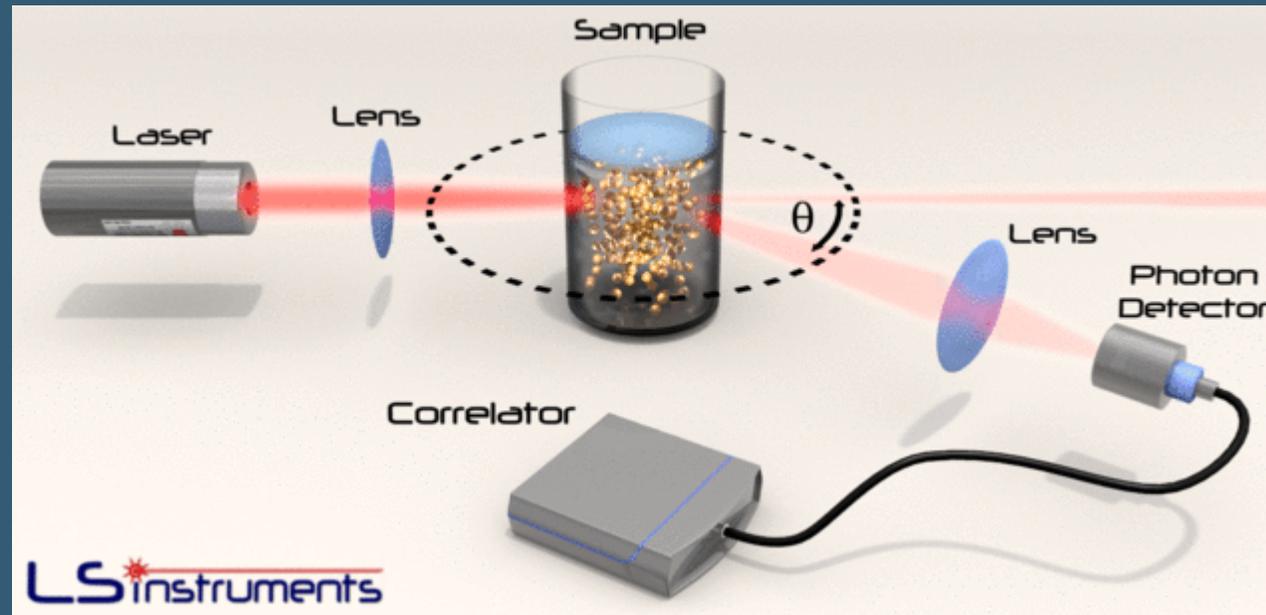
EXAMPLE 4

- Internal strain

$2dsin\theta=\lambda$

- Tensile stress increase d

- As d increase peak shifts to the right

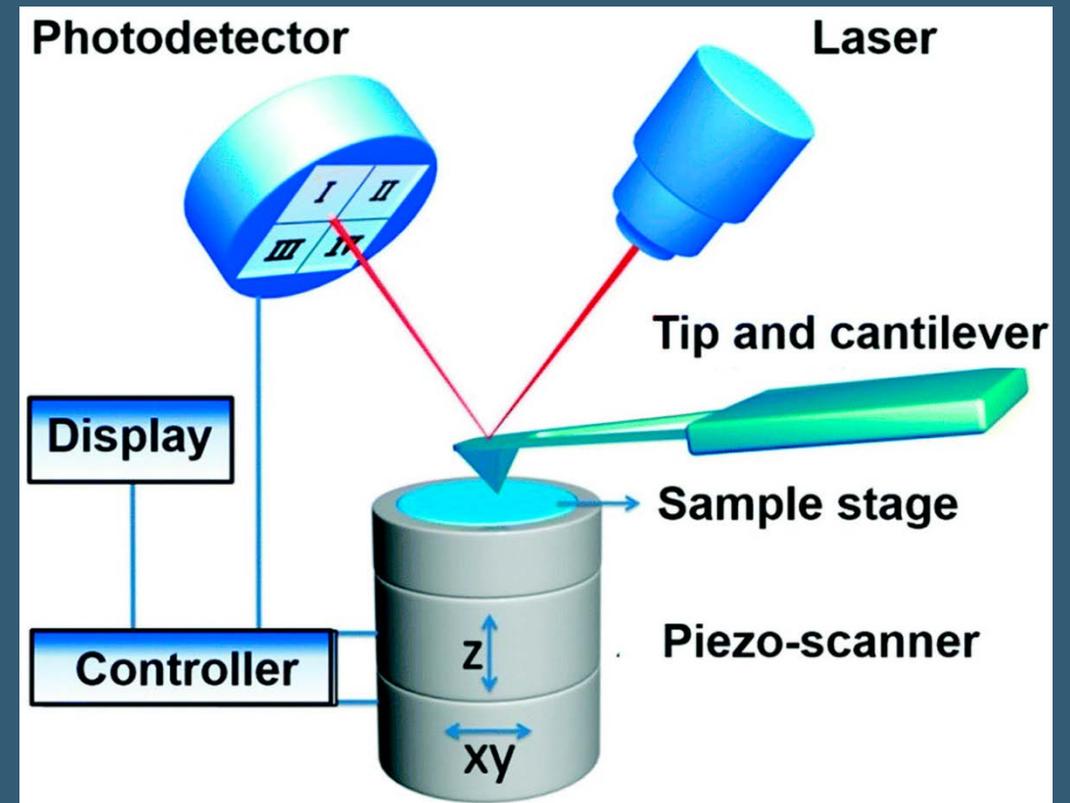- Compressive stress decrease d

  - shift peak to the left

Diffraction Line

d_0

d_1

Shifts to lower angles

RMS Strain

$2\theta \longrightarrow$

Exceeds d_0 on top, smaller than d_0 on the bottom

Elements of X-RAY Diffraction By B.D.Cullity and S.R.Stock
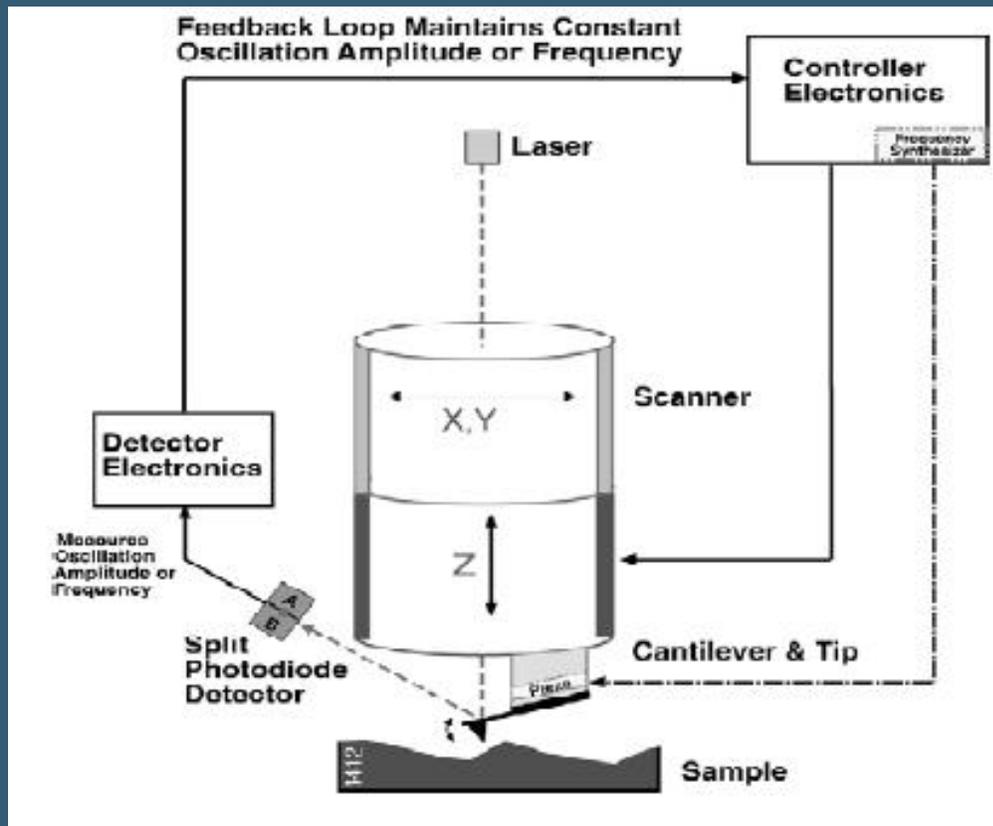
DYNAMIC LIGHT SCATTERING (DLS)

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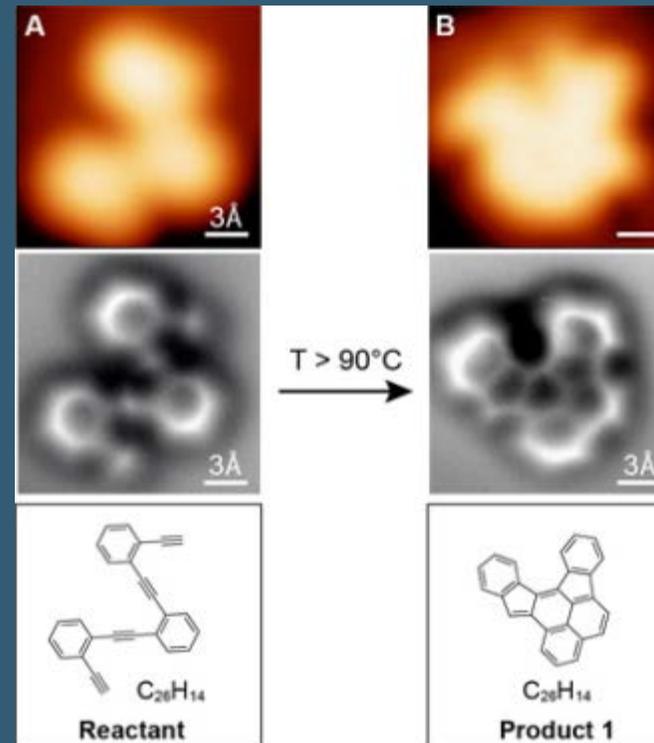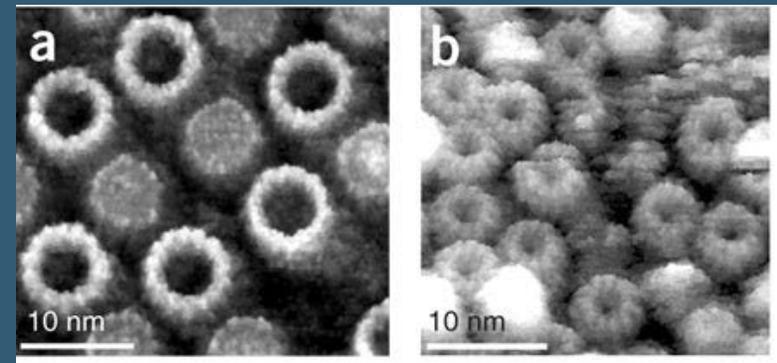
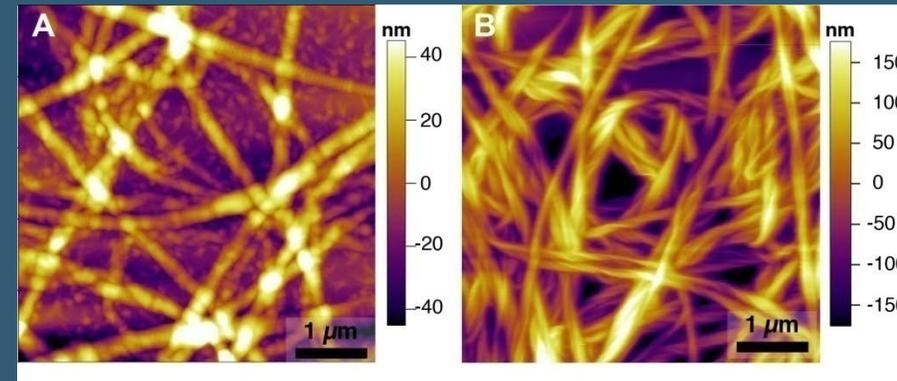# ATOMIC FORCE MICROSCOPE

APPLICATIONS OF AFM

- Take Atomic-Scale Picture of Chemical Bonds

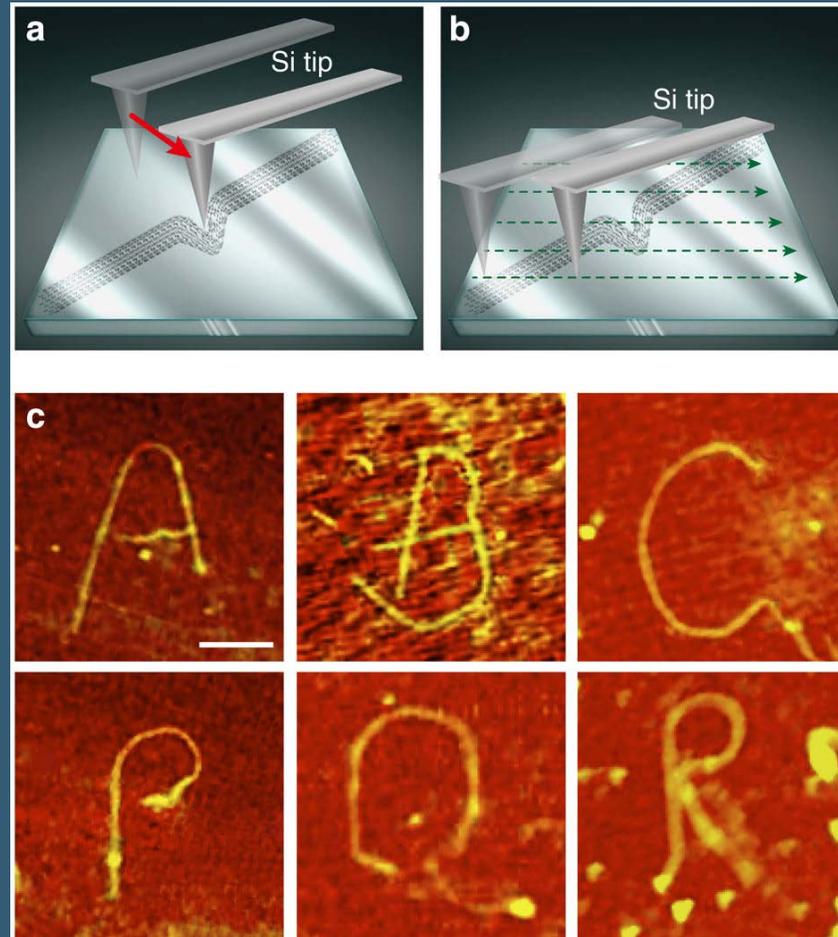- Bond length and molecular structure

APPLICATIONS OF AFM

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

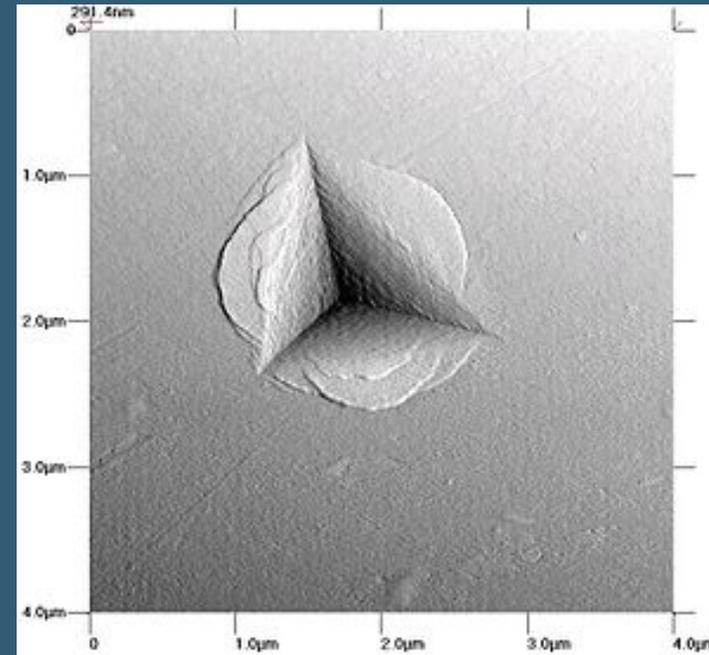- Size, Diameter, Physical and chemical properties

APPLICATIONS OF AFM
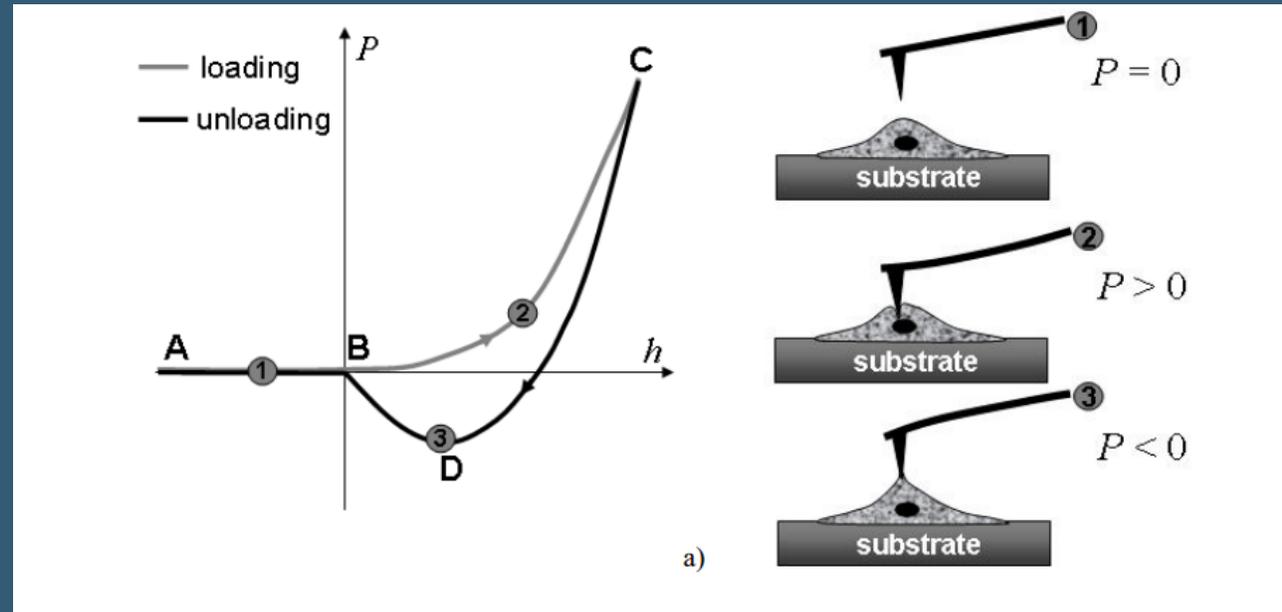
- Manipulation

- 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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