Characterization for Nanostructures

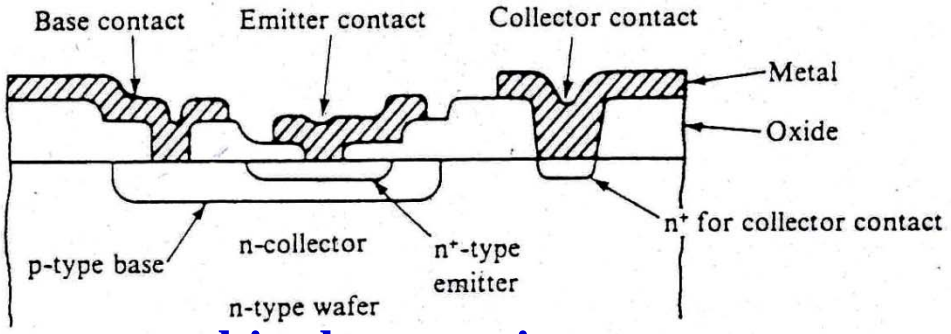
Byungwoo Park

Department of Materials Science and Engineering
Seoul National University

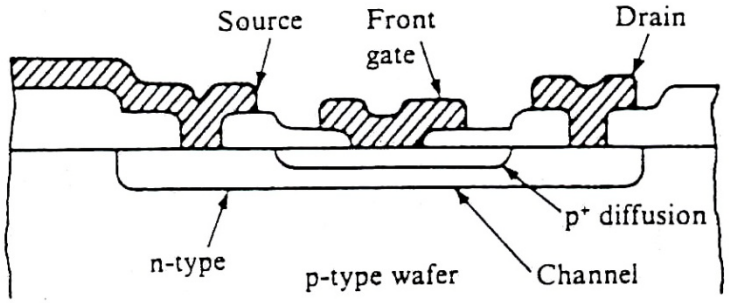
http://bp.snu.ac.kr

성공적인 집적회로

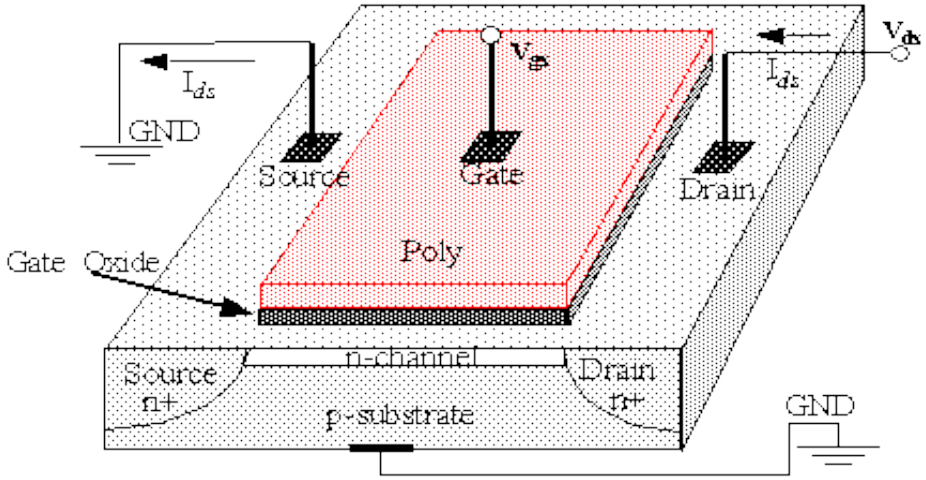
- Accurate Control of Composition and Phase
- Accurate Size Control
- Accurate Solute-Distribution Control



***n-p-n* bipolar transistor**



***n*-channel junction field effect transistor**

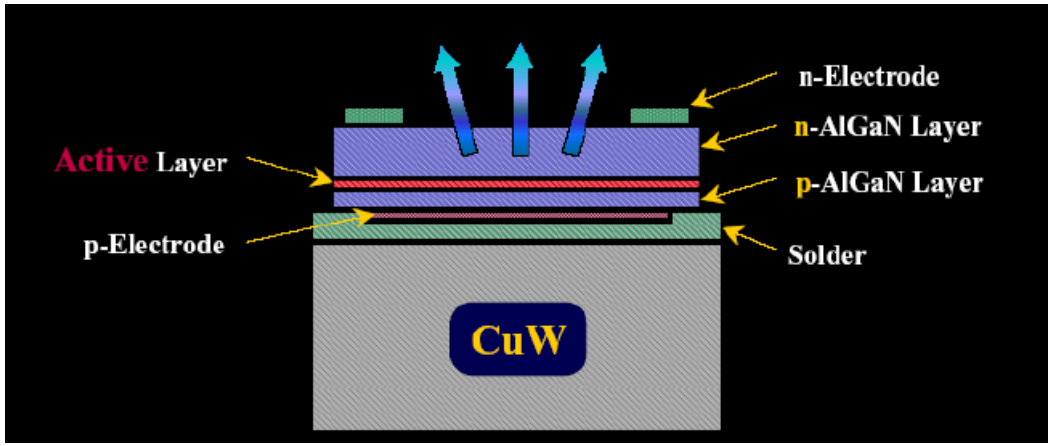


***n*-channel MOS transistor**

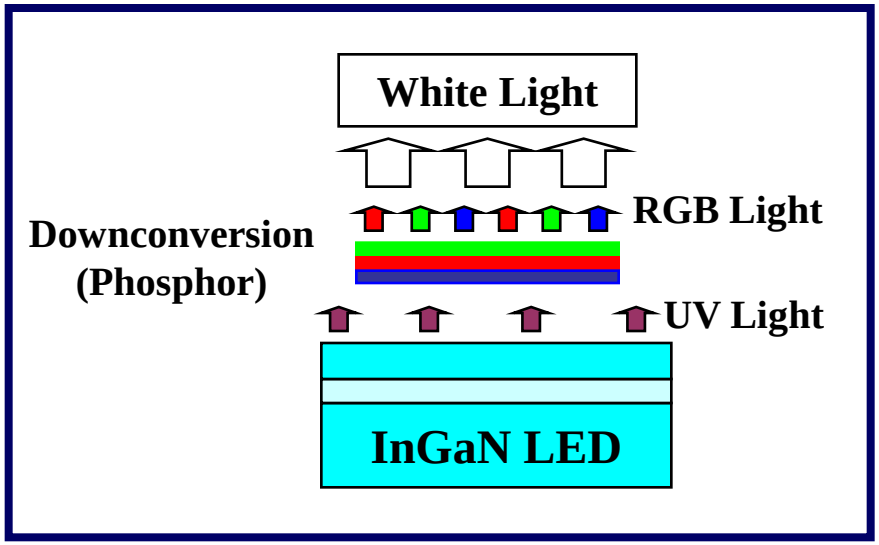
PL Nanoparticles on UV Epilayer

- **White LED**

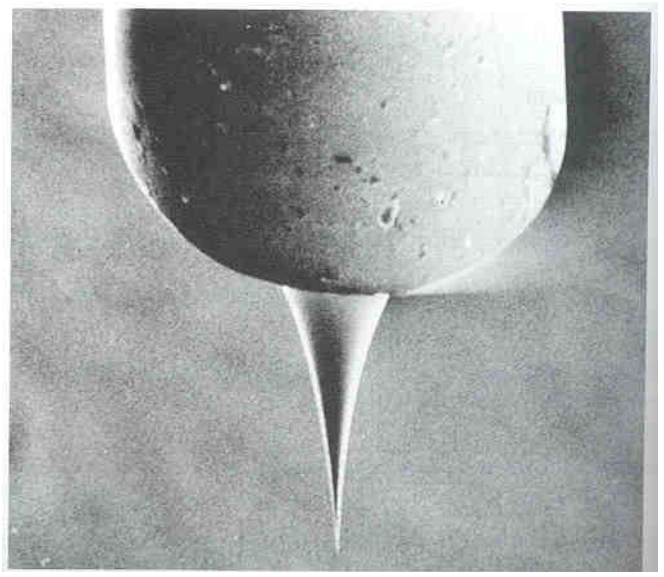
- Nichia High-Power LED



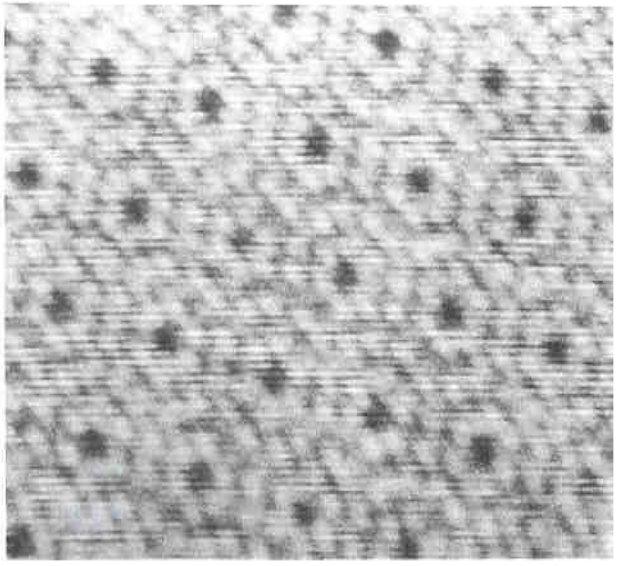
- UV LED & RGB Phosphor



Scanning Tunneling Microscopy



The tungsten probe of
a scanning tunneling microscope.



Silicon atoms on Si (111) surface of a silicon single crystal form a repeated pattern (produced by STM).

Growth Characteristics – Silicon (001) Surface

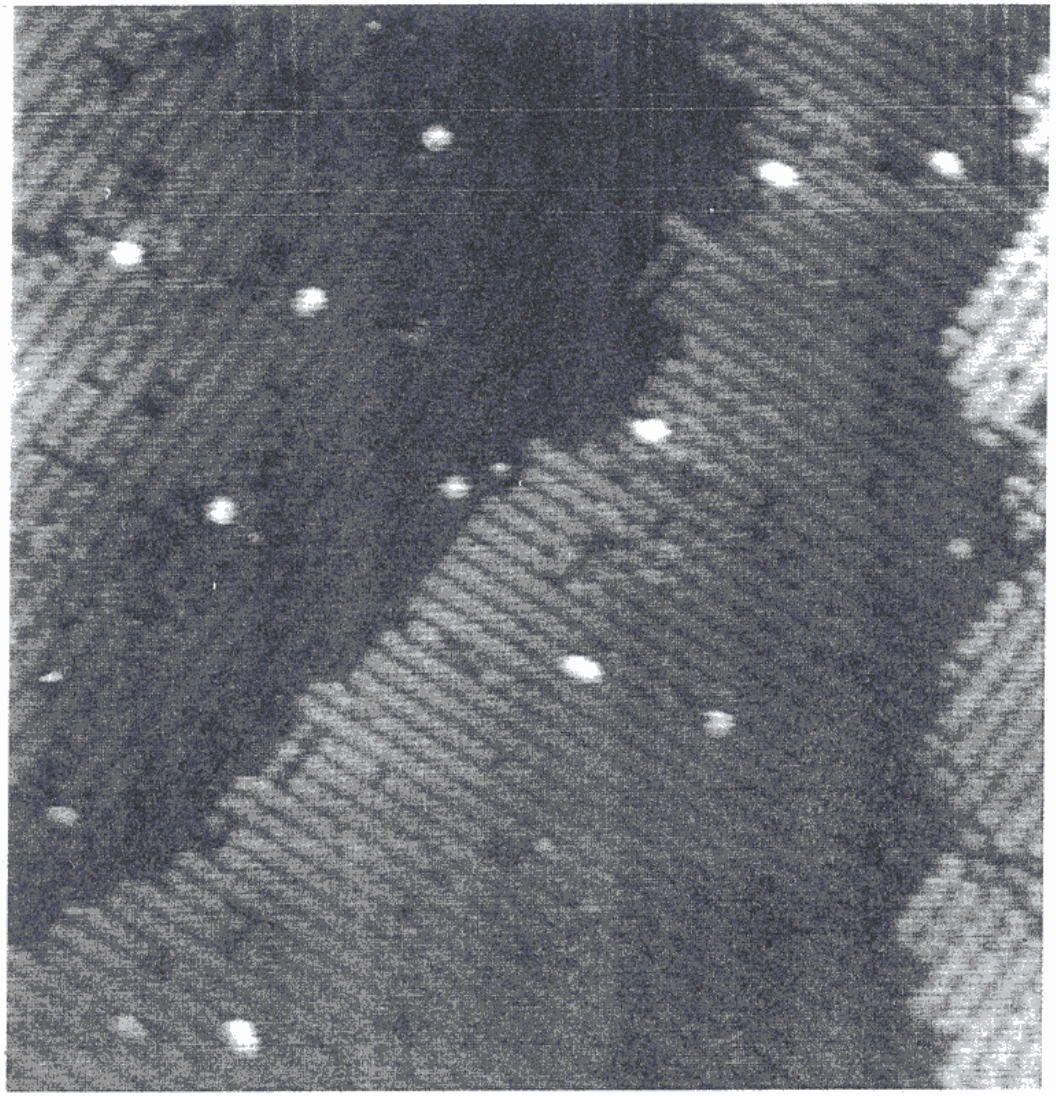
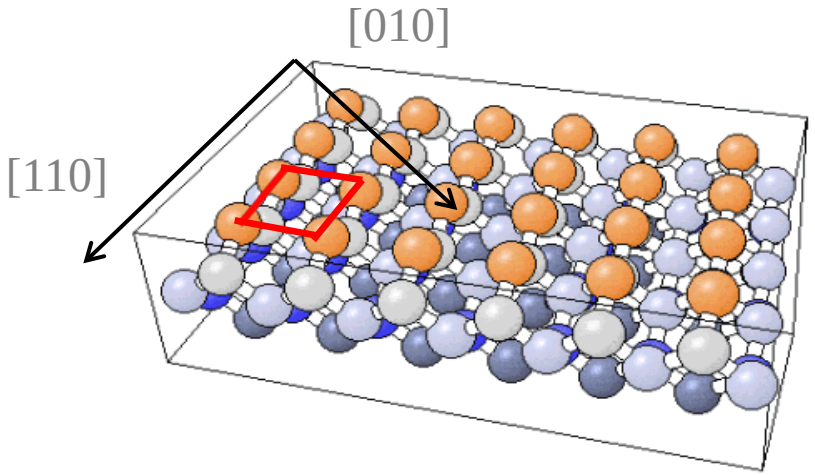
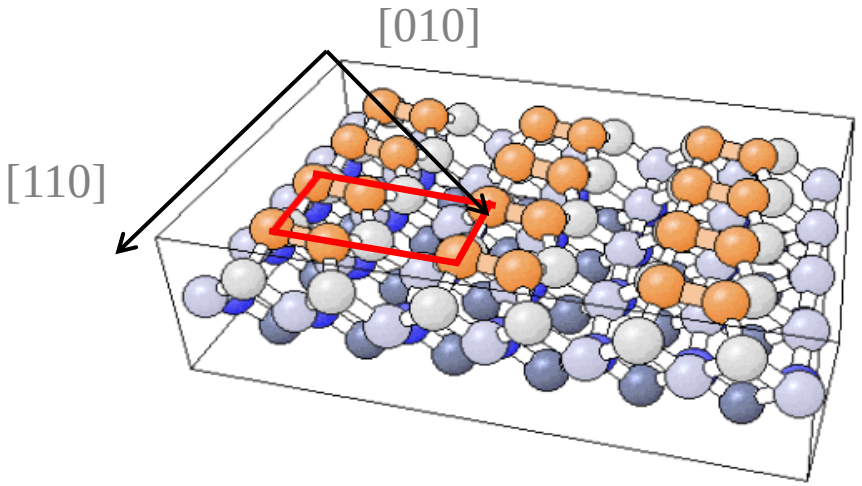


FIGURE 1. A SCANNING tunneling microscope image of a silicon (001) surface after the deposition of a small amount of Si at room temperature. The image shows two single-layer steps (the jagged interfaces) separating three terraces. Because of the tetrahedral bonding configuration in the silicon lattice, dimer row directions are orthogonal on terraces joined by a single-layer step. The area pictured is 30 × 30 nm.

The Si(001)-(2 ×1) Reconstruction



Unreconstructed Si(001)-(1×1) surface.
- Si atoms of the topmost layer highlighted in orange.
- These atoms are bonded only two other Si atoms, both of which are in the second layer (shaded grey).

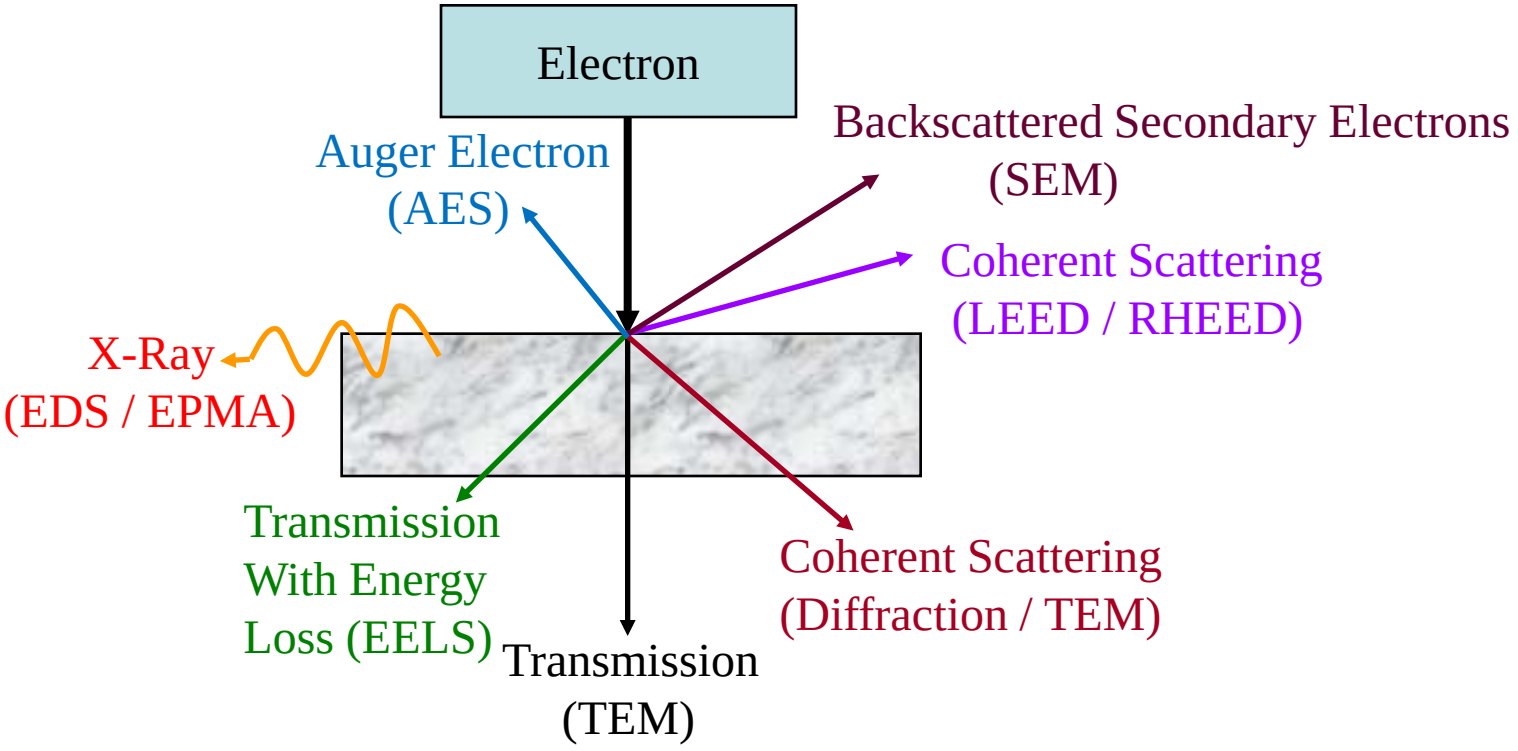


Reconstructed Si(001)-(2×1) surface.
- The Si atoms of the topmost layer form a covalent bond with adjacent surface atoms.
- Drawn together as pairs.

Z. Zhang *et al*. (Oak Ridge National Laboratory)
Annual. Rev. Mater. Sci. **27**, 525 (1997).

http://www.chem.qmul.ac.uk/surfaces/scc/scat1_6a.htm

Electron Method



Electron Method

- **SEM (Scanning Electron Microscopy)**:
  The surface of solid is swept in a raster pattern with a finely focused beam of electrons: physical nature and chemical composition of the surfaces.

- **TEM (Transmission Electron Microscopy)**:
  TEM is used to obtain nanostructural information by diffraction and imaging from a thin specimen (thin enough to transmit electrons).

- **EDS (Energy Dispersive Spectroscopy)**:
  A specimen, excited by the incident electrons, emits the energy released by one of the higher level electrons coming down as a characteristic x-ray (i.e., same as in an x-ray tube). A dedicated instrument for chemical analysis with EDS is an electron microprobe (EPMA). EDS is often **used in conjunction with SEM and TEM**.

Electron Method

- AES (Auger Electron Spectroscopy):

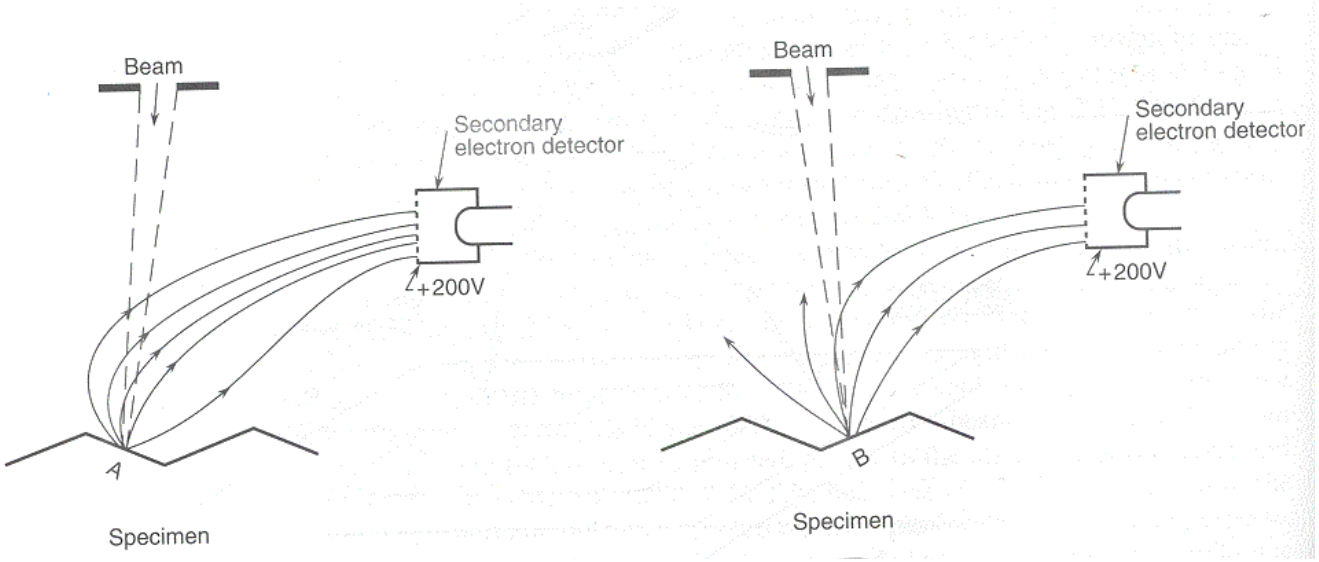
  A specimen atom, excited by the incident electron, emits some of the energy by one of the higher level electrons coming down, by emitting a second electron with a characteristic energy. This is a surface analysis technique.

- EELS (Electron Energy Loss Spectroscopy):

  The characteristic energy losses of the incident electron beams penetrating through a film or reflected from a surface can give important information on the nature of the solid and the relevant binding energies.

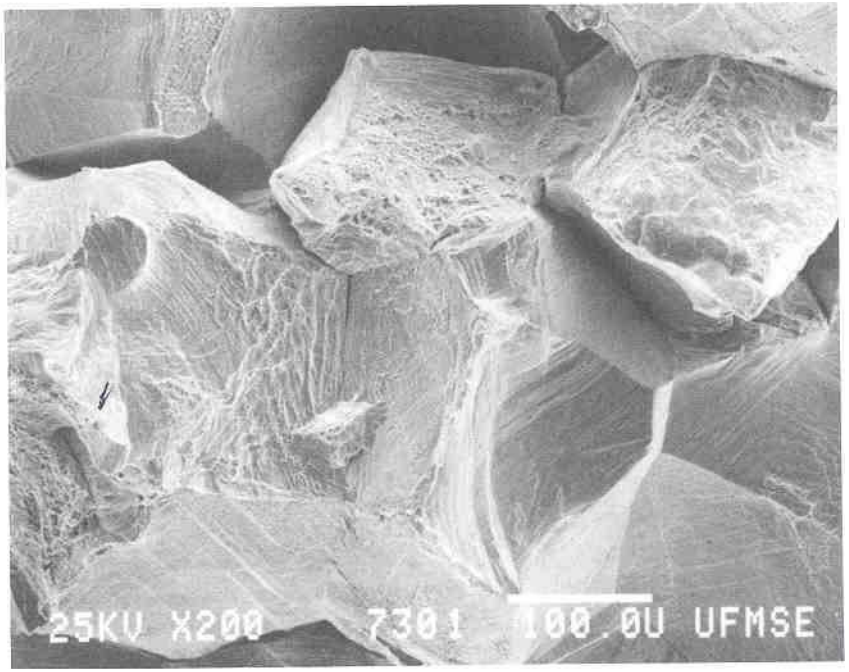
Scanning Electron Microscopy

- Incident beam of high-speed electrons (20 keV).
- Energetic electrons in this beam cause the emission of low-energy secondary electrons from the surface.

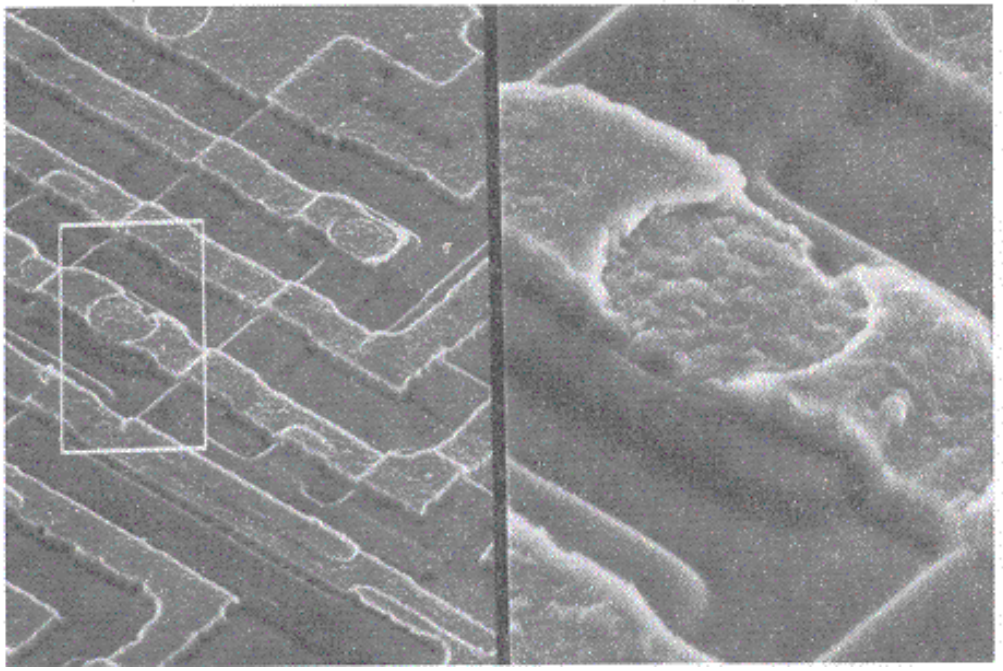


An illustration of how the scanning electron microscope can reveal surface relief when used with a secondary electron detector.

SEM Image

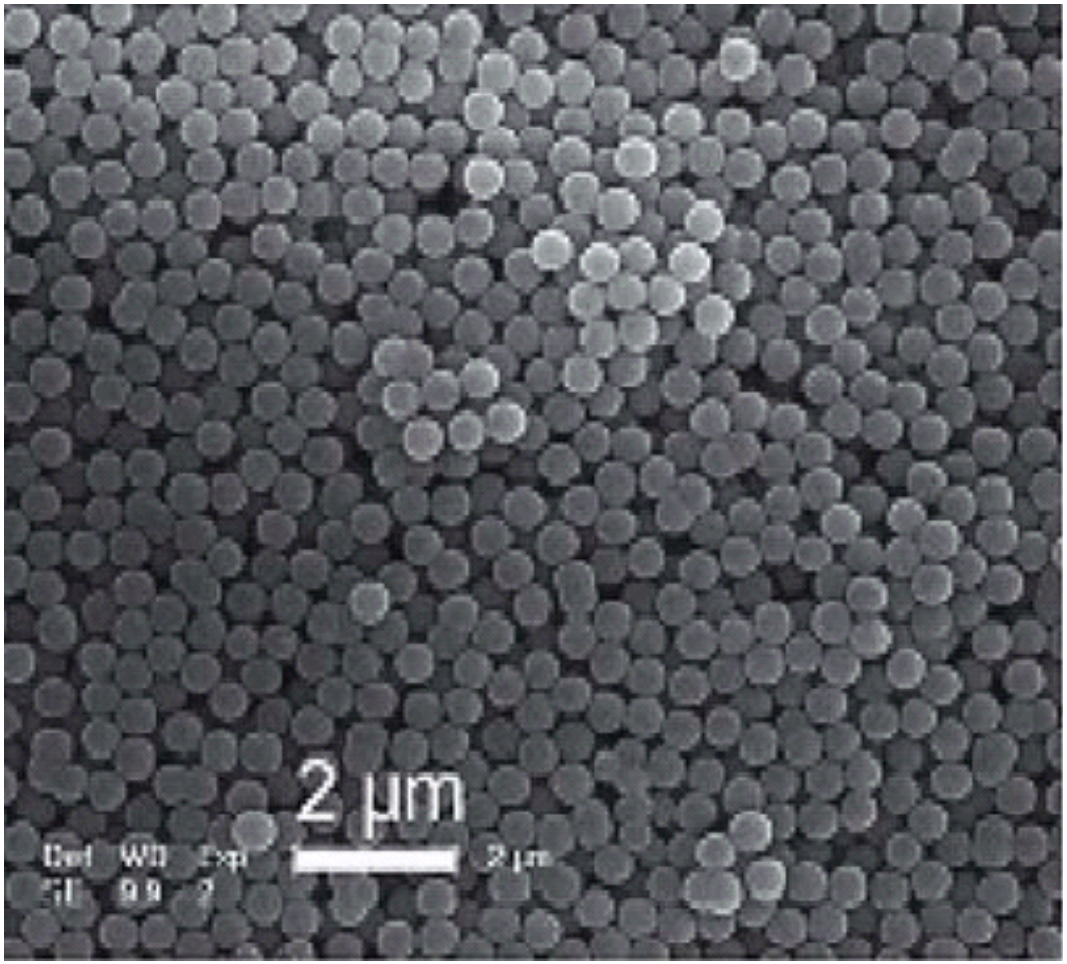


An SEM micrograph of a fractured Cu-4.9 at. % Sn specimen.



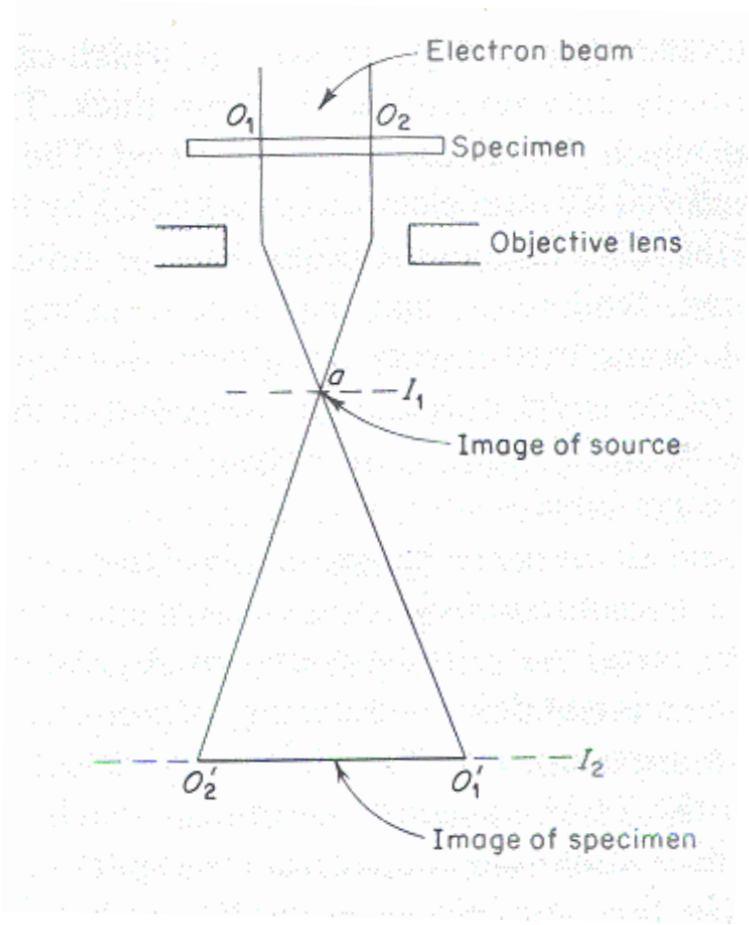
Left side is an image of part of an integrated circuit, right side is an enlargement of the highlighted rectangle on the left: (magnification = ×850 left, ×3300 right, accelerating voltage = 10.0 keV).

Field-Emission Scanning Electron Microscopy

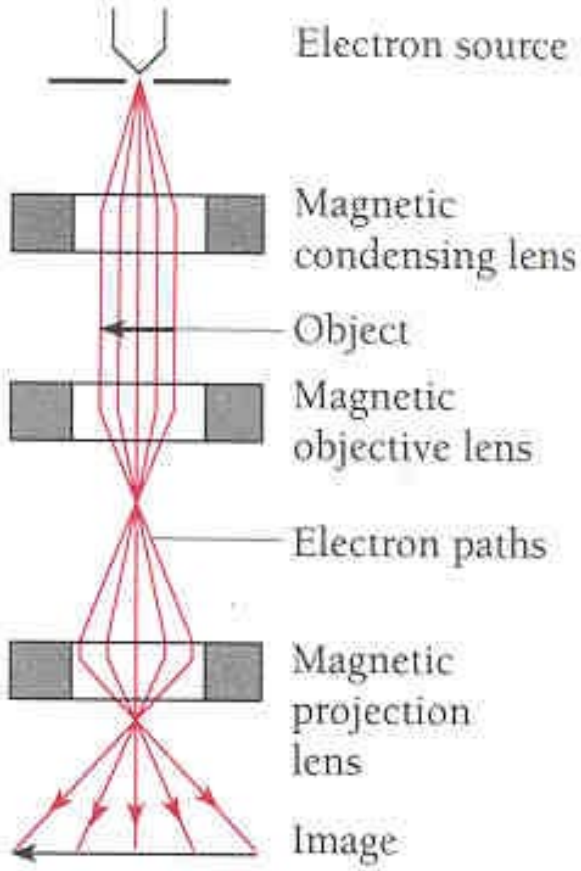


- SiO_2 Spherical Particles, *APL* (2005)

Transmission Electron Microscopy

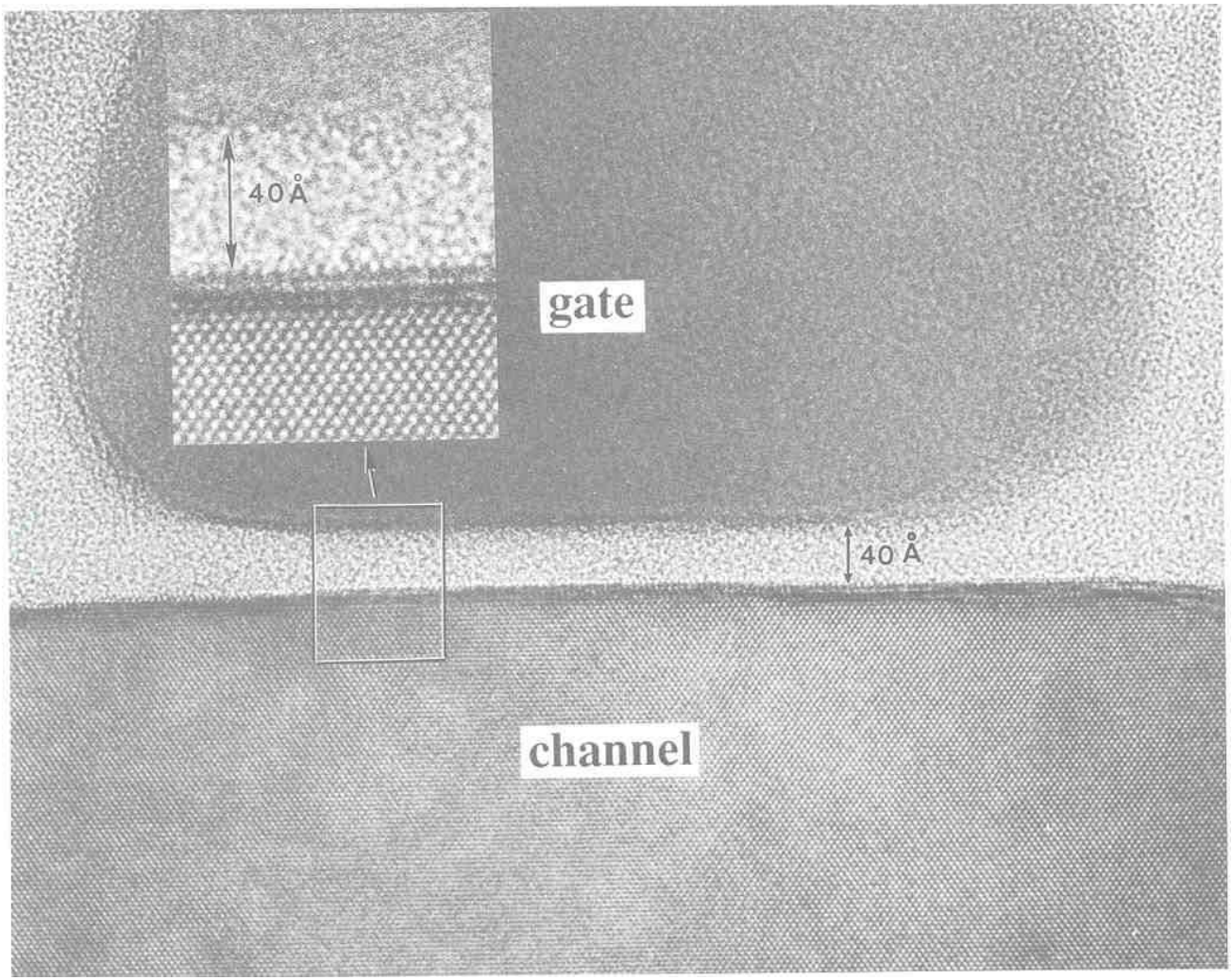


Schematic drawing of a transmission electron microscope.



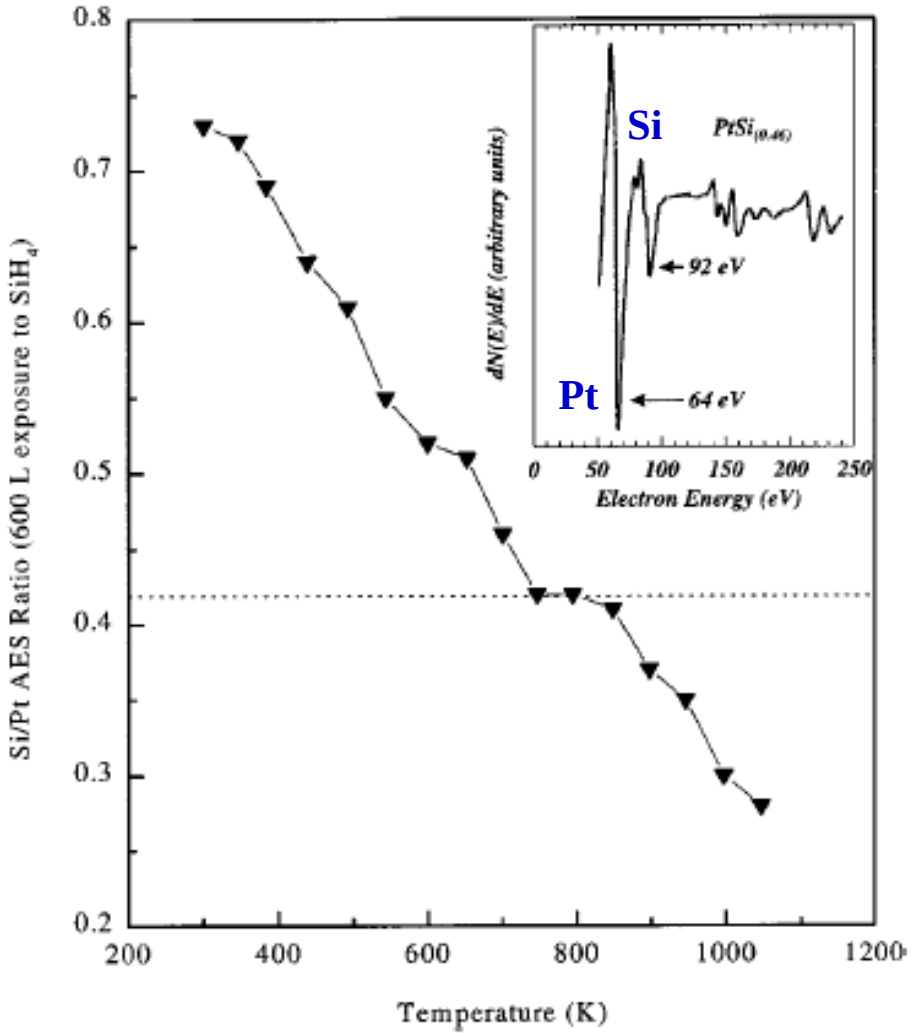
The electron beam in an electron microscope is focused by magnetic fields.

High-Resolution TEM



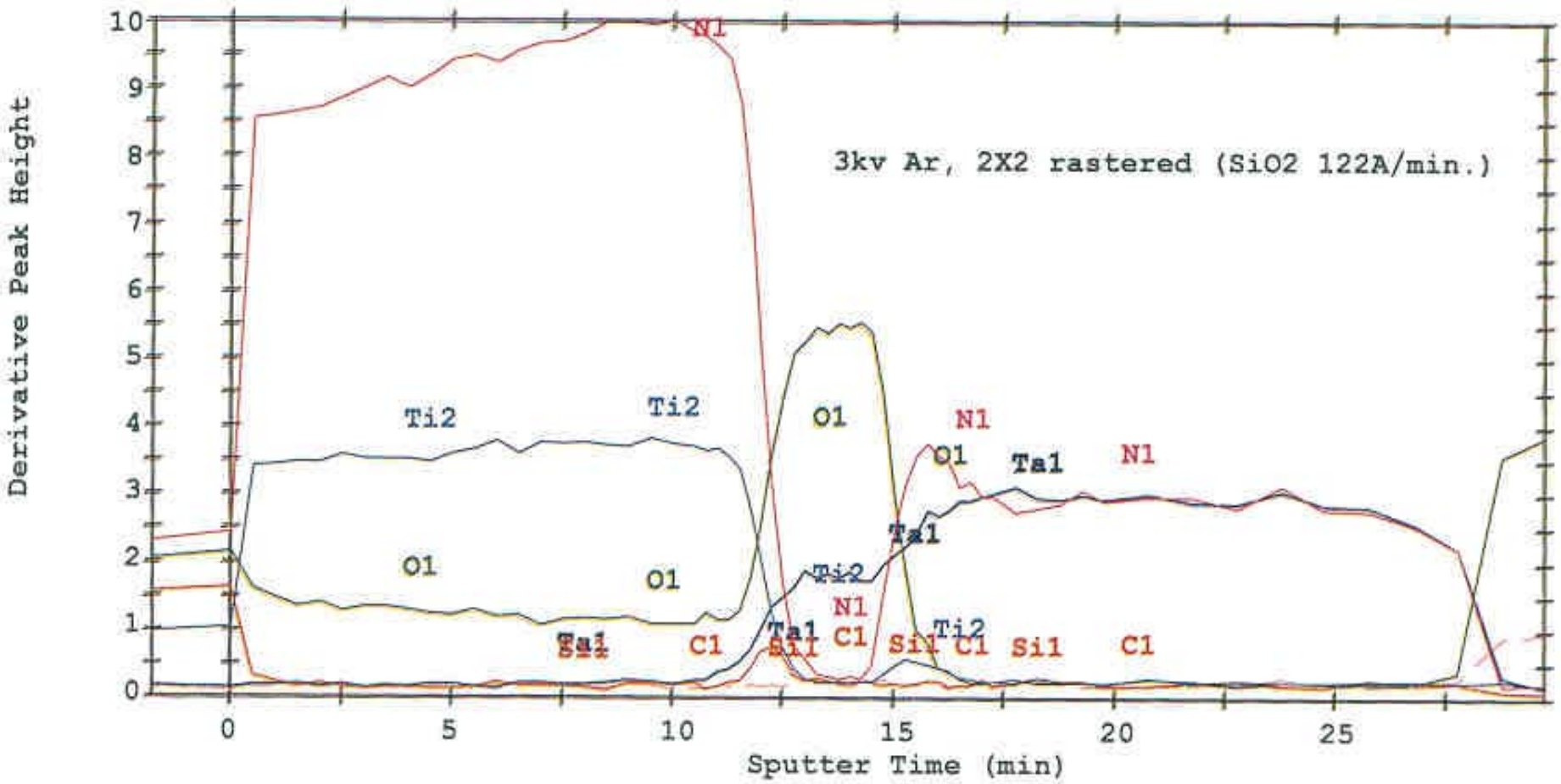
High-resolution cross-sectional TEM, showing an experimental silicon metal-oxide field effect transistor (MOFET). Each white blob represents a pair of atom columns. The gate is only a few hundred atoms long, and the **gate oxide** is 4 nm thick. Such devices, fabricated by a team at AT&T Bell Laboratories, have demonstrated intrinsic speeds in excess of **100 GHz** at room temperature.

Auger Electron Spectroscopy



- Si saturated Pt (100) surface, silicide as interconnects in FET, *JACS* (1999)

Depth Profile by AES



Sample : Layer of TiN/TaO/TaN on SiO_2 film

Ion Method

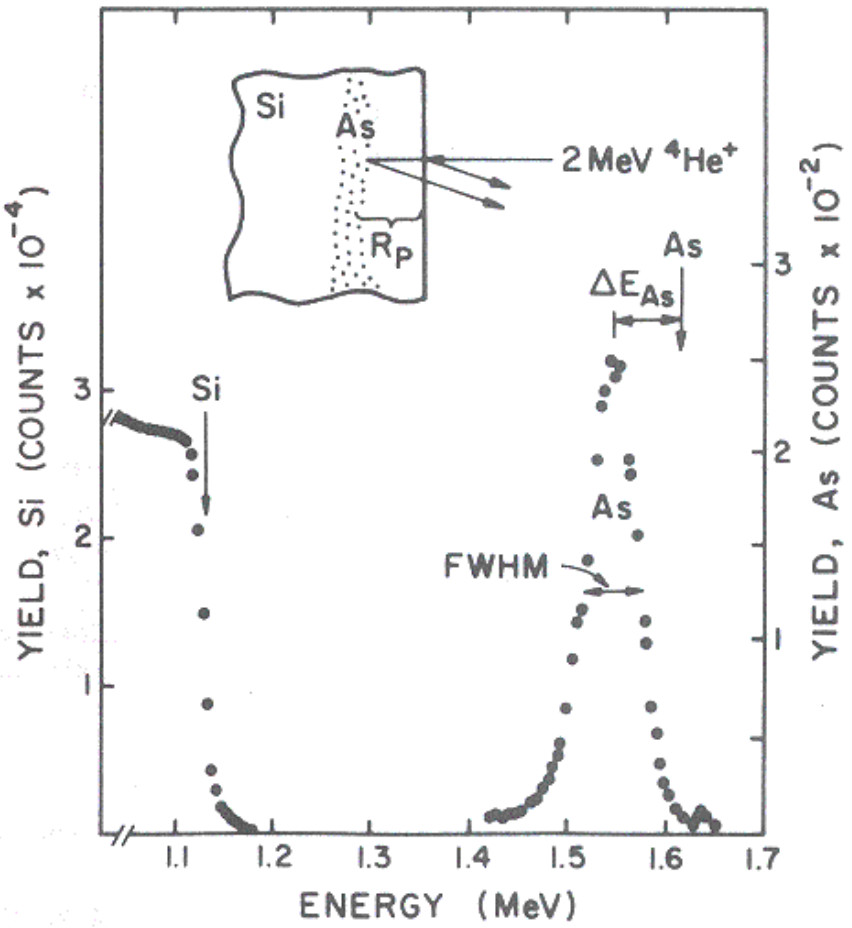
- RBS (Rutherford Backscattering Spectroscopy):
  Through the measurements of intensity and energy of the scattered ions, it is possible to infer the composition and depth of thin films.

- SIMS (Secondary Ion Mass Spectroscopy):
  The incident ion beam knocks off atoms from the specimen surface, which are then analyzed in a mass spectrometry.

- FIM (Field Ion Microscopy):
  The specimen is made into a fine tip in a local electric field. The imaging gas atoms are ionized by an individual atom on the tip. The ion travels to the negative side of the chamber. This was the finest instrument with atomic resolution.

- Ion Scattering (or He Scattering):
  Diffraction effect to study the surface structure.

Rutherford Backscattering Spectroscopy (RBS)



Energy spectrum of 2 MeV ^{4}He ions backscattered from a silicon crystal implanted with a normal dose of 1.2×10^{15} As^+/cm^2 at 250 keV. The vertical arrows indicate the energies of particles scattered from surface atoms of ^{28}Si and ^{75}As.

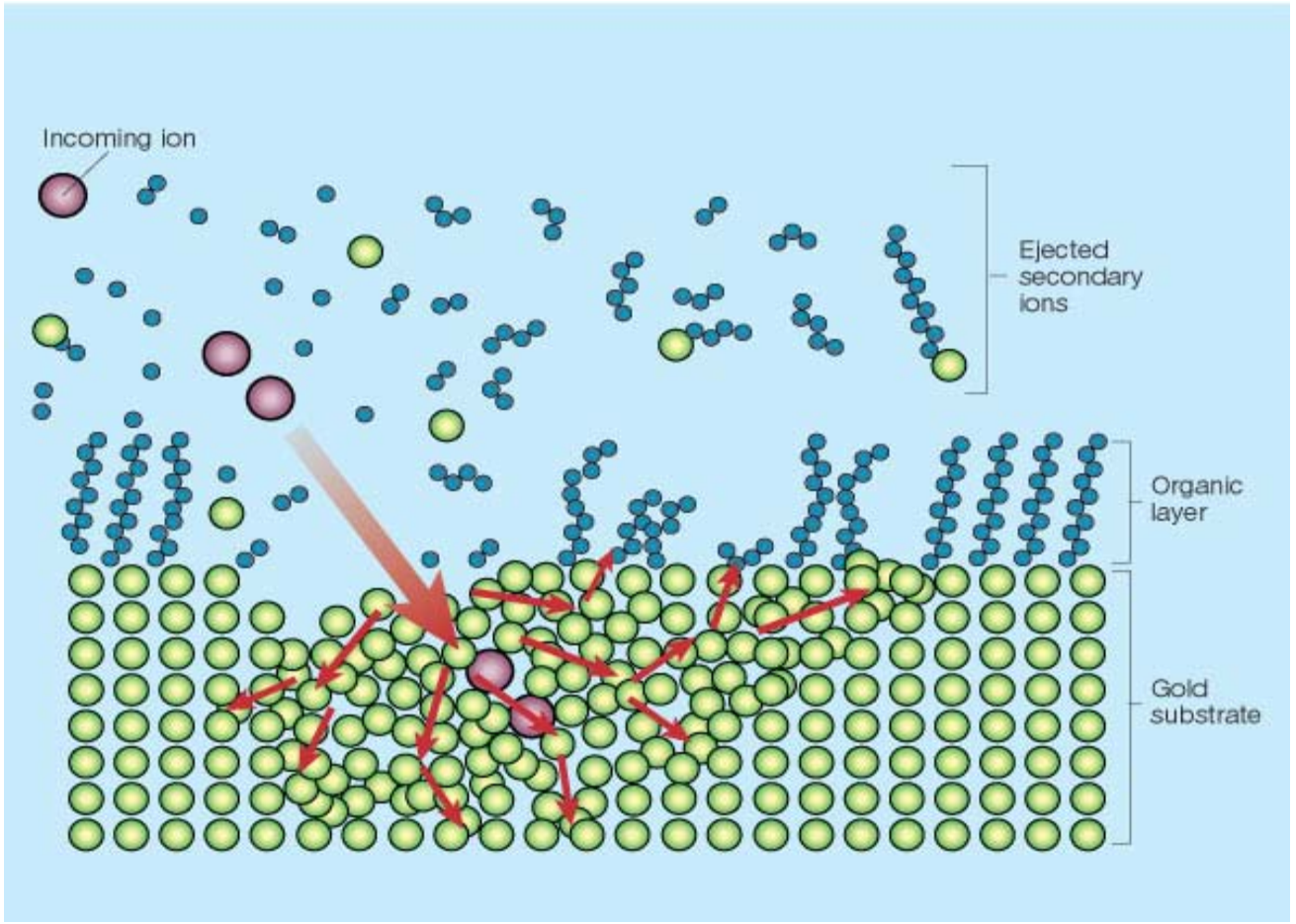
Secondary Ion Mass Spectroscopy (SIMS)

- Atoms and molecules are knocked (sputtered) out of the target.

- A mass spectrometer, where excited particles or ions can be separated according to their mass/charge ratio.

- It is a destructive technique because the surface atoms have to be knocked out of the solid.

Secondary-Ion Mass Spectrometry (SIMS)

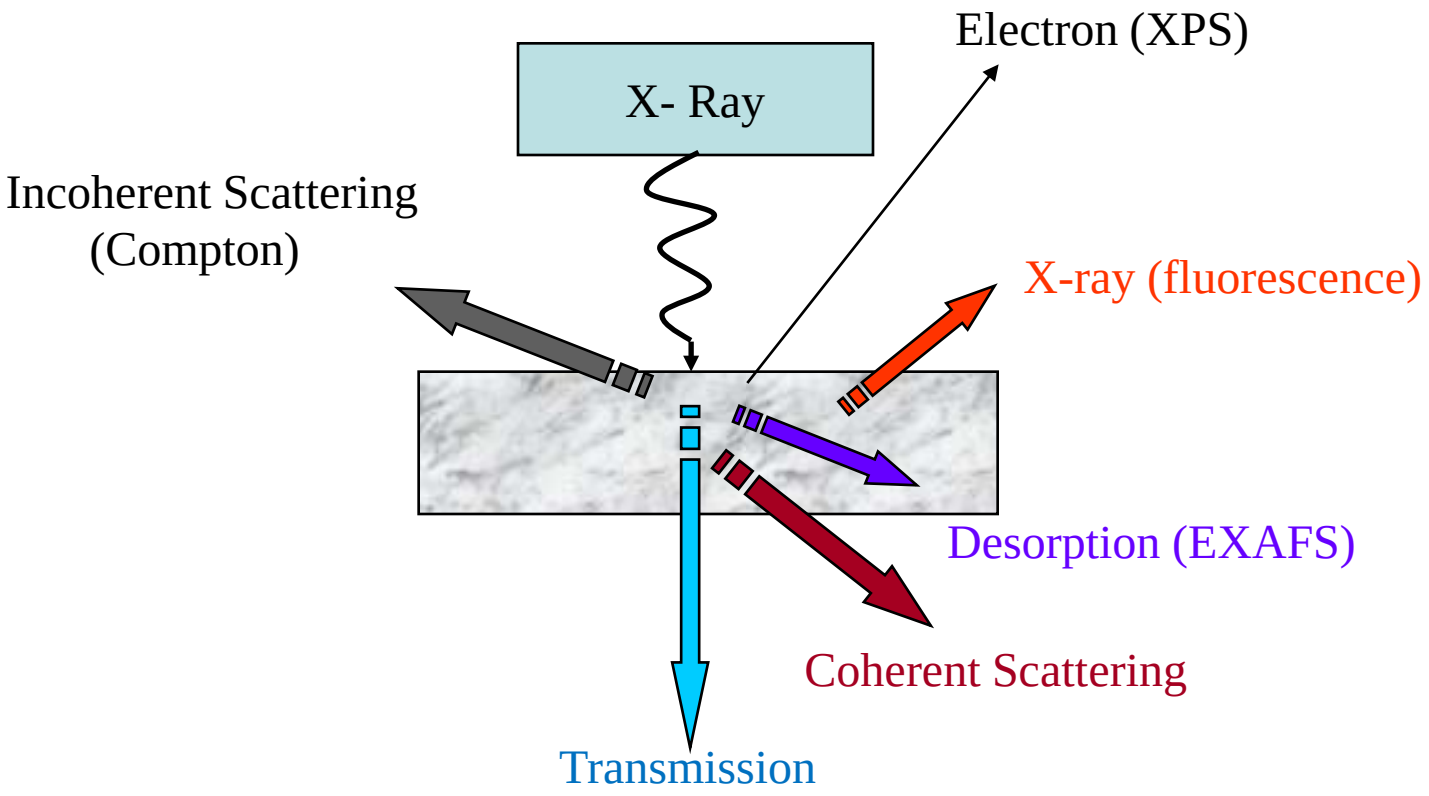


"View from the Edge"
David G. Castner
University of Washington
Nature **422, 129 (2003).**

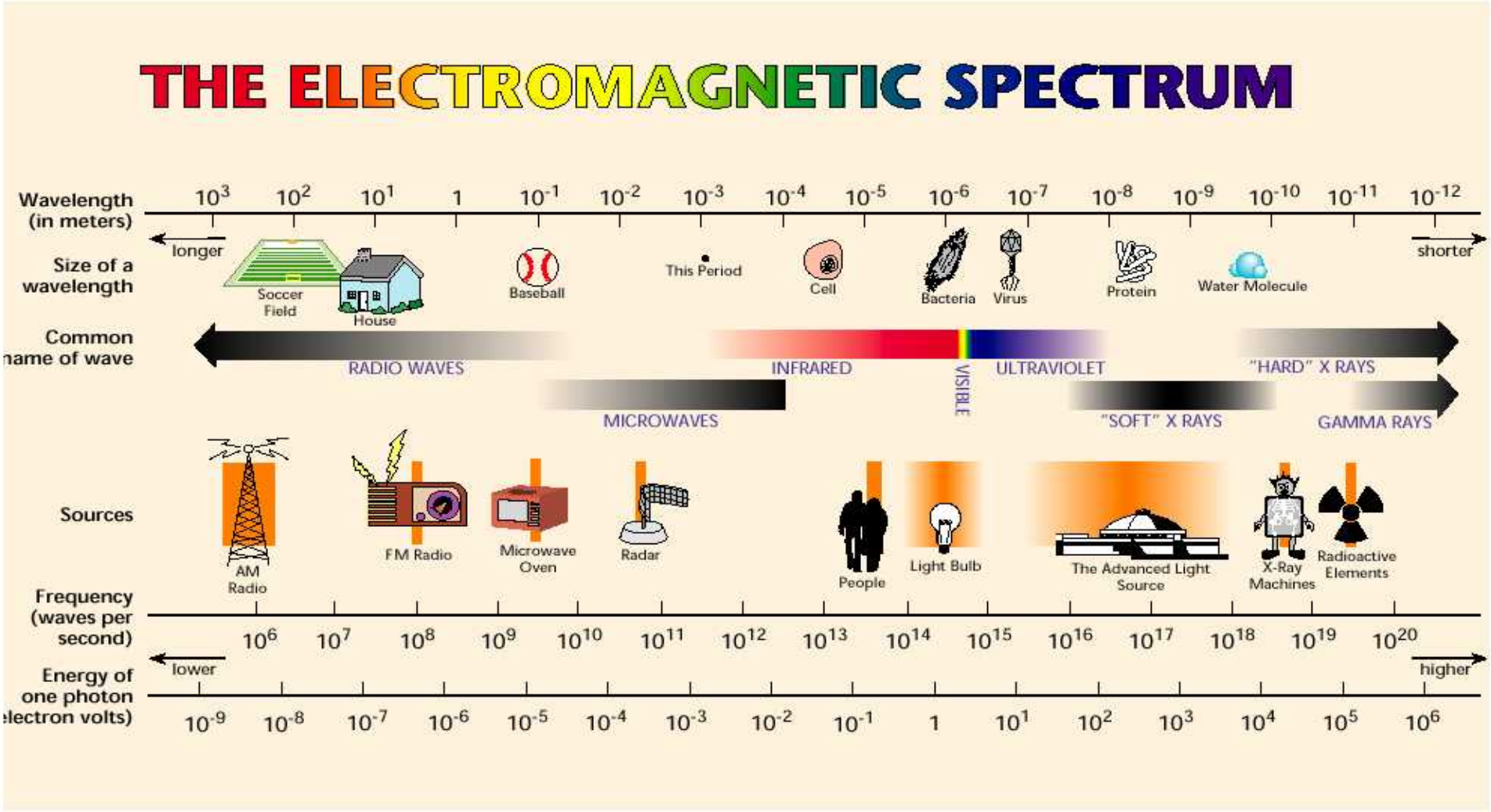
Ions are fired into an organic self-assembled monolayer on a gold substrate. The energy deposited in the surface region from the incoming primary ions produces a collision cascade. This results in the ejection of a wide range of atomic and molecular fragments, of which **about 1% are ions**. **Mass analysis of the ejected secondary ions is the key** to exploring the structure of the surface.

Survey of Analytic Techniques: X-Ray

X-Ray Method



Photon = Electromagnetic Wave



X-Ray Method

- **Diffraction :**

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

- **XPS (X-Ray Photoemission Spectroscopy)**:
  The incident x-ray causes emission of one of the core electrons of the specimen atom.

- Fluorescence:
  Specimen atoms, excited by x-ray absorption, emit the energy as a characteristic x-ray. Used for chemical analysis.

- Tomography:
  Differential absorption due to the presence of chemical inhomogeneity, yielding photographic images of the internal structure of a device.
  Used for medical, industrial quality control, and electronic devices.

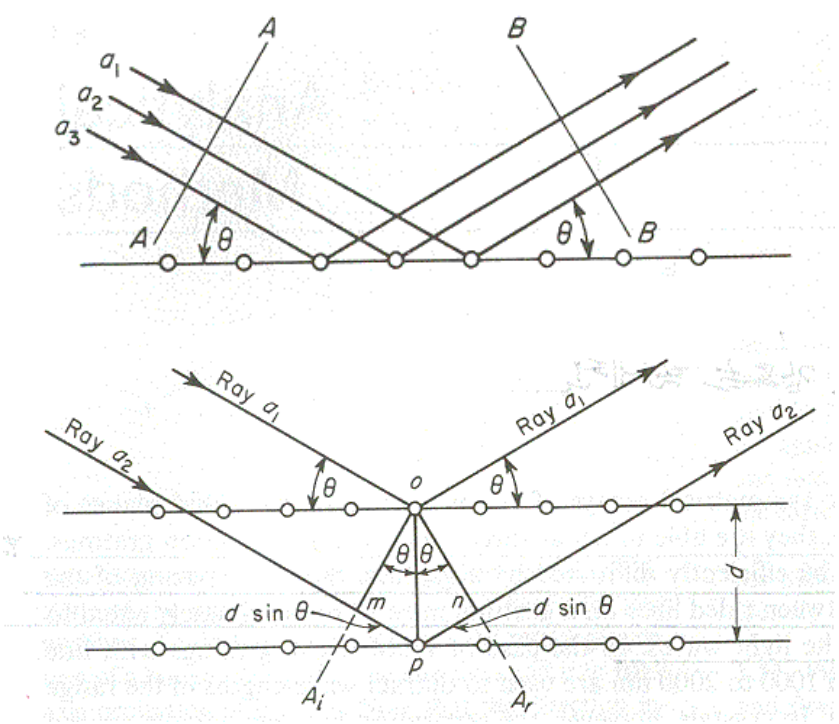
X-Ray Method

- Topography:
  The lattice distortion can give various diffraction conditions.
  A photographic recording of the transmitted radiation reveals the portion of defects.

- Compton Scattering:
  Incoherent scattering

- **EXAFS (Extended X-Ray Absorption Fine Spectroscopy)**:
  Measurements of the absorption coefficient as a function of incident x-ray energy show atomic structures due to diffraction of the ejected electron by neighboring atoms.

Diffraction: Bragg's Law



Constructive and destructive interferences

Bragg's Law

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

where n = 1, 2, 3…

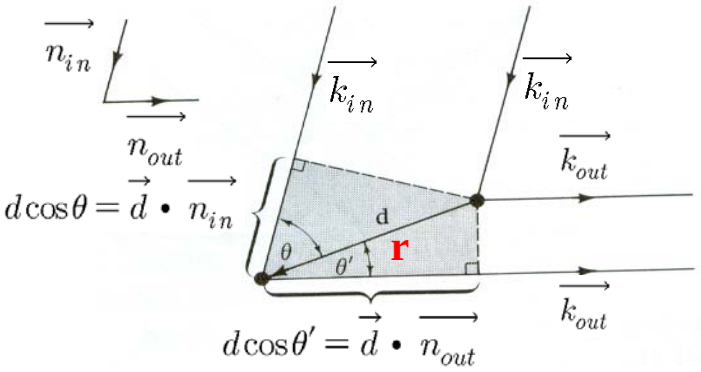
λ = wavelength

θ = scattering angle

General Theory of Diffraction

$$d\cos\theta + d\cos\theta' = \vec{d} \cdot (\overrightarrow{n_{in}} - \overrightarrow{n_{out}})$$

Path difference: *n* is unit vector.



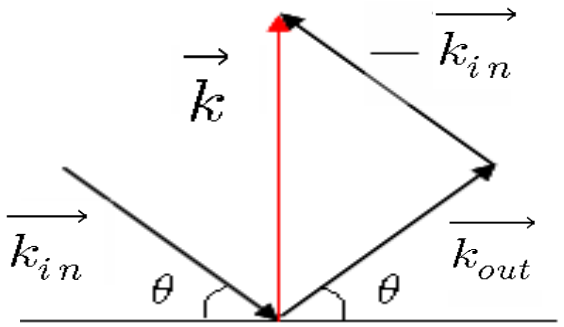
$\vec{k}$ **Reciprocal Lattice**

Reciprocal Space

***k* Space**

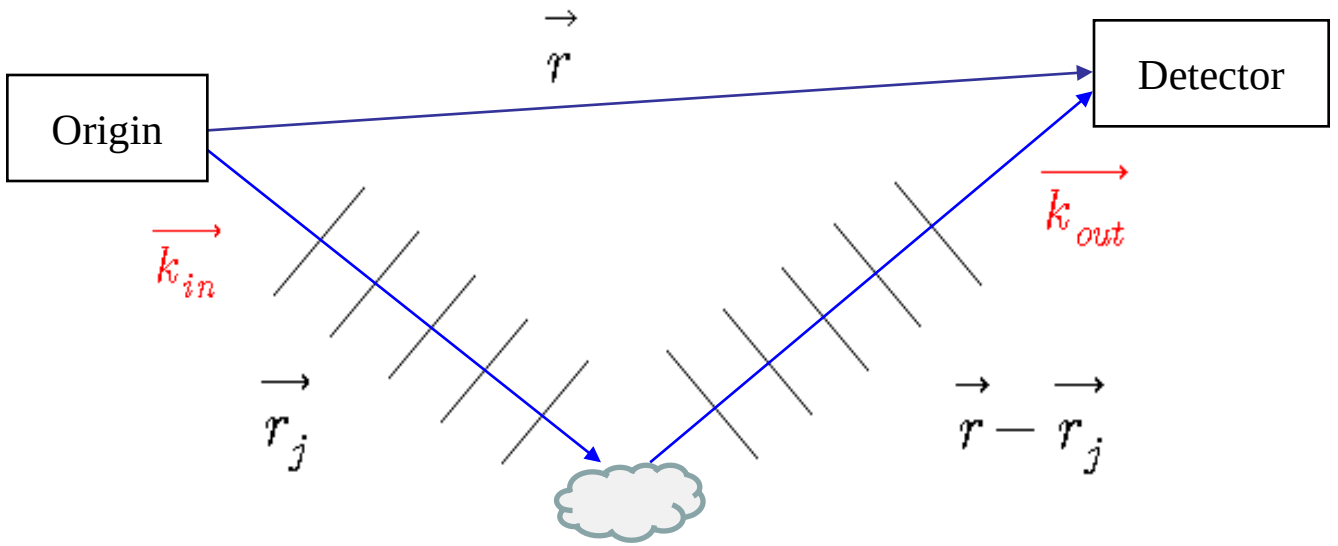
Scattering Vector

With $\vec{k} = \overrightarrow{k_{out}} - \overrightarrow{k_{in}}$ and $|\vec{k}| = |\overrightarrow{k_{in}}| = |\overrightarrow{k_{out}}| = \frac{2\pi}{\lambda}$



Constructive Interference

• Assumption: Incoming plane wave + Scattered plane wave.



$\vec{k}_{in}$: incident plane wave vector

$\vec{k}_{out}$: scattered plane wave vector

$$|\vec{k}_{in}| = |\vec{k}_{out}| = \frac{2\pi}{\lambda}$$

$\Psi(\vec{r}) = Ae^{i\vec{k}_{in} \cdot \vec{r}}$: incident plane wave function

Constructive Interference

- Scattered wave function (if there are N atoms in r_j position)

$$\Psi_{sc} = \sum^{N} A e^{i\overrightarrow{k_{in}} \cdot \vec{r}_j} f_i(\theta) e^{i\overrightarrow{k_{out}} \cdot (\vec{r} - \vec{r}_j)}$$

$f_j(\theta)$: Atomic form factor

$$\Psi_{sc} = A e^{i\overrightarrow{k_{out}} \cdot \vec{r}} \sum_{j=1}^{N} f_j(\theta) e^{-i\vec{r}_j \cdot (\overrightarrow{k_{out}} - \overrightarrow{k_{in}})}$$

$$\Psi_{sc} = \sum_{j=1}^{N} f_j(\theta) e^{-i\vec{r}_j \cdot (\overrightarrow{k_{out}} - \overrightarrow{k_{in}})}$$

Fourier Transform
=
Diffraction

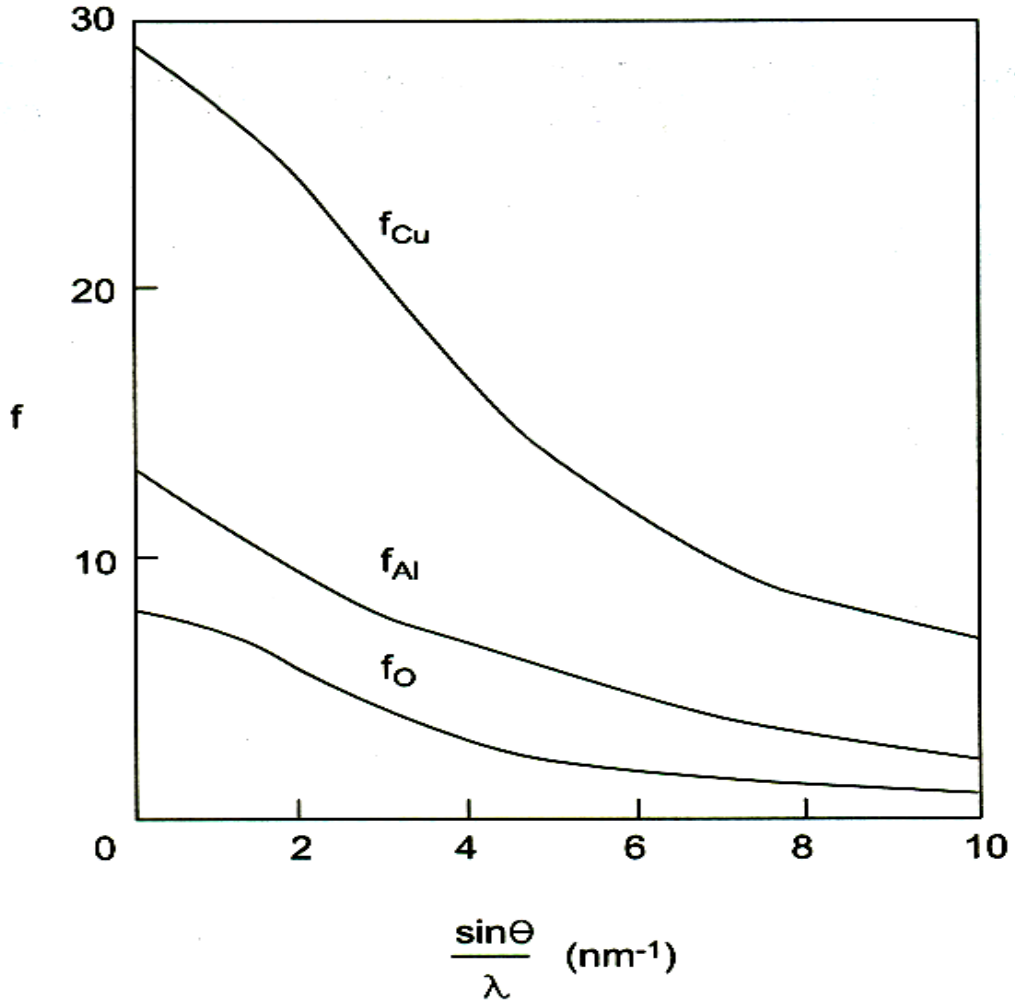
$\vec{k} = \overrightarrow{k_{out}} - \overrightarrow{k_{in}}$: Reciprocal wave vector (diffraction condition)

$$\longrightarrow \quad \boxed{\Psi_{sc} = \sum_{j=1}^{N} f_j(\theta) e^{-i\vec{r}_j \cdot \vec{k}}}$$

Atomic Form Factor

<Atomic form factor>

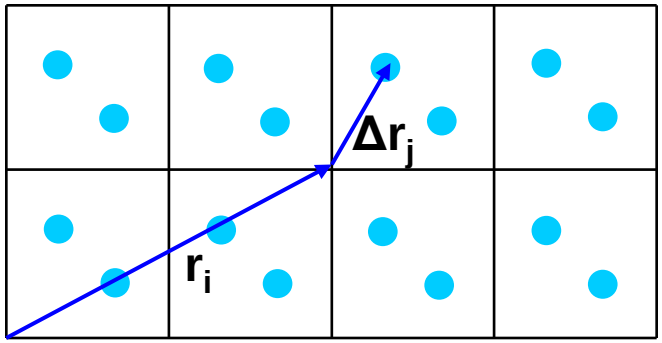
$f(\theta)$ = Amplitude scattered by an atom / Amplitude scattered by a single electron



Structure Factor

<Structure factor>

F_{hkl} = Amplitude scattered by a unit cell / Amplitude scattered by a single electron



$$\vec{r} = \vec{r_i} + \Delta\vec{r_j}$$

$$\vec{r_i} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

$$\Delta\vec{r_j} = x_j\vec{a} + y_j\vec{b} + z_j\vec{c}$$

$$\psi_{sc} = \sum_{j=1}^{N} \sum_{n_1,n_2,n_3}^{\infty} f_i(\theta) e^{-2\pi i \vec{K}\cdot(\vec{r_i}+\Delta\vec{r_j})}$$

$$= \left(\sum_{j=1}^{N} f_i(\theta) e^{-2\pi i \vec{K}\cdot\Delta\vec{r_j}} \right) \times \left(\sum_{n_1,n_2,n_3}^{\infty} e^{-2\pi i \vec{K}\cdot\vec{r_i}} \right)$$

Atomic form factor

Structure factor (= F_{hkl})

Assumption: $\overrightarrow{k_{in}} = \frac{1}{\lambda}$

Sorry for the different definition of k_{in} ($2\pi/\lambda$ or $1/\lambda$) on page 30.

Fourier Transform and Diffraction

- Recall Kinematical electron diffraction

$$\Psi_{sc} = \sum_{j=1}^{N} f_j(\theta) e^{-2\pi i \vec{K}\cdot\vec{r}_j}$$ → The formula is a Fourier series.

Fourier Transformation of f(r) → F {f(r)} = F(K) = $\int_{-\infty}^{\infty} f(r)\, e^{-2\pi i K r}\, dr$

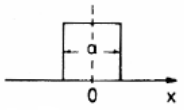
The diffraction amplitude is the Fourier transform of a real lattice.

✓ Special Example

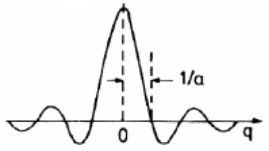
1 a) One-dimensional slit

$$f_1(x) = \begin{cases} 1 & \text{if } |x| < a/2 \\ 0 & \text{if } |x| > a/2 \end{cases}$$

$$F_1(q) = a\frac{\sin \pi a q}{\pi a q}$$



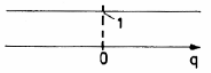
Transformation



1 b) Point source ($a \to 0$)

one-	two-dimensional
$f_1(x) = \delta(x)$	$f_1(\boldsymbol{r}) = \delta(\boldsymbol{r})$
$\int \delta(x)\mathrm{d}x = 1$	$\int\int \delta(\boldsymbol{r})\mathrm{d}^2\boldsymbol{r} = 1$

$F_1(q) = 1$ (isotropic scattering)



Assumption: $\overrightarrow{k_{in}} = \frac{1}{\lambda}$

Sorry for the different definition of k_{in} ($2\pi/\lambda$ or $1/\lambda$) on page 31.

Convolution

- At the infinite point condition

11) Infinite point row $N \to \infty$

$$f_{11} = \sum_{n=-\infty}^{+\infty} \delta(x - nd) \qquad F_{11}(q) = \sum_{n=-\infty}^{+\infty} \delta\left(q - \frac{n}{d}\right)$$

12) Infinite periodic function

$$f_{12}(x) = f_{11}(x) \otimes f_1(x) \qquad F_{11}(q) = F_{12}(q) \cdot F_1(q) = \sum_{n=-\infty}^{+\infty} F_1(q_n)\delta(q - q_n)$$

Assumption: $\overrightarrow{k_{in}} = \frac{1}{\lambda}$

Sorry for the different definition of k_{in} ($2\pi/\lambda$ or $1/\lambda$) on page 32.

Convolution

- Convolution Theorem

$$C(x) = \int_{-\infty}^{+\infty} f(\xi) g(x-\xi) d\xi = f(x) \otimes g(x)$$

$$F\{f \otimes g\} = F(k) \cdot G(k)$$

$$F\{f \cdot g\} = F(k) \otimes G(k)$$

1 a) One-dimensional slit

$$f_1(x) = \begin{cases} 1 & \text{if } |x| < a/2 \\ 0 & \text{if } |x| > a/2 \end{cases}$$

$$F_1(q) = a \frac{\sin \pi a q}{\pi a q}$$

7) One-dimensional point lattice

$$f_7(x) = \sum_{n=1}^{N} \delta(x - x_n)$$

$$F_7(q) = \frac{\sin \pi q N d}{\sin \pi q d}$$

- Convolution Atomic Form Factor $f_1(x)$ ⊗ Point array $f_7(x)$

8) N slits of width a

$$f_8(x) = f_1(x) \otimes f_7(x)$$

$$F_8(q) = F_1(q) \cdot F_7(q) = a \frac{\sin \pi a q}{\pi a q} \frac{\sin \pi q N d}{\sin \pi q d}$$

Assumption: $\overrightarrow{k_{in}} = \frac{1}{\lambda}$

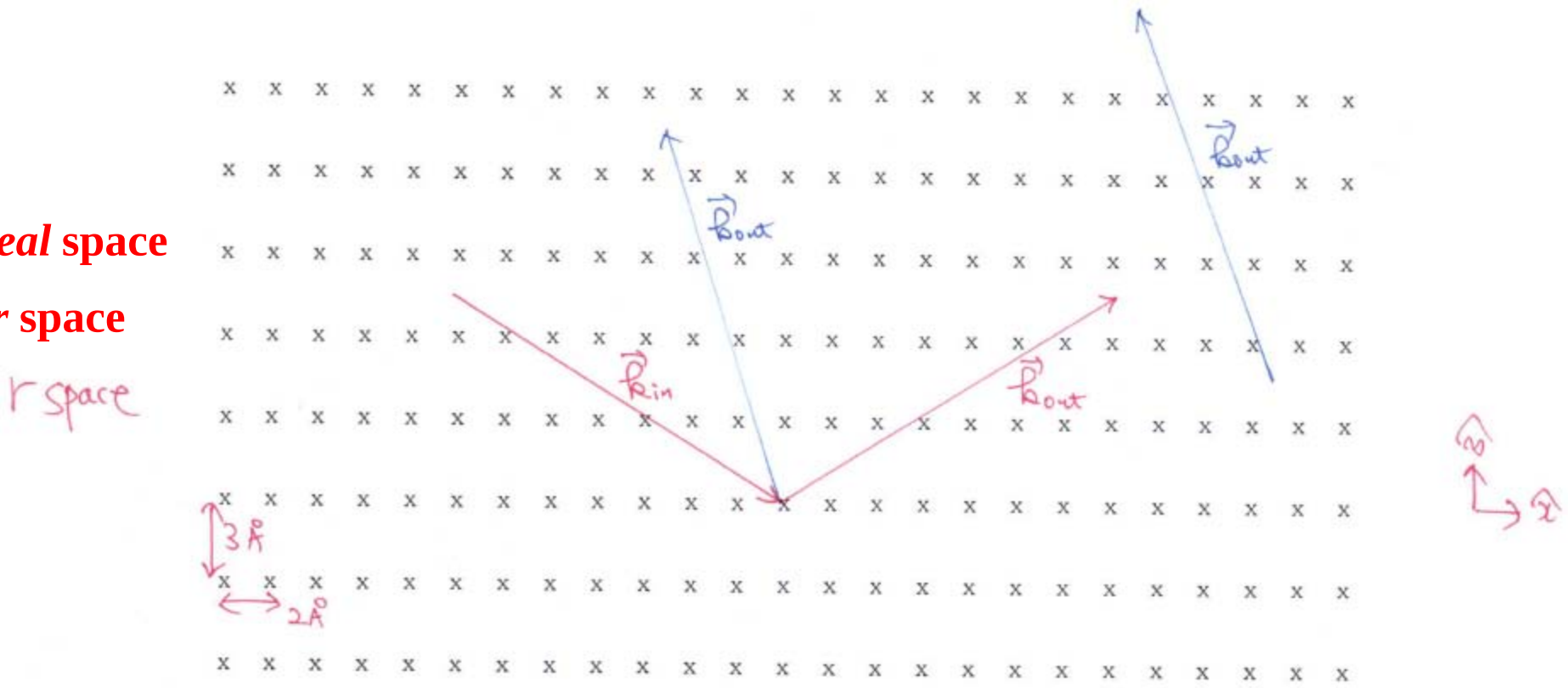
Sorry for the different definition of k_{in} ($2\pi/\lambda$ or $1/\lambda$) on page 33.

- 2010-10-18

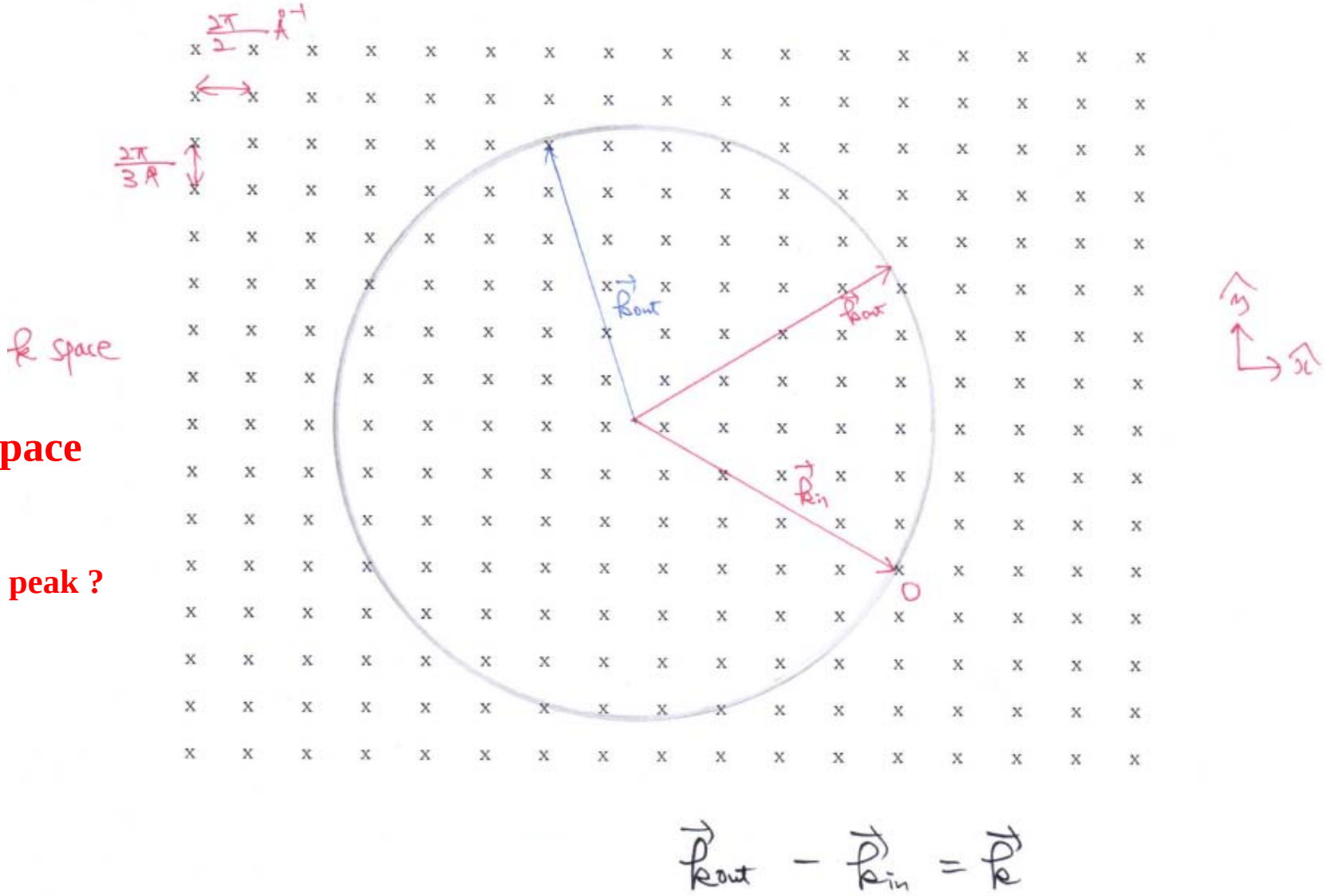
Real Space

***real* space**

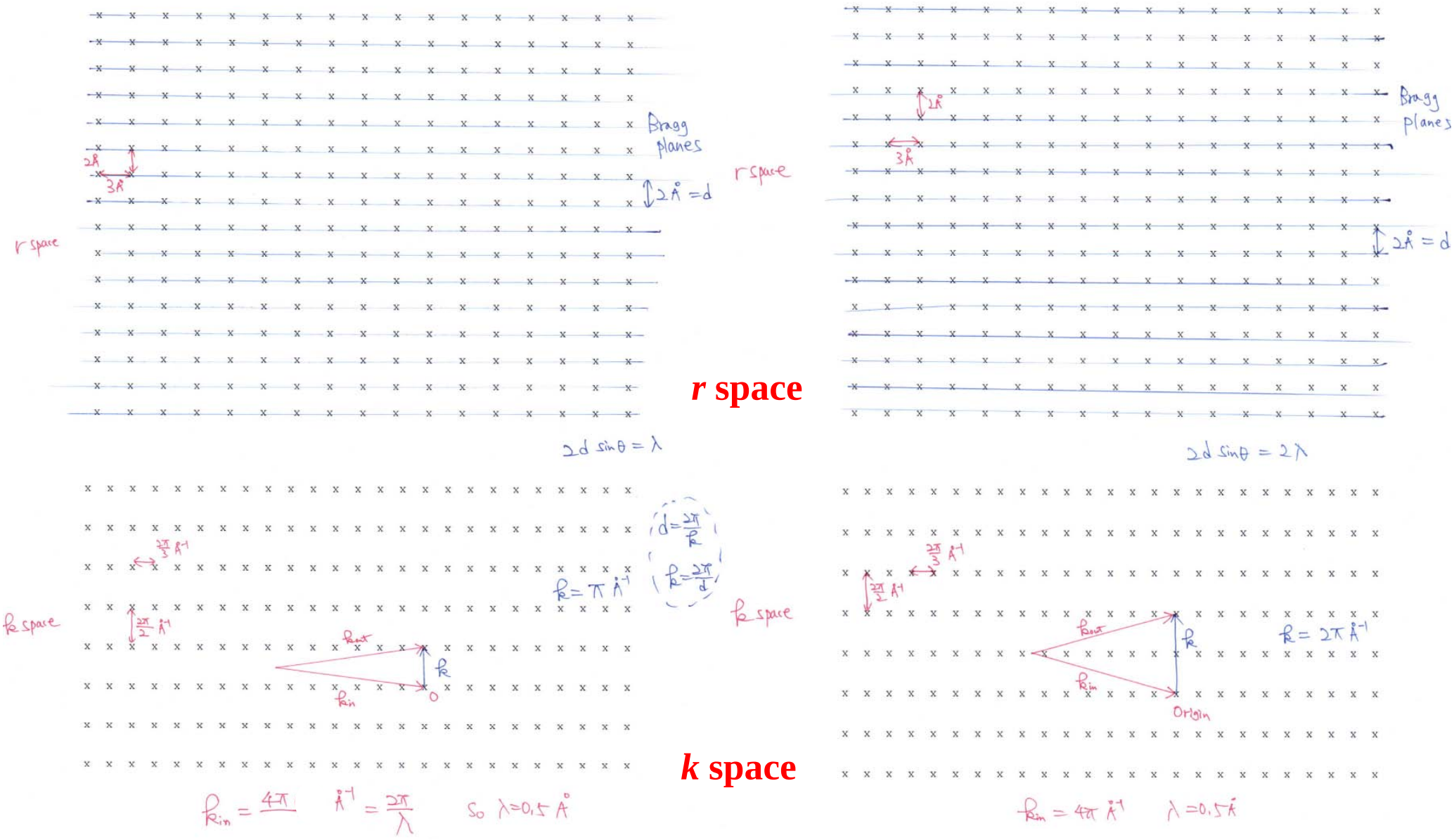
***r* space**



Ewald Sphere



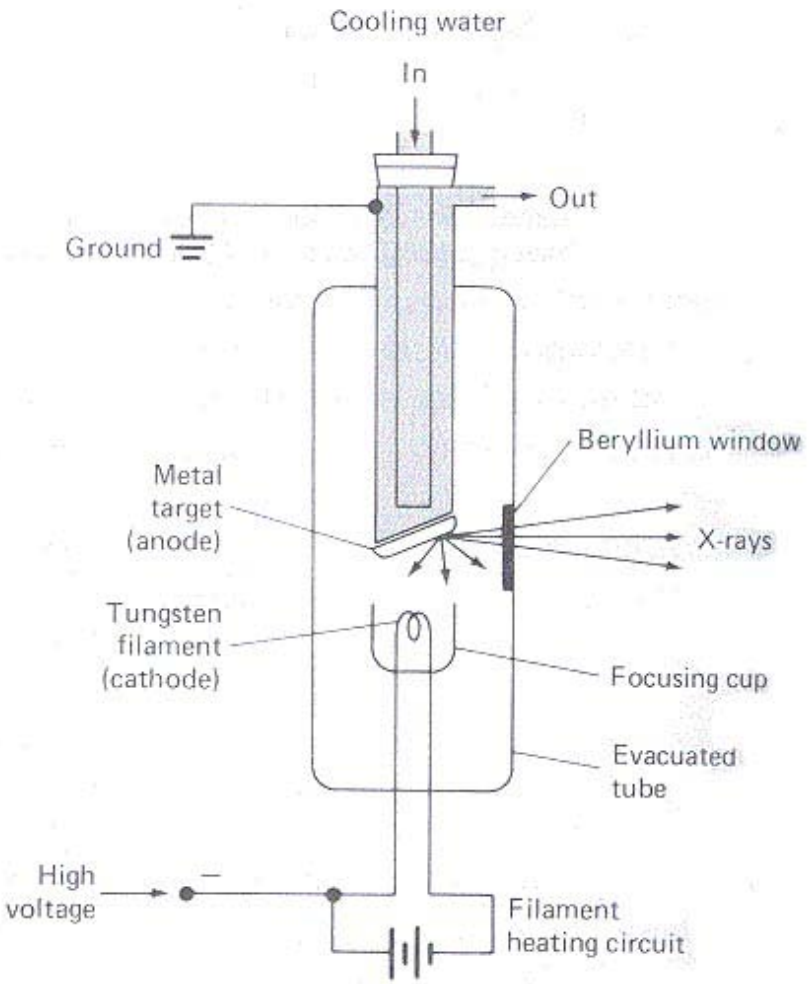
Laue Condition



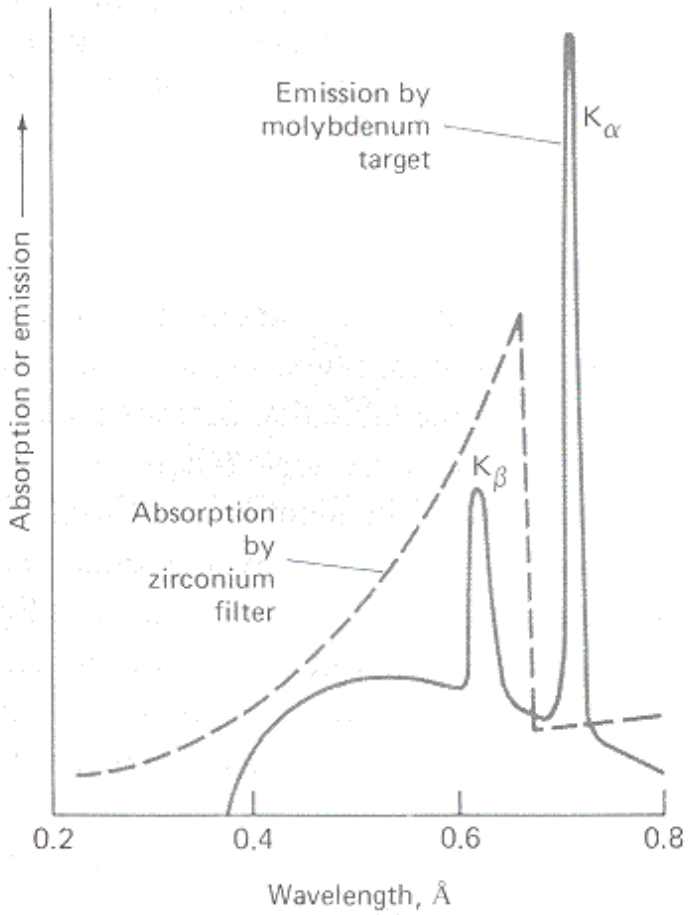
***r* space**

***k* space**

X-Ray Source

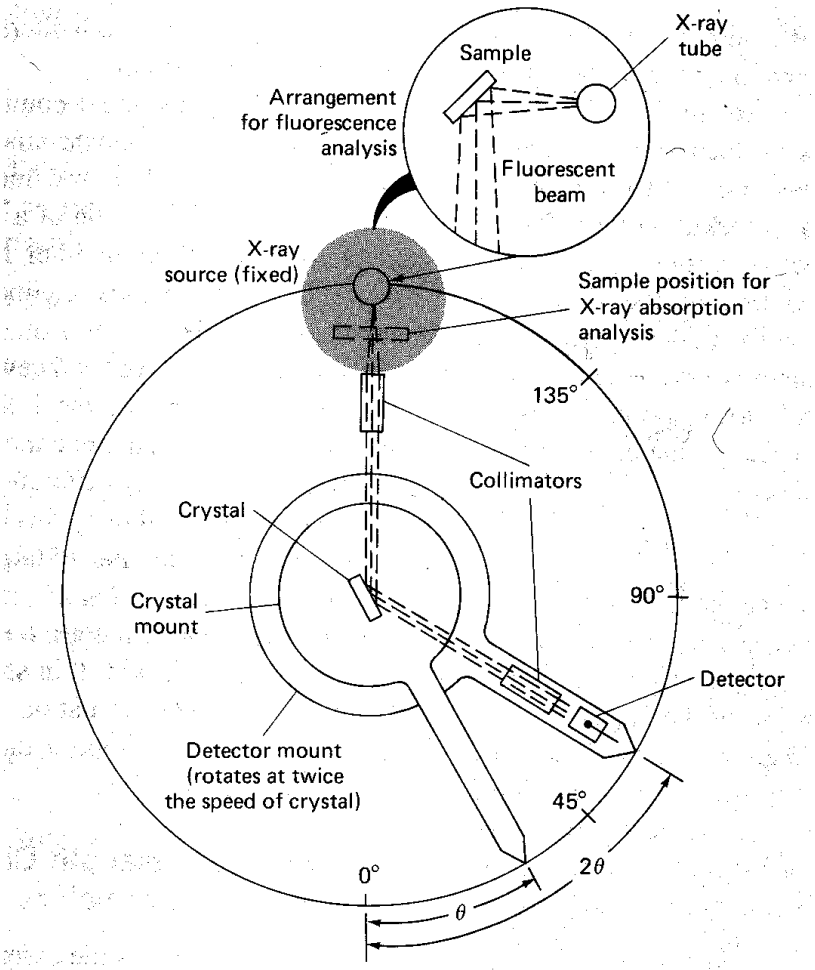


Schematic of an x-ray tube



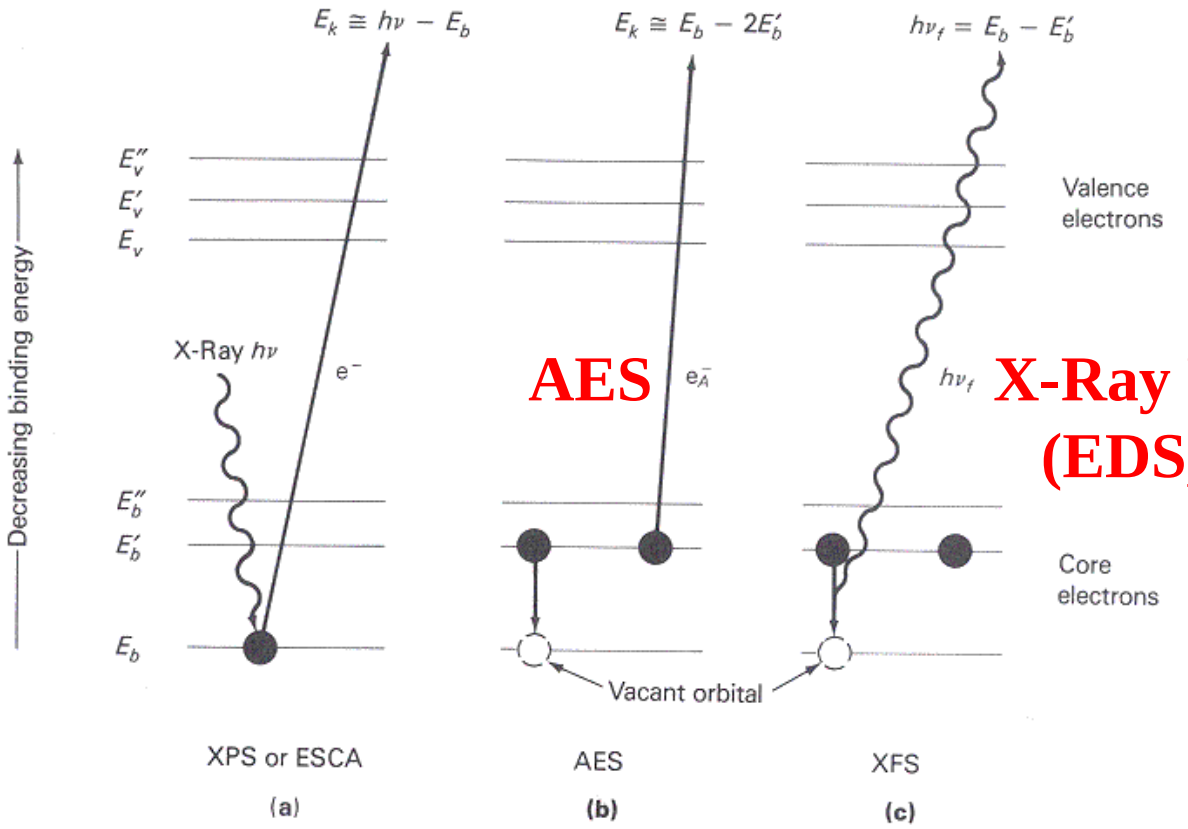
Filter to produce monochromatic radiation

θ-2θ Diffraction



An x-ray monochromator and detector. Note that the angle of the detector with respect to the beam (2θ) is twice that of the crystal face.

Principles of Electron Spectroscopy



AES

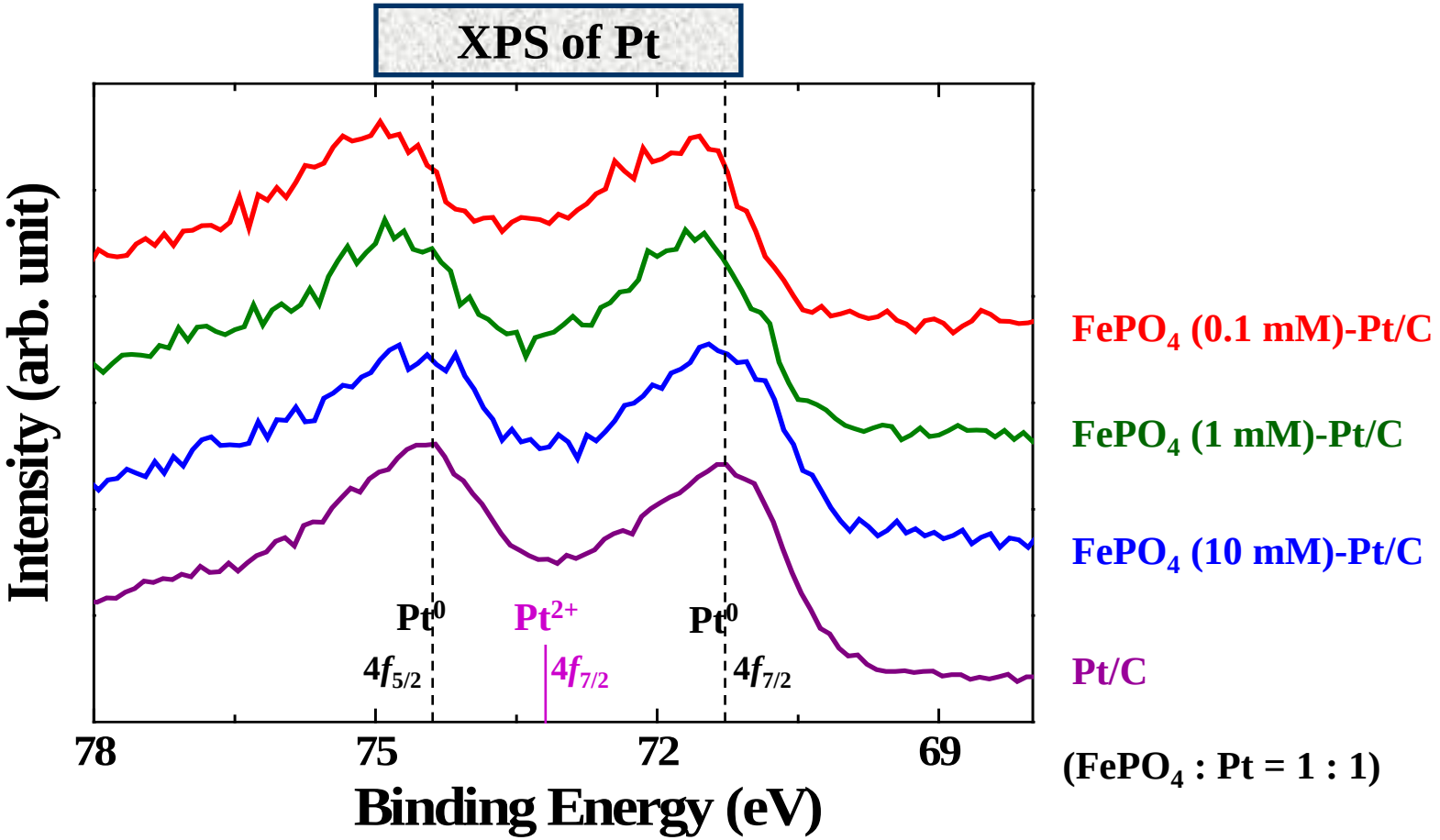
X-Ray Fluorescence (EDS, EPMA)

XPS, ESCA

The first two electron spectroscopes require the measurement of the emitted electron E_k.

The third (competing with AES) requires the energy measurement of the emitted x-ray photon.

X-Ray Photoelectron Spectroscopy

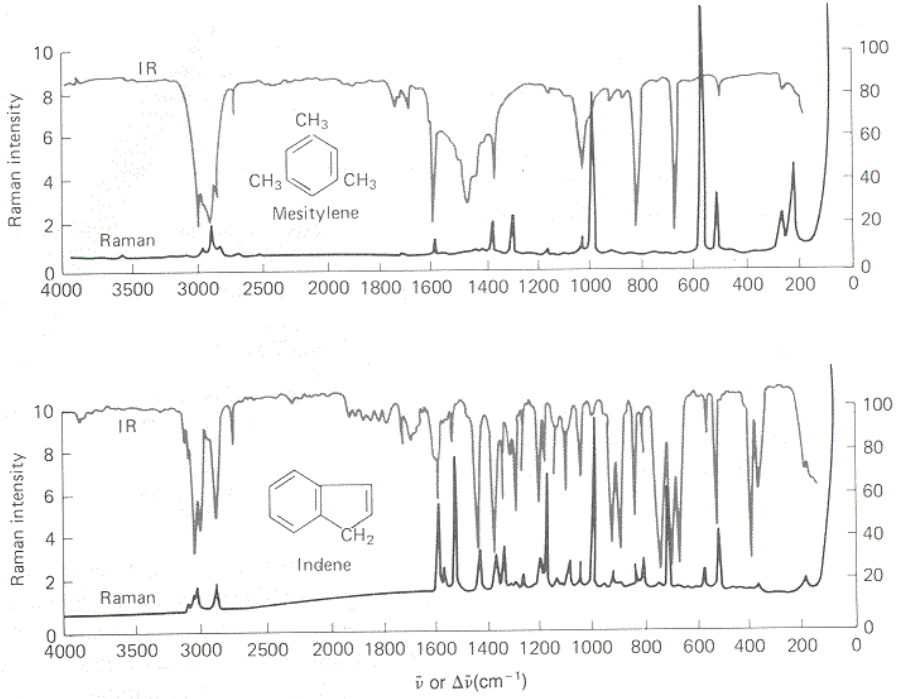


Slight Peak Shift of Pt in $FePO_4$-Pt/C Nanocomposites

- **Zero-Valent Metallic Pt Phase**
- **Charge Transfer of Pt**
- **The Largest Interfacial Contacts in $FePO_4$ (0.1 mM)-Pt/C**

Raman Spectroscopy

- Quantized vibrational changes are associated with infrared absorption.
- The difference in wavelength between the incident and scattered radiation corresponds to wavelengths in the mid-infrared region.
- Enough differences between the kinds of groups that are infrared active and those that are Raman active to make the techniques complementary rather than competitive.



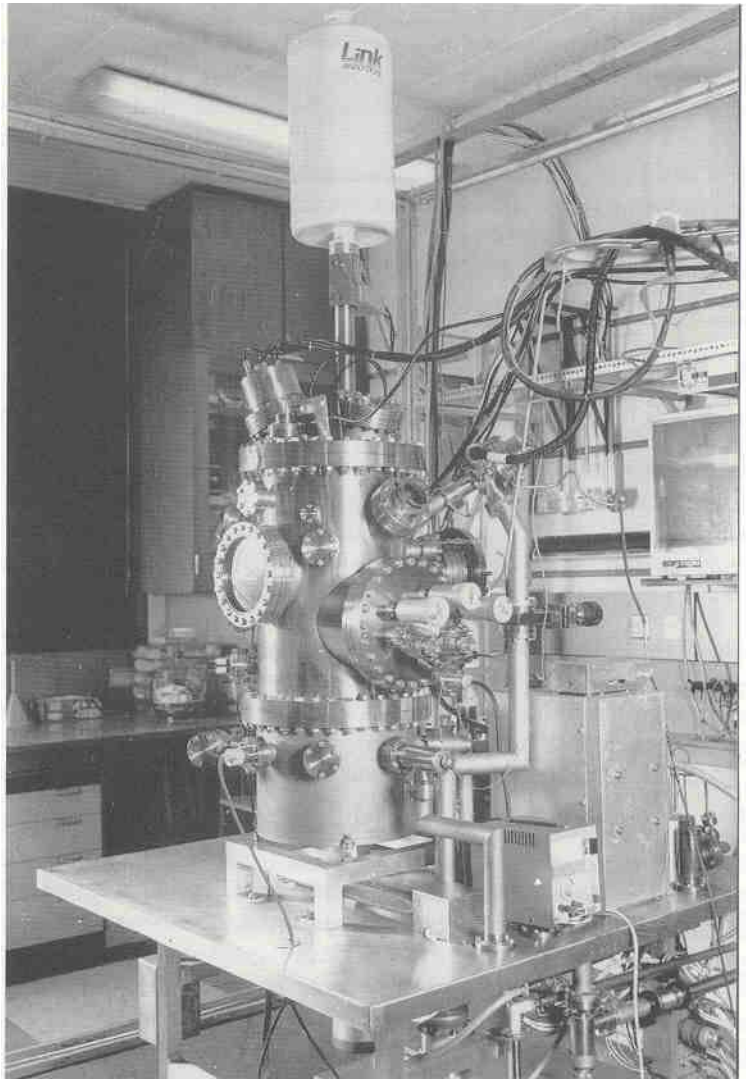
Comparison between

Raman and FTIR

Fourier Transform Infrared Absorption Spectroscopy (FTIR)

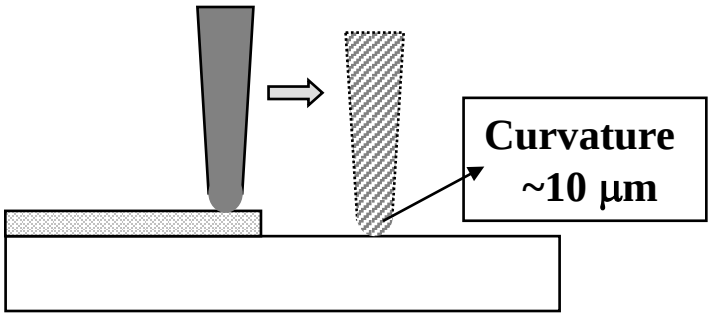
- Resolution: 0.026 cm^{-1}
- Spectral range: 5 - 4500 cm^{-1}
- IR source:
  - Mercury (원적외선)
  - Globar (중적외선)
  - Quarts-Halogen (근적외선 및 가시광선)
- Detector:
  - MCT detector (450 - 4500 cm^{-1}) : operating at 77 K
  - DTGS detector (350 - 7000 cm^{-1}) : operating at R.T.
  - Si:B detector (450 - 4500 cm^{-1})
  - Si Bolometer detector (50 - 380 cm^{-1})
  - Pumped Si Bolometer detector (5 - 100 cm^{-1})

Multi-Technique UHV System



A multi-technique UHV system in use for surface studies and microscopy, backscattered electron detection, ion bombardment, and characteristic x-ray detection. The apparatus is surrounded by a cube of coil pairs designed to cancel out the earth's magnetic field in the region of sample and detectors around it.

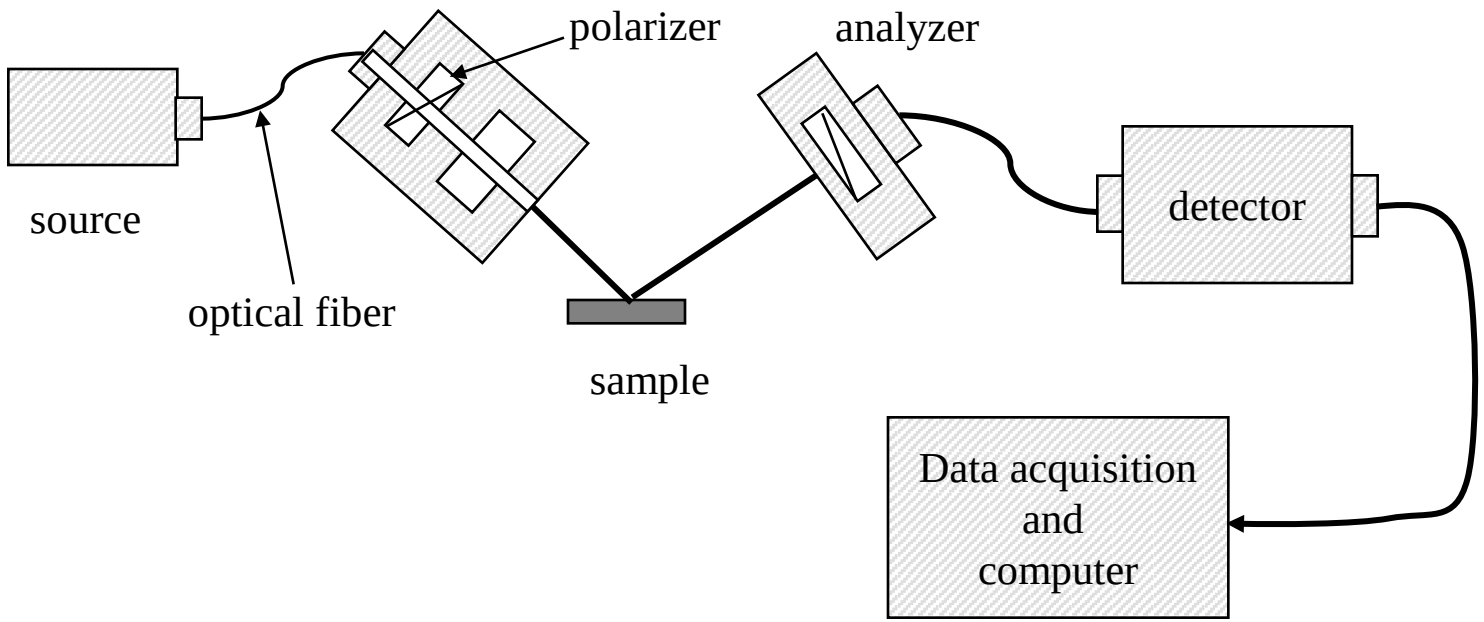
α-step (Thickness Measurement)



- Detection limit: ~1 nm
- Methods of Step Generation
  - chemical etching
  - mask
- Measurements:
  - step heights
  - etch depths
  - coating thickness
- Problems:
  - substrate roughness
  - film softness

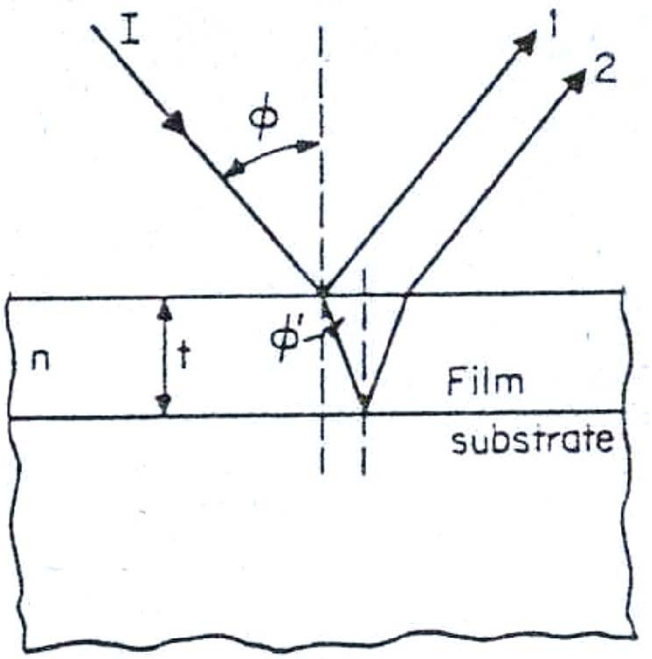
Ellipsometry (Thickness Measurement)

- Using the change of polarization and amplitude (phase shift)



Color Chart (Thickness Measurement)

Color	SiO2 Thickness (A)	Si3N4 (A)
Silver	270	200
Brown	530	400
Yellow-brown	730	550
Red	970	730
Deep blue	1000	770
Blue	1200	930
Pale blue	1300	1000
Very Pale blue	1500	1100
Silver	1600	1200
Light yellow	1700	1300
Yellow	2000	1500
Orange-red	2400	1800
Red	2500	1900
Dark Red	2800	2100
Blue	3100	2300
Blue-green	3300	2500
Light green	3700	2800
Orange-yellow	4000	3000
Red	4400	3300

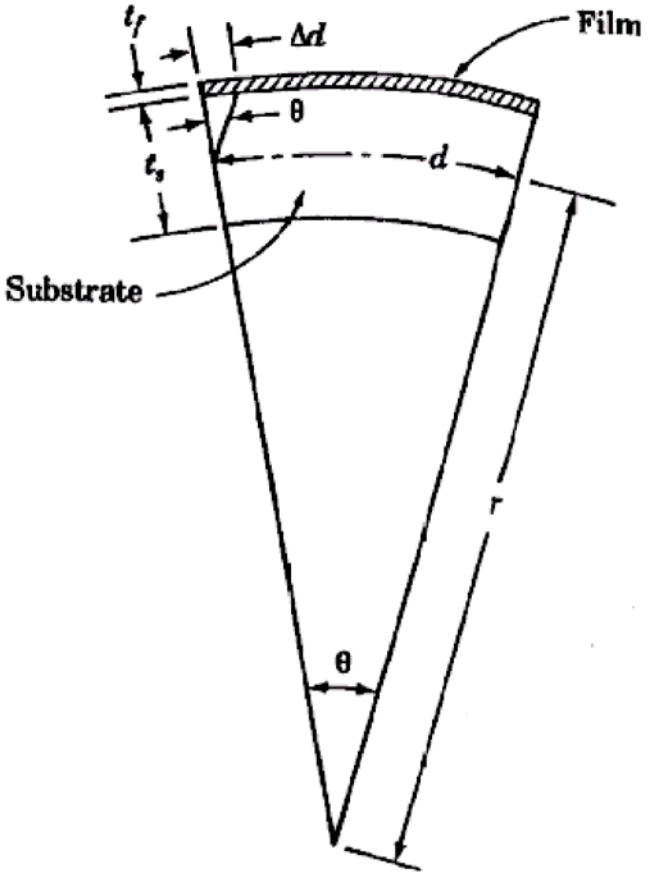


Color chart for thermal dioxide (refractive index of 1.48) and silicon nitride (1.97)

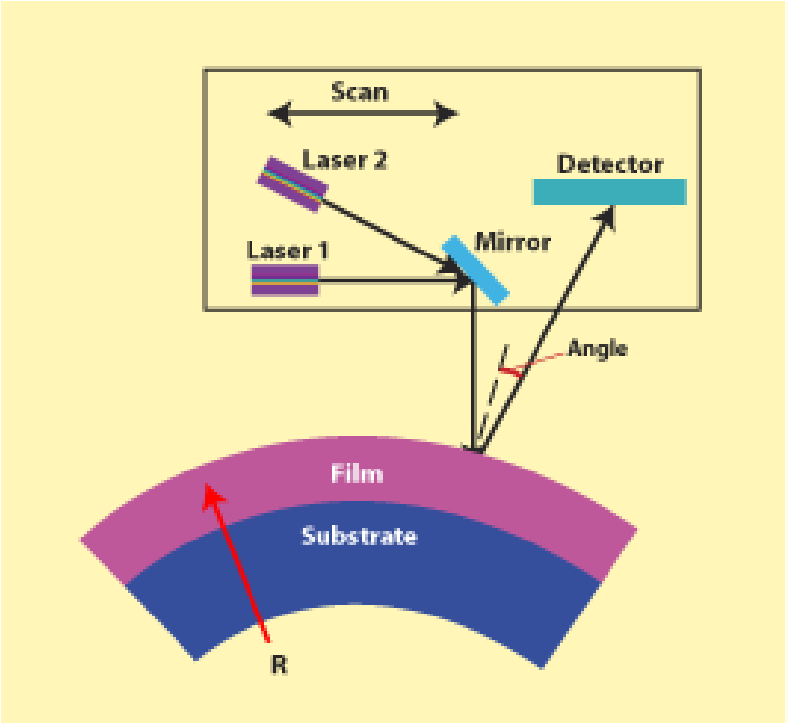
From Stephen A. Campell, The Science and Engineering of Microelectronic Fabrication, Oxford University Press, 1996

Film Stress

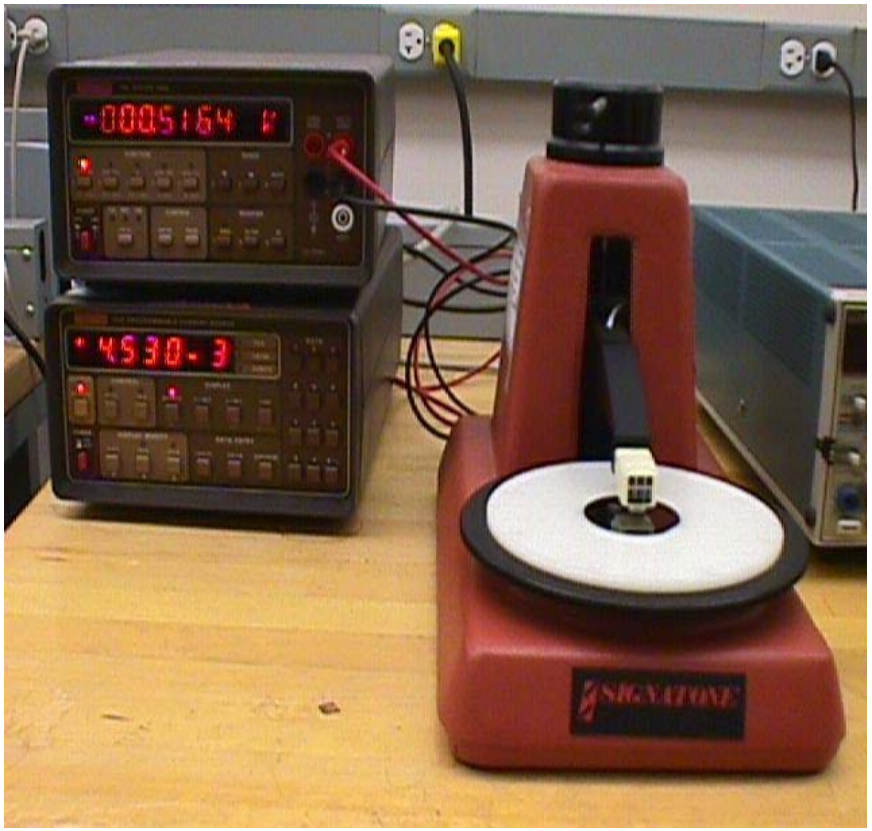
❖ Deflected Substrate & Film

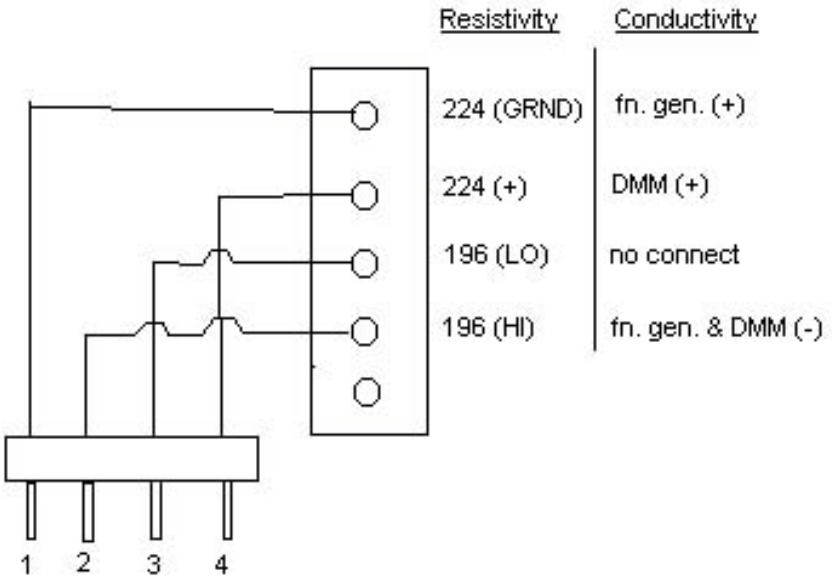


❖ Laser Scanning Measurement



4 Point Probe (Conductivity Measurement)





The four point probe consists of two current-carrying probes (outside), and two voltage-measuring probes (inside)

Resistivity Measurement by 4-Point Probe

4-point probe manual,
Robert A. Weller (2001)

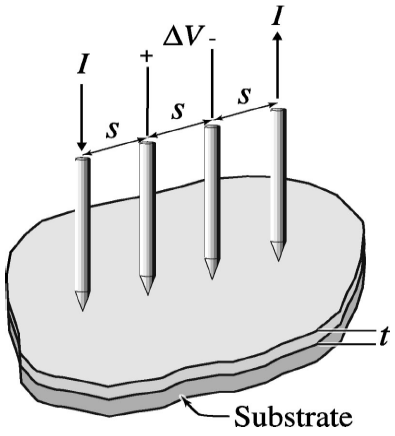


FIG. 1. Schematic of the linear four-point probe geometry for measuring the resistivity of a uniform film with thickness t on a substrate that may be either an insulator or conductor.

$$F_1 = \frac{t/s}{2\ln\{[\sinh(t/s)]/[\sinh(t/2s)]\}} = \frac{t/s}{2\ln(2)}$$

(t ≤ s/2 인 경우, t < 400 μm 인 경우)

$$\rho = 4.532 t \frac{V}{I} F_2$$

4-point probe 장비로 측정할 수 있는 Sheet resistance 값의 최대허용치는 $9.9\times10^{8}\,\Omega/\square$ 입니다.
(장비에서 읽을 수 있는 최대값)
따라서 thin film의 두께가 200 nm $(2\times10^{-5}\,\mathrm{cm})$ 일 경우 가능한 Resistivity 값은 $\rho \approx 1.0\times10^{4}\,\Omega\mathrm{cm}$ 이 최대치가 됩니다.

$$F_2 = \frac{\ln(2)}{\ln(2) + \ln\{[(D/2)^2 + 3]/[(D/s)^2 - 3]\}}$$

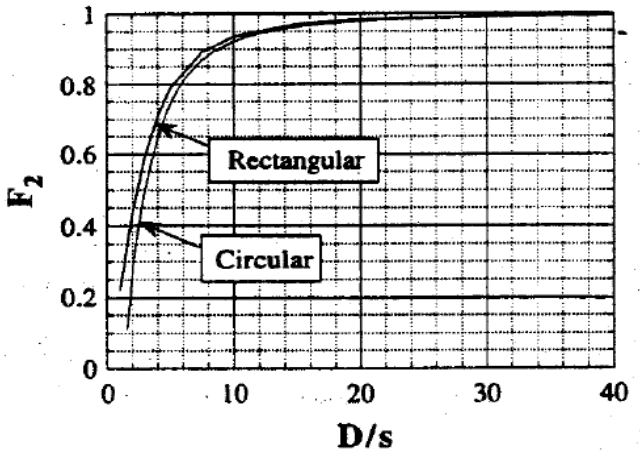
(sample 이 circle 일 때
→ D : sample 의 직경
sample 이 square 일 때
→ D : sample 한 변의 길이)

$$\rho = 2\pi s F\left(\frac{V}{I}\right)$$

ρ : resistivity
s : probe spacing (1 mm)
F : correction factor

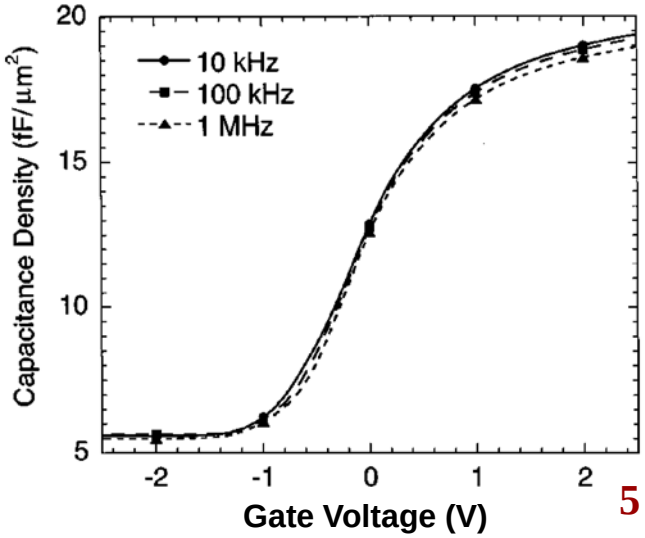
$$F = F_1 F_2 F_3$$

F_1 : sample thickness에 의한 factor
F_2 : sample size에 의한 factor
F_3 : temperature에 의한 factor
(room temperature에서 F_3 =1)

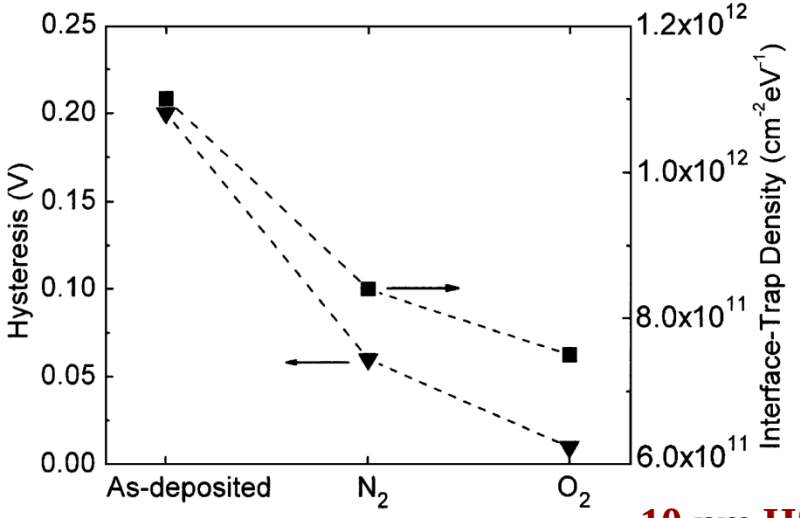


D/s	Circle	Square
3.0	2.2662	2.4575
4.0	2.9289	3.1127
5.0	3.3625	3.5098
7.5	3.9273	4.0095
10.0	4.1716	4.2209
15.0	4.3646	4.3882
20.0	4.4364	4.4516
32.0	4.4791	4.4878
40.0	4.5076	4.5120
infinity	4.5324	4.5324

Capacitance-Voltage Measurements

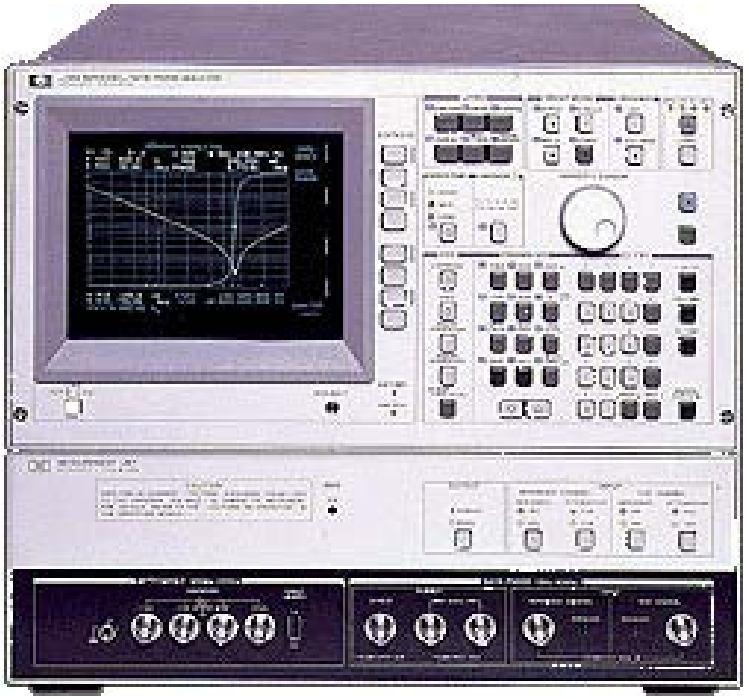


5 nm $HfSi_xO_y$ *APL* (1999)

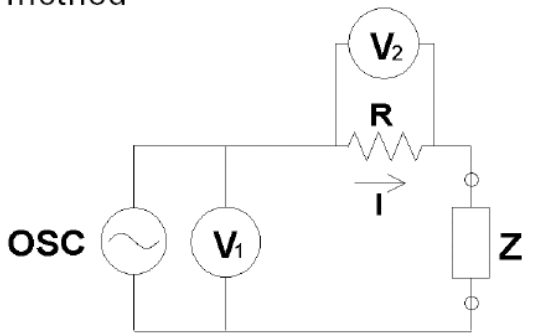


10 nm HfO_2 *APL* (2005)

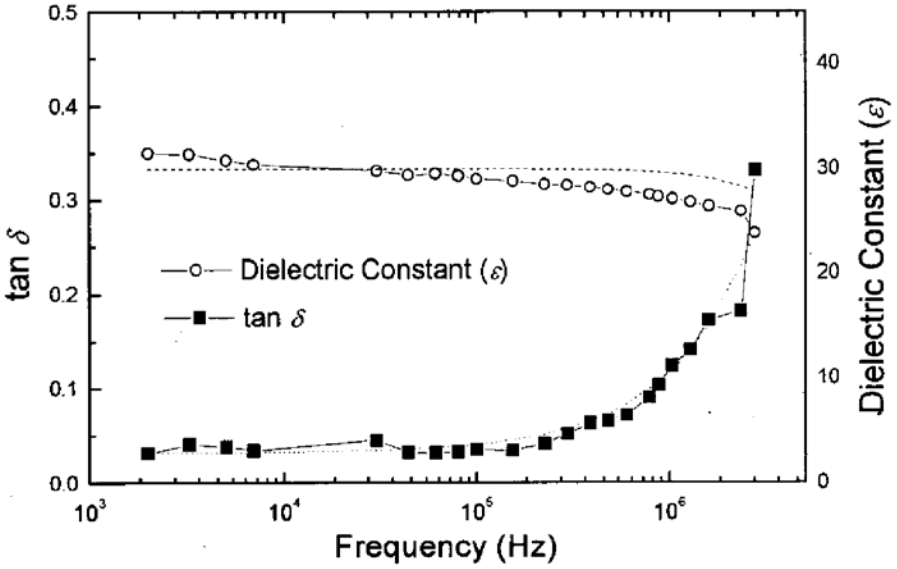
Impedance Analyzer



I-V method

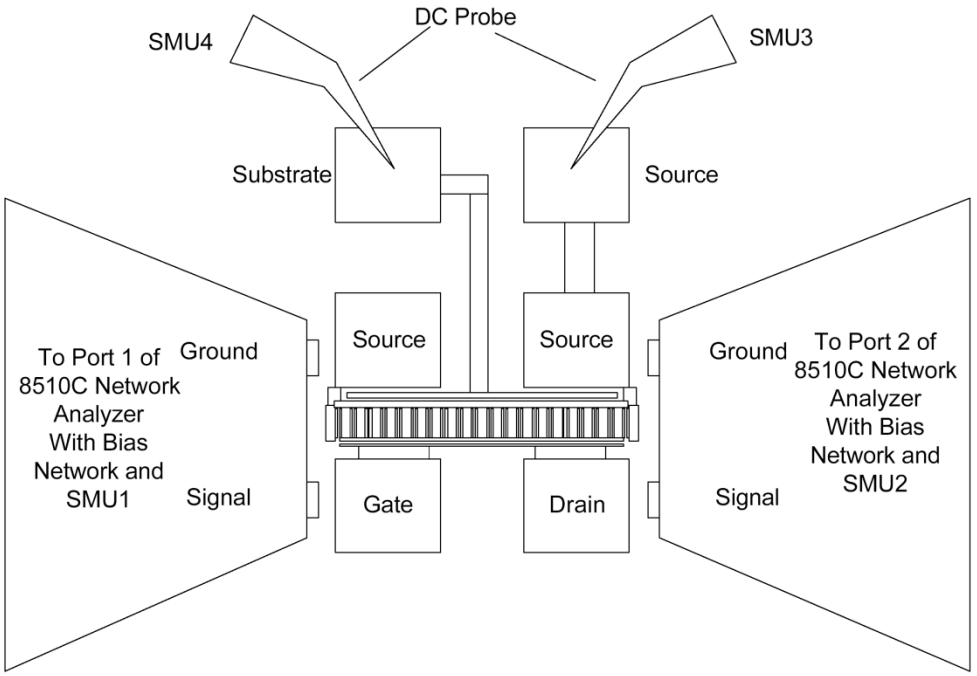


$$Z = \frac{V_1}{I} = \frac{V_1}{V_2} R$$

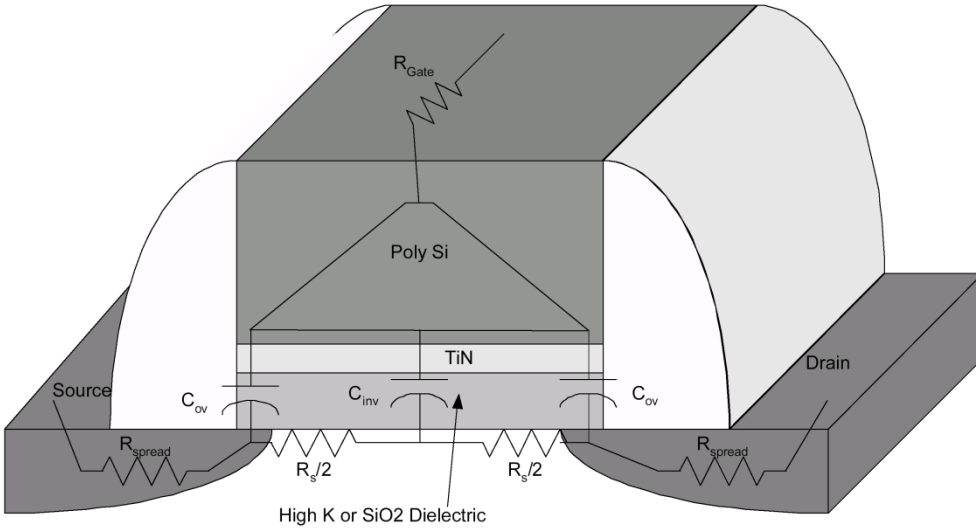


- *APL* (2000)

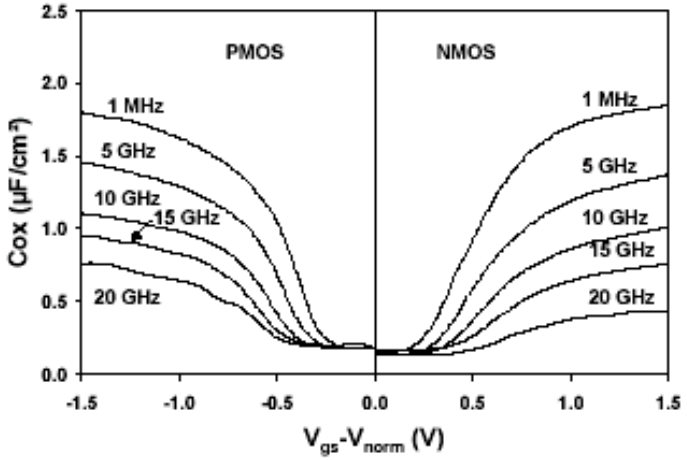
Network Analyzer

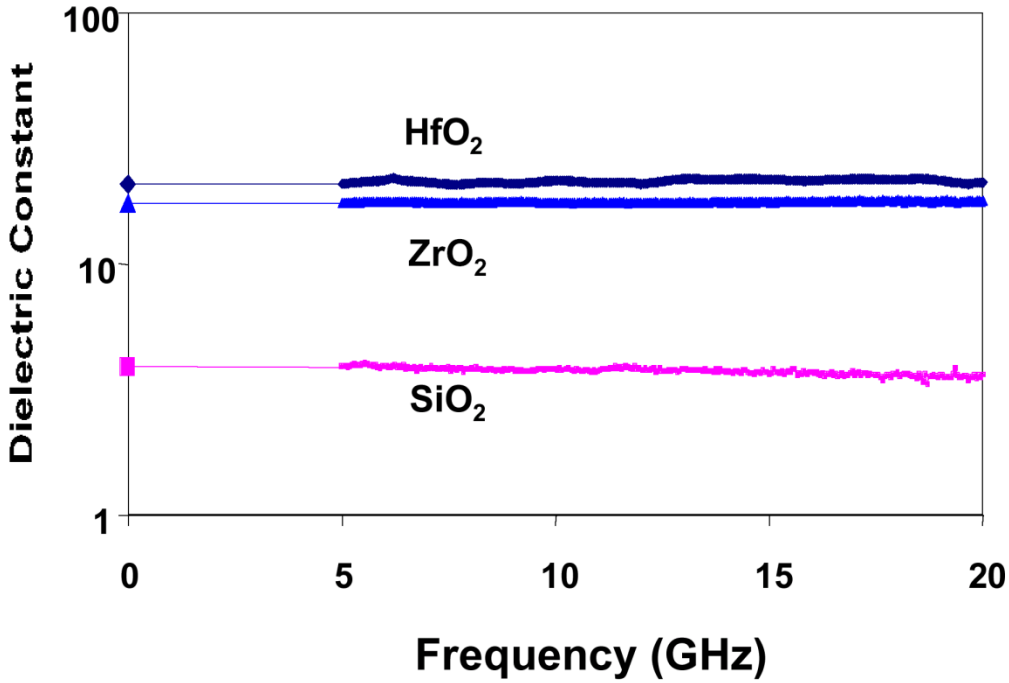


Network Analyzer



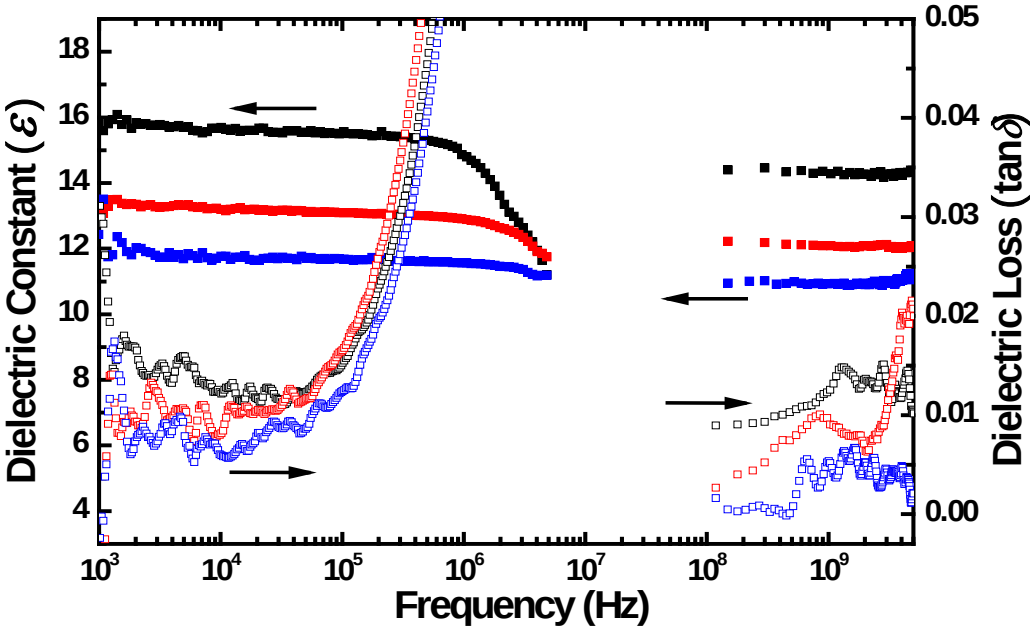
$R_{spread} < R_{gate} < R_s/2$

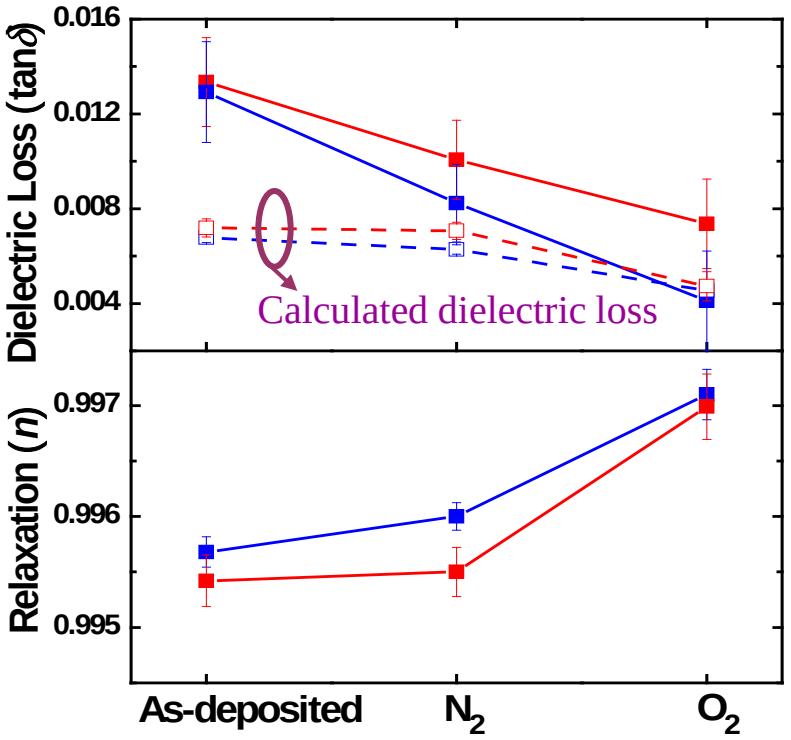




- Intel, *IEEE* (2001)

ALD HfO_2 Thin Film-Dielectric Relaxation

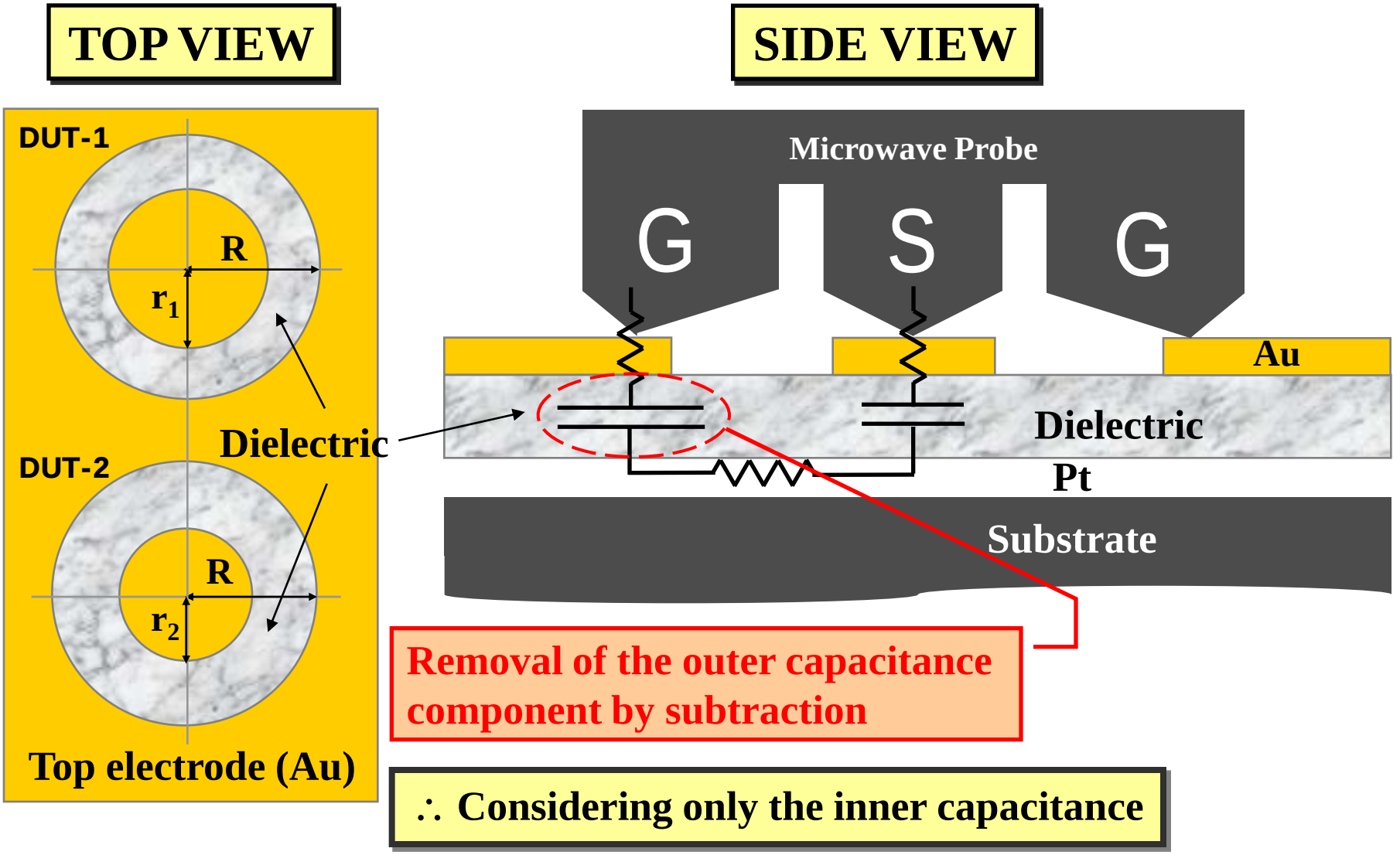




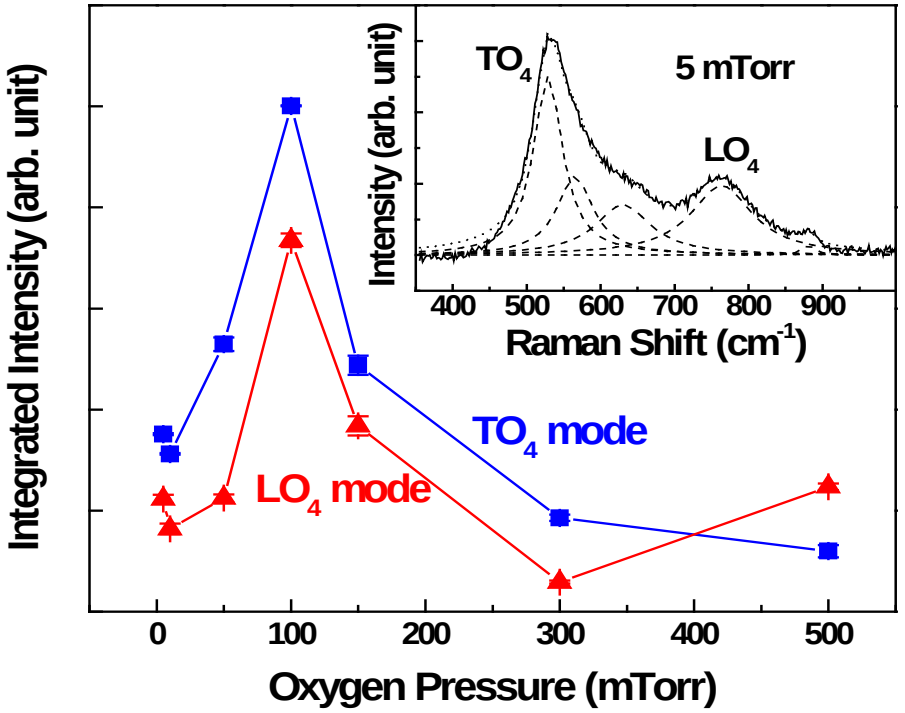
- Curie-von Schweidler relaxation from 1 kHz to 5 GHz.
- Dielectric relaxation depends on the annealing condition.
- Various defects in the HfO_2 layer and/or interface.

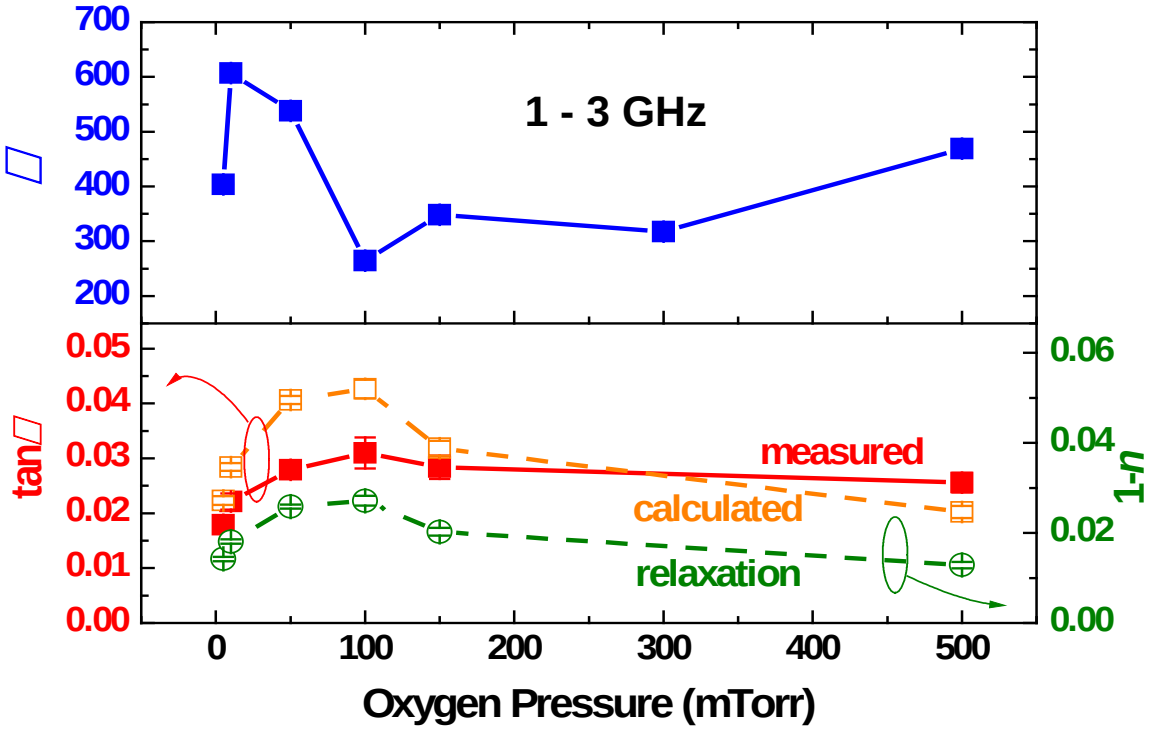
➢ B. Lee, T. Moon, T.-G. Kim, D.-K. Choi, and B. Park *Appl. Phys. Lett.* **87**, 012901 (2005).

Measurement Technique at GHz-Frequency Ranges



$(Ba,Sr)TiO_3$ Thin Film: Microwave Dielectric Relaxation





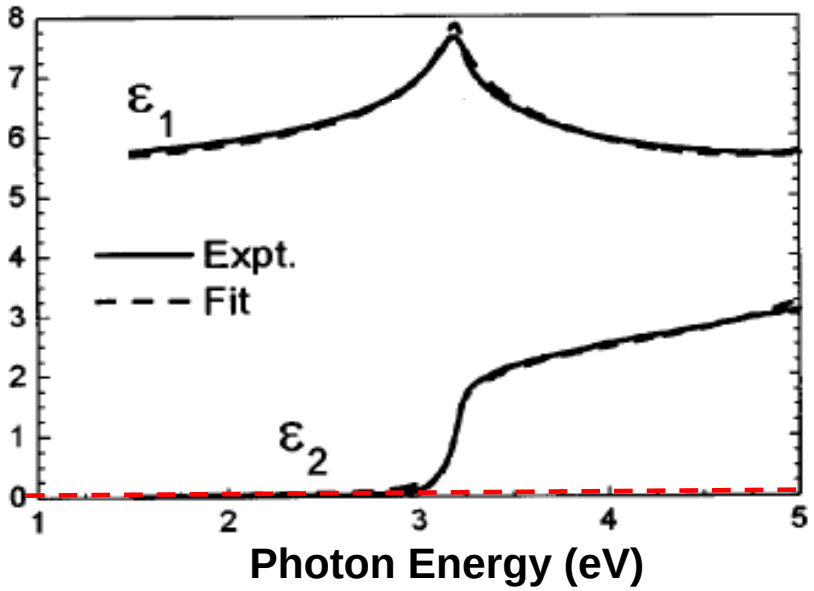
- Ferroelectric fluctuation
- Nanopolar reorientation
- Defect dipole related oxygen vacancy ($Vo^{\cdot\cdot}$)

➢ T. Moon, B. Lee, T.-G. Kim, J. Oh, Y. W. Noh, S. Nam, and B. Park *Appl. Phys. Lett.* **86**, 182904 (2005).

Dielectric Constant vs. Photon Energy

$$\varepsilon = \varepsilon_1 + i\varepsilon_2$$

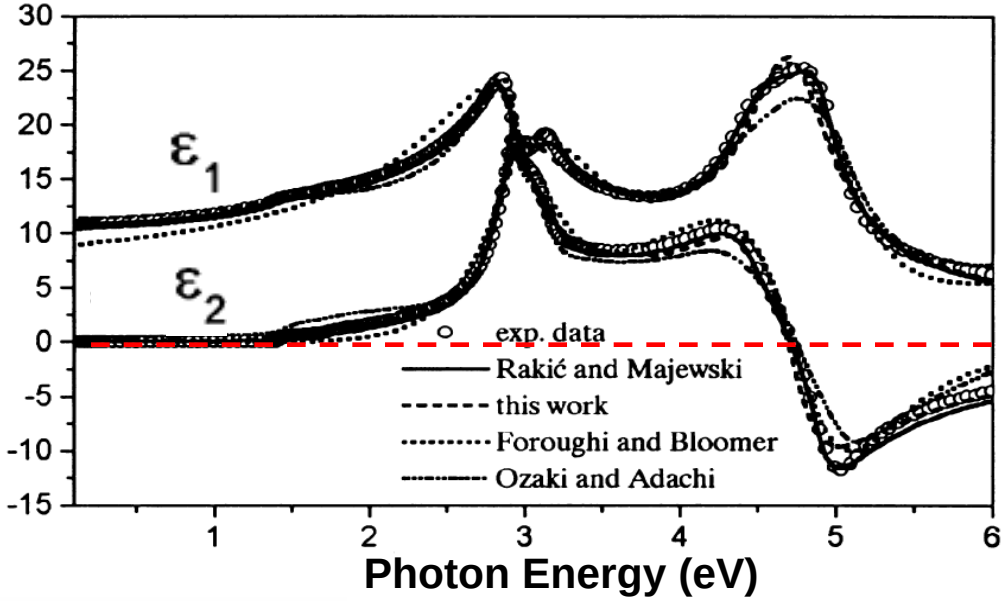
c-GaN



E_g ~3.2 eV

Pollak's Group
J. Appl. Phys. (2003)

c-GaAs



E_g ~1.4 eV

Djurisic's Group
Thin Solid Films (2000)

$$\mathscr{E} = \mathscr{E}_0 \, e^{-i\omega(t-\tilde{n}x/c)}$$

with a complex refractive index

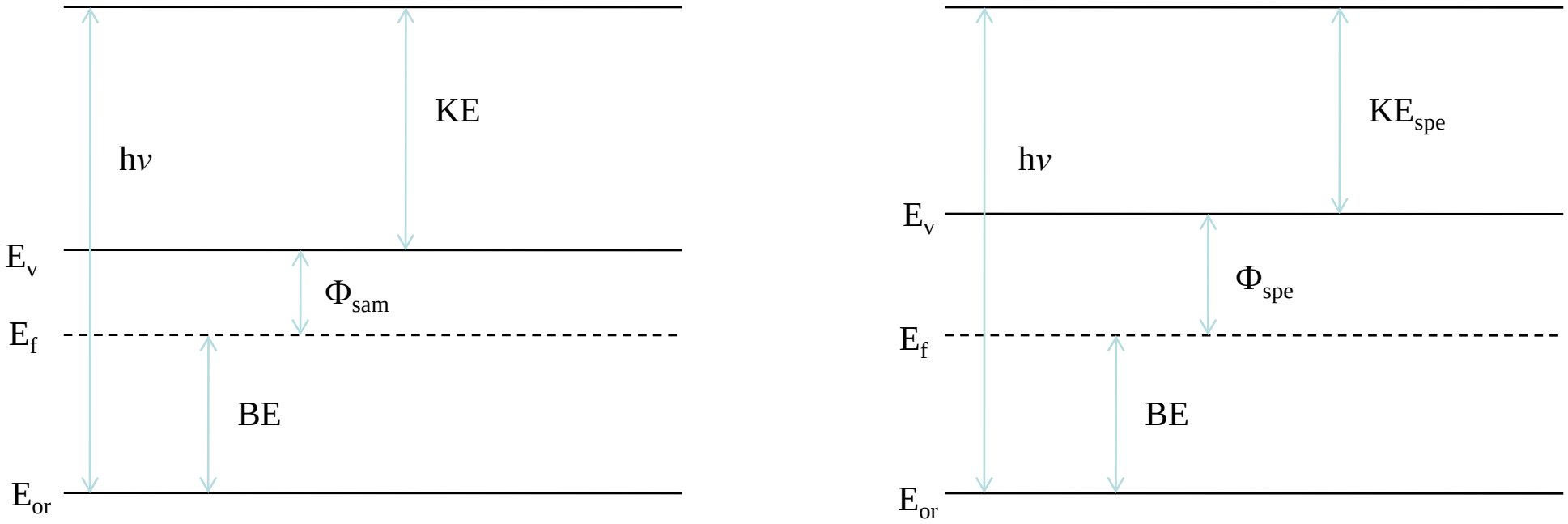
$$\tilde{n}(\omega) = n + i\kappa = \sqrt{\varepsilon(\omega)} \, ,$$

$$n^2 - \kappa^2 = \varepsilon_1 \, ,$$

$$2n\kappa = \varepsilon_2 \, .$$

Sample

Spectrometer



E_v: Vacuum level, E_f : Fermi level,

E_{or}: 특정 orbital에 binding 되어 있는 electron의 energy level

hν: Incident photon energy, KE: Kinetic energy in vacuum

BE: Binding energy, Φ_{sam}: Work function of sample

KE_{spe}: detector에서 관측되는 Kinetic energy, Φ_{spe}: Work function of spectrometer

일반적으로 sample에 hν 만큼의 에너지를 가진 photon을 쏘아줬을 때 관계식은 다음과 같습니다.

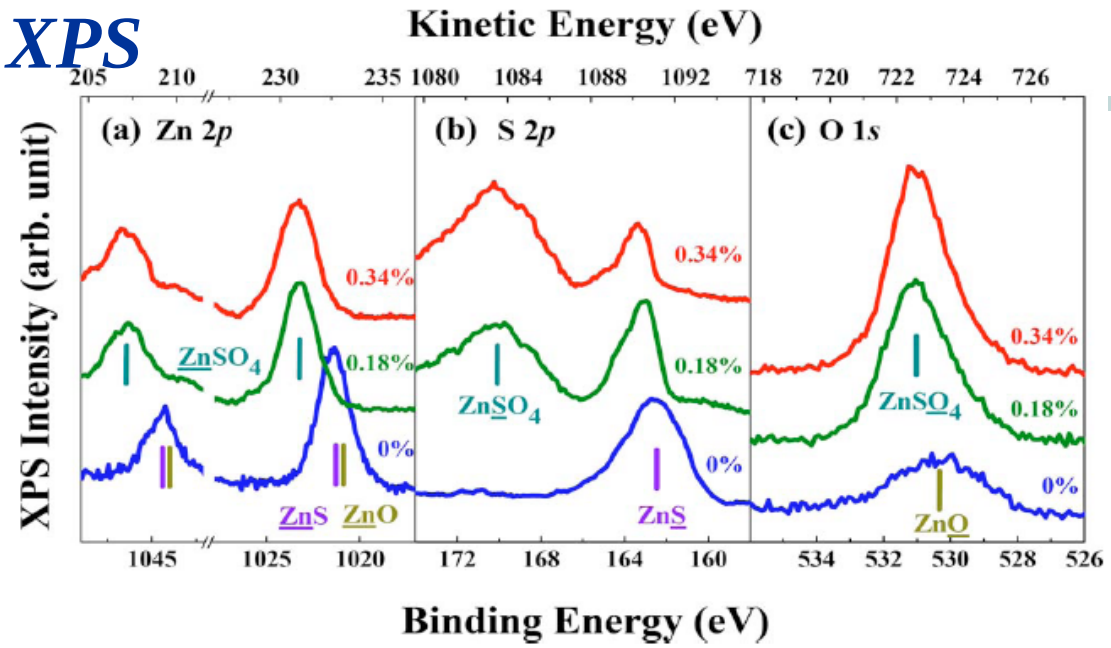
$$h\nu = KE + BE + \Phi_{sam}$$

반면 spectrometer의 detector는 sample과는 다른 값의 vacuum level을 갖기 때문에 detector에서 인식하는 Kinetic energy는 실제 Kinetic energy 값과는 다르게 됩니다. 하지만 sample의 Fermi level과 spectrometer의 Fermi level은 동일하기 때문에 (sample과 spectrometer의 detector는 외부 circuit으로 연결되어 있기 때문) 다음의 관계식 또한 성립함을 알 수 있습니다.

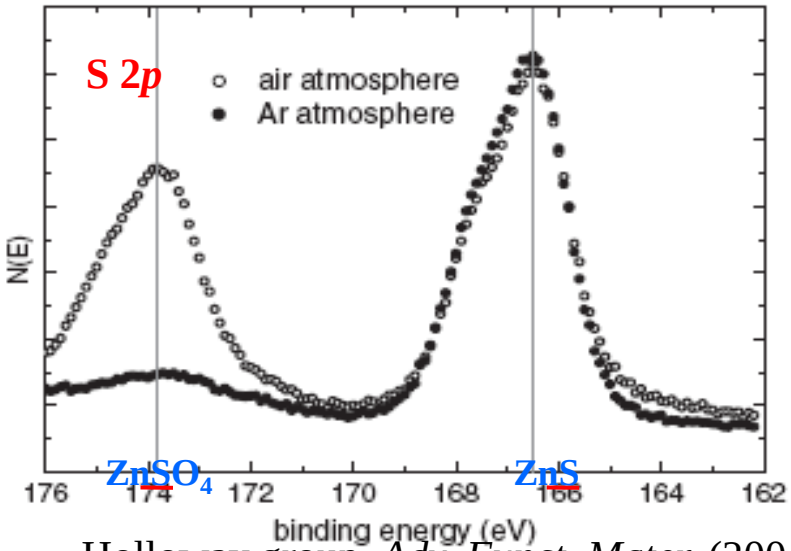
$$h\nu = KE_{spe} + BE + \Phi_{spe}$$

우리는 detector에서 관측되는 (실제와는 다른) kinetic energy 값과 spectrometer의 work function 값을 알 수 있기 때문에 위 두 관계식을 통해 생각해 보면 이론적으로는 실제 물질이 갖는 binding energy을 측정할 수 있게 됩니다.

또한 만약 sample에서 벗어나 vacuum을 통과하는 실제 kinetic energy를 알기 위해서는 그 물질의 work function을 알아야 함을 알 수 있습니다.



BP group, *Appl. Phys. Lett.* (2008).

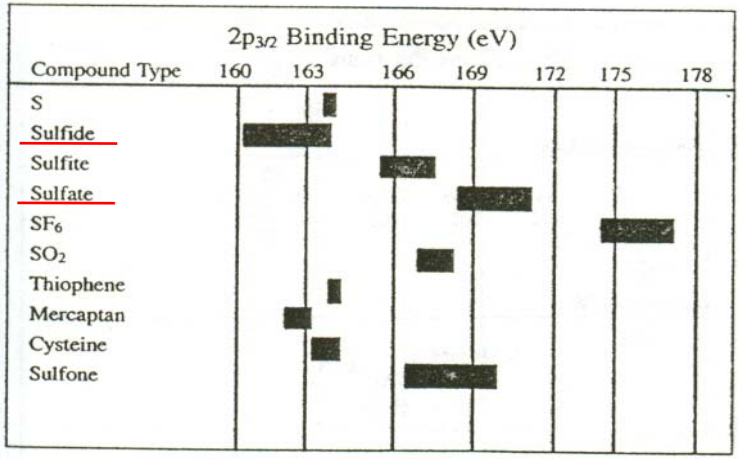


Holloway group, *Adv. Funct. Mater.* (2004).

저희 논문의 경우는 S 2*p*에서 binding energy 기준으로 sulfide peak이 ~162.5 eV, sulfate peak이 ~170 eV로 handbook에 나와 있는 range에 들어있음을 알 수 있습니다.

하지만 Holloway group의 경우에는 sulfide peak이 ~166.5 eV, sulfate peak이 ~174 eV로 handbook에 나와 있는 수치와 차이가 남을 알 수 있습니다.

XPS data는 C 1*s* peak을 이용하여 반드시 peak 위치를 보정해야 하는데 제 생각에는 아마도 Holloway Group에서 보정 과정을 수행하지 않아 이런 문제가 발생한 것으로 보입니다.



Handbook of X-ray Photoelectron Spectroscopy (Perkin-Elmer Corporation, 1992).