# Characterization for Nanostructures

***Byungwoo Park***

**Department of Materials Science and Engineering**
**Seoul National University**

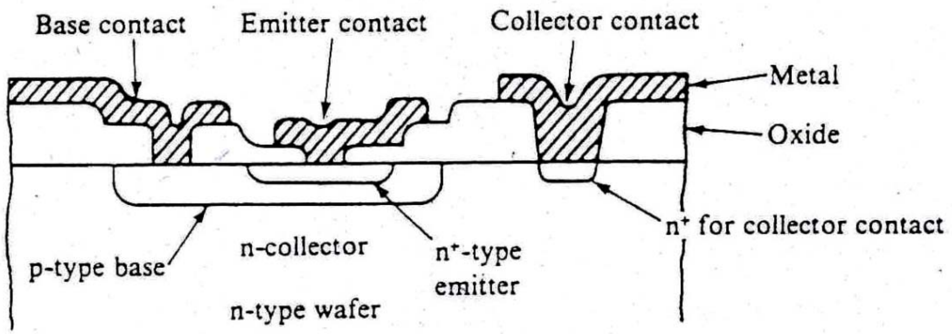
**http://bp.snu.ac.kr**

# 성공적인 집적회로

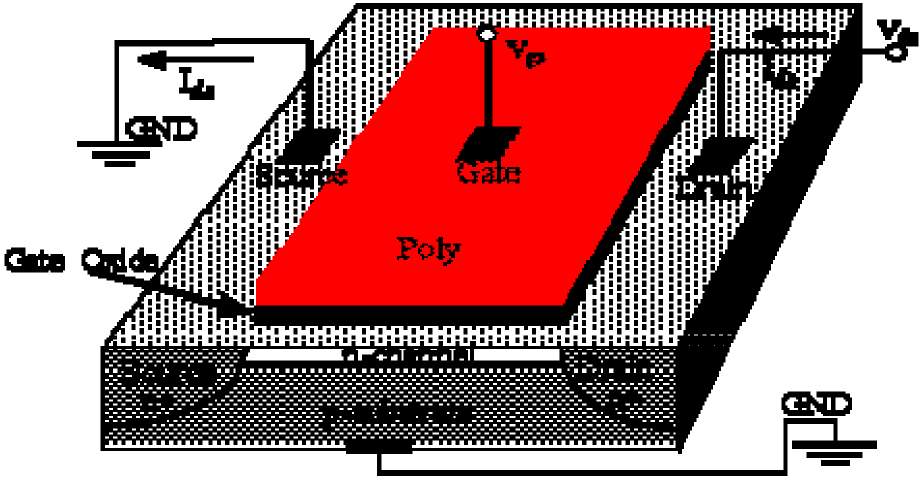
**- Accurate Control of Composition and Phase**

**- Accurate Size Control**

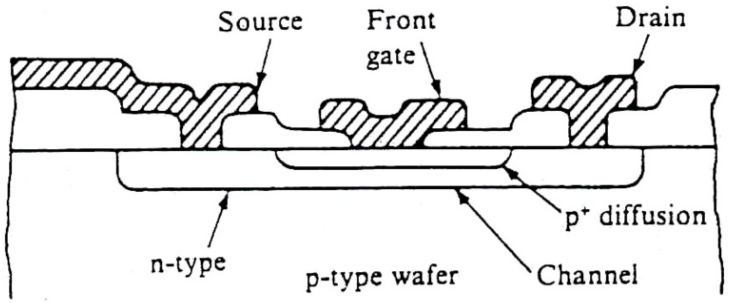
**- Accurate Solute-Distribution Control**



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



***n*-channel MOS transistor**

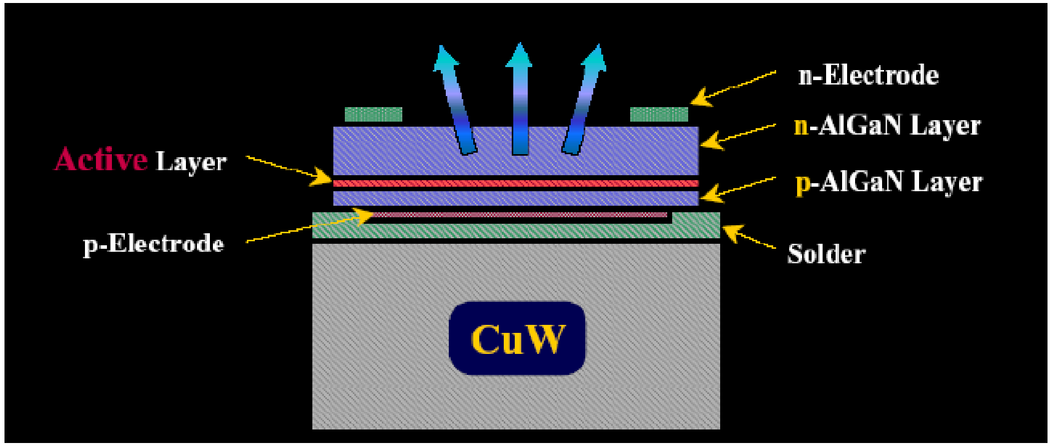


***n*-channel junction field effect transistor**

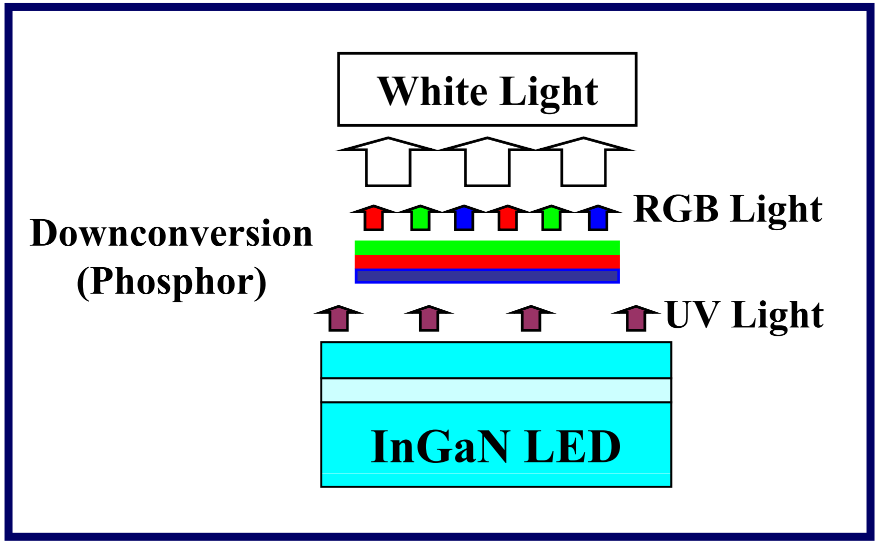
# *PL Nanoparticles on UV Epilayer*

- **White LED**

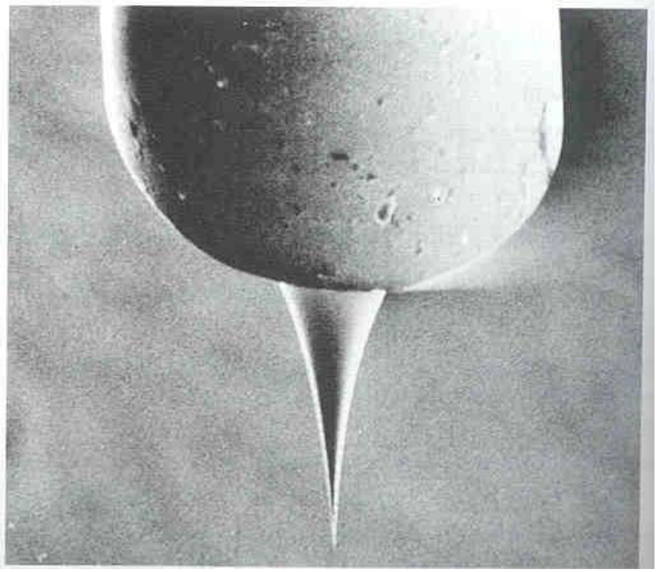
**- Nichia High-Power LED**



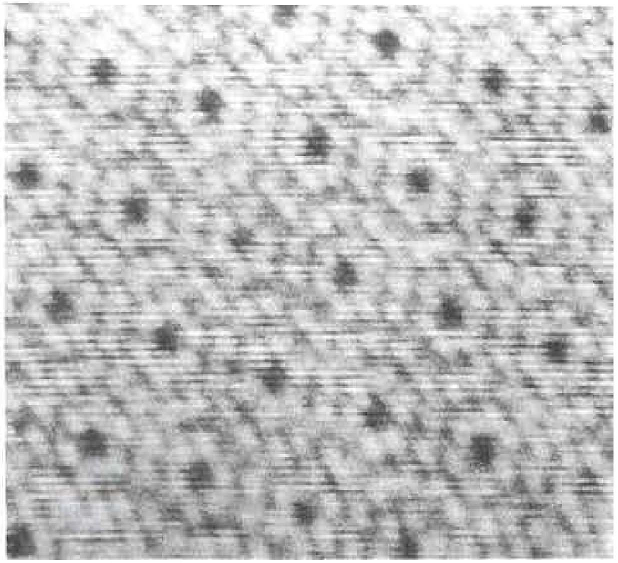
**- UV LED & RGB Phosphor**



# *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*

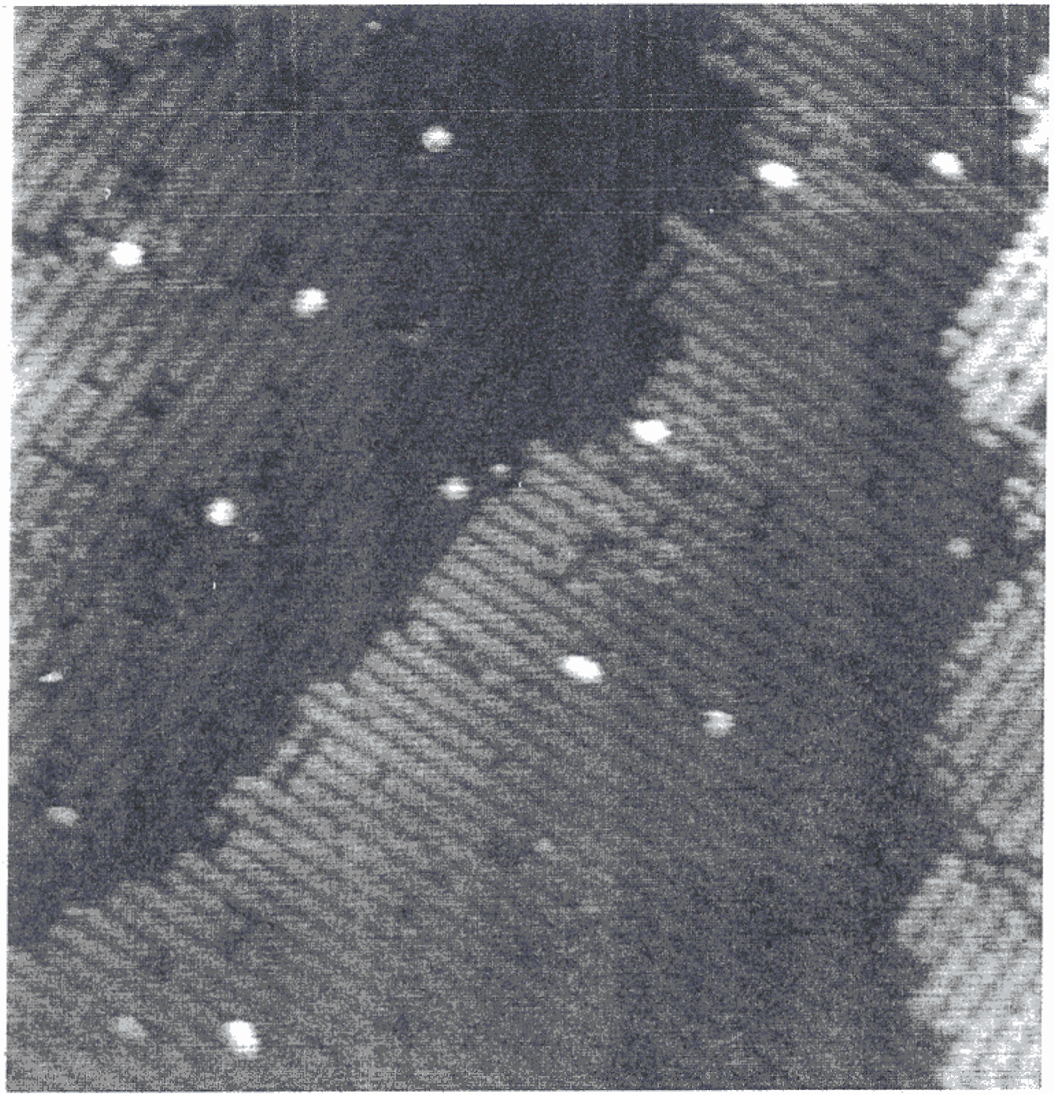
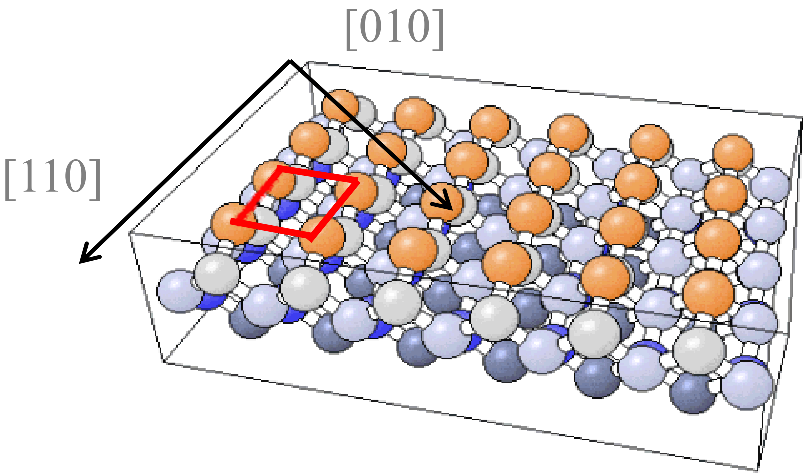
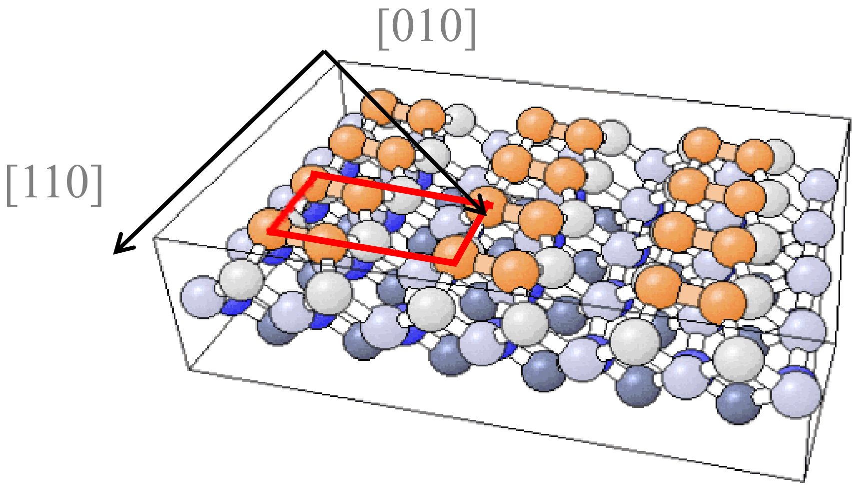


FIGURE 1. A SCANNING tunneling microscope image of a silicon (001) surface after the deposition of a small amount of Si at room temperature. The image shows two single-layer steps (the jagged interfaces) separating three terraces. Because of the tetrahedral bonding configuration in the silicon lattice, 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).



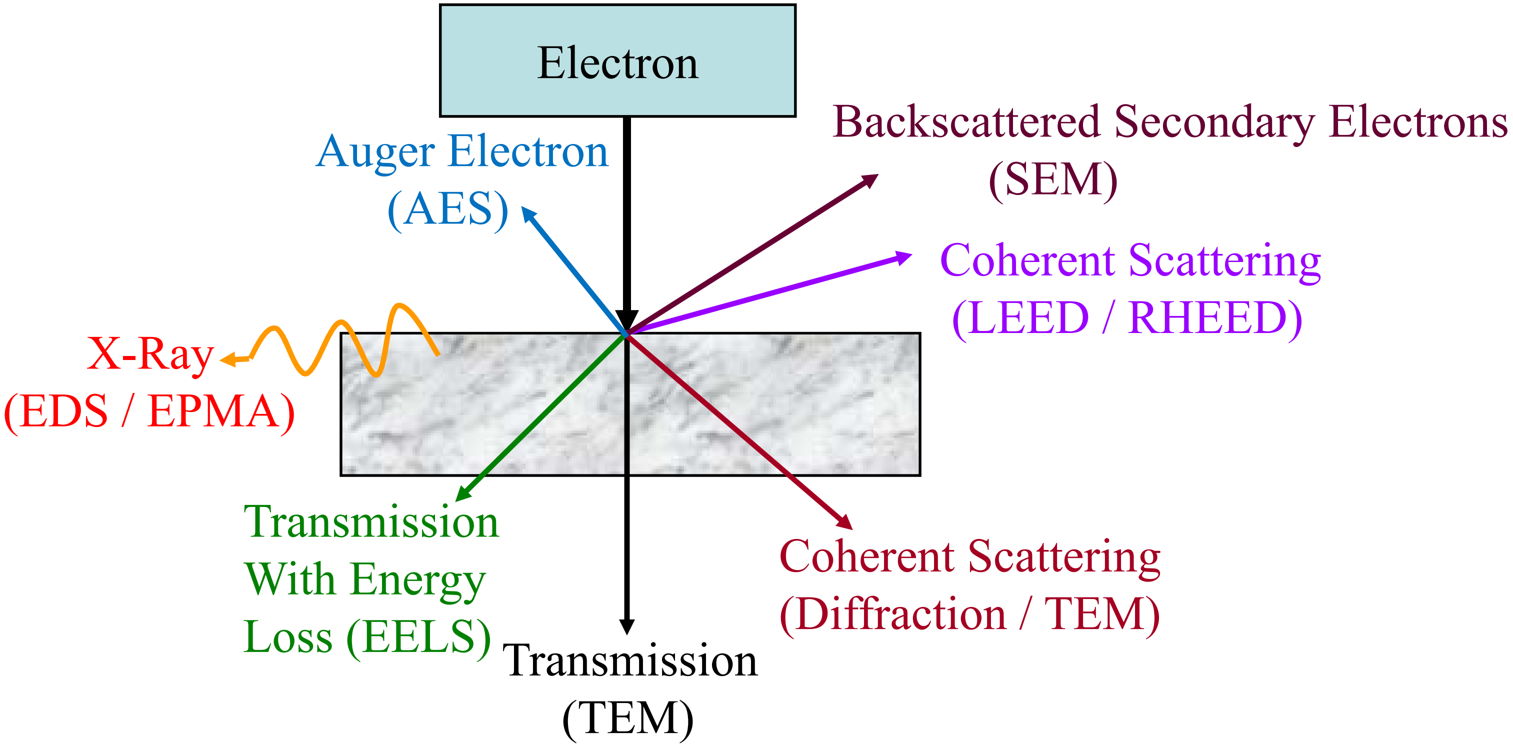
Reconstructed Si(001)-(2×1) surface.
- The Si atoms of the topmost layer form a covalent bond with adjacent surface atoms.
- Drawn together as pairs.

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

# *Survey of Analytic Techniques*

## 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):

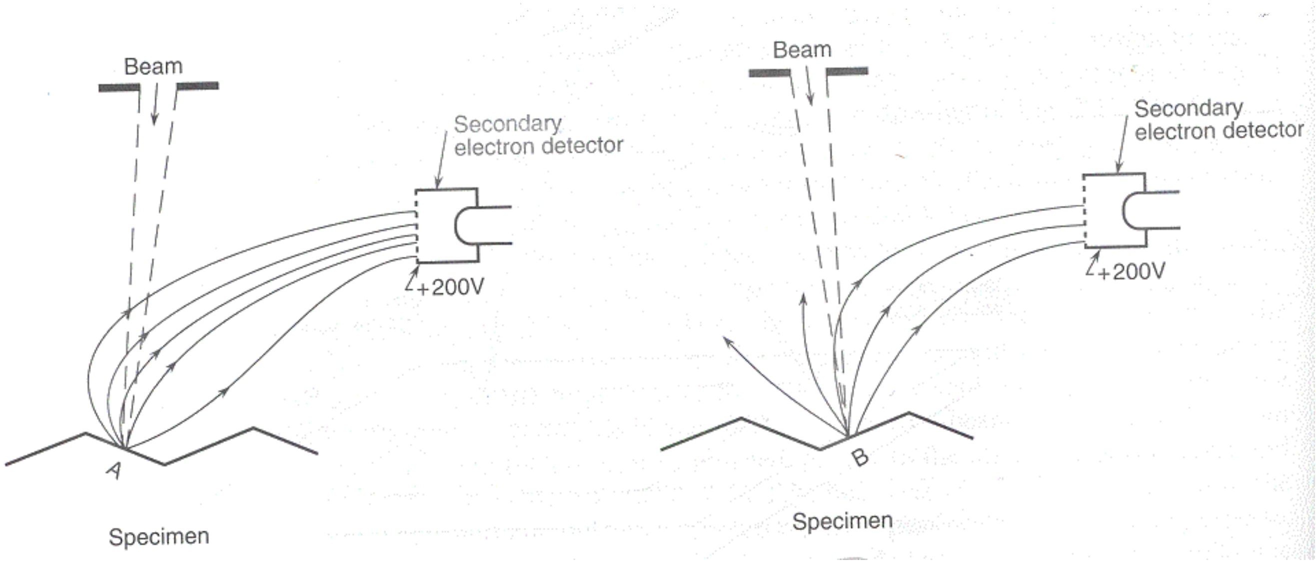
  A specimen atom, excited by the incident electron, emits some of the energy by one of the higher level electrons coming down, by emitting a second electron with a characteristic energy. This is a surface analysis technique.

- 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.

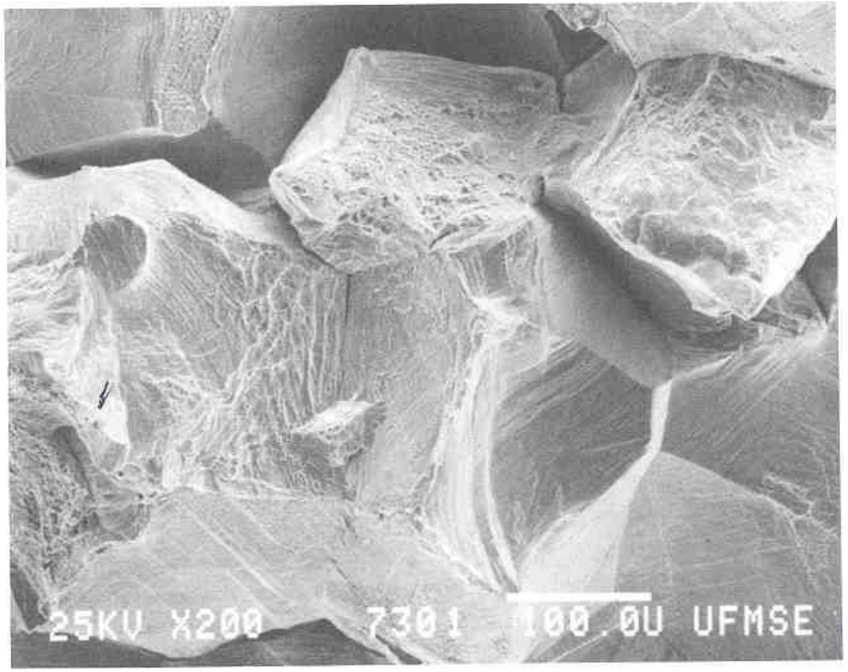
# *Scanning Electron Microscopy*

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

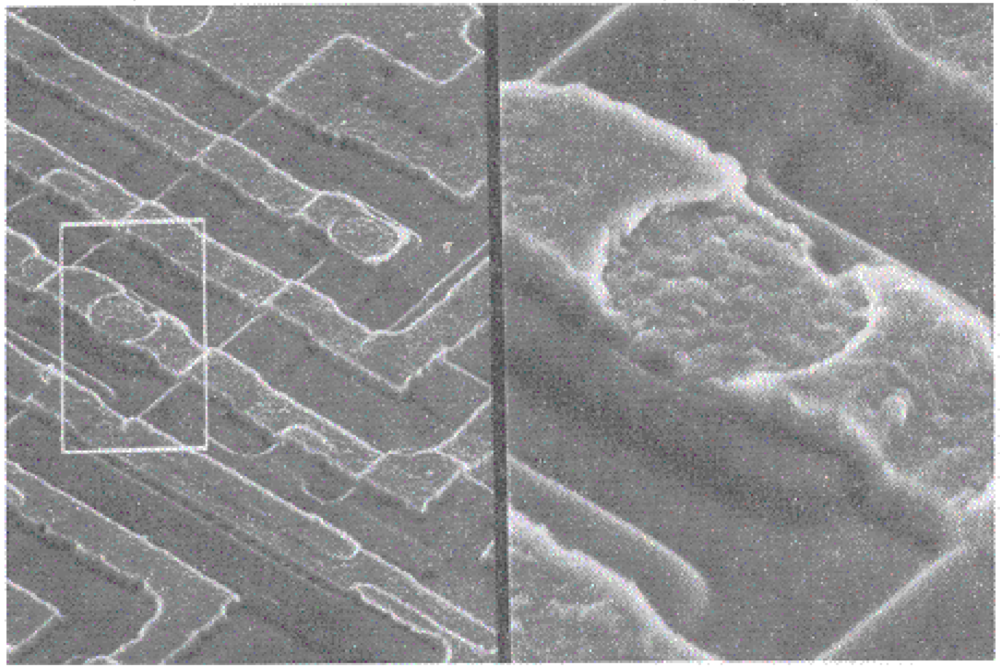


An illustration of how the scanning electron microscope can reveal surface relief when used with a secondary electron detector.

# SEM Image

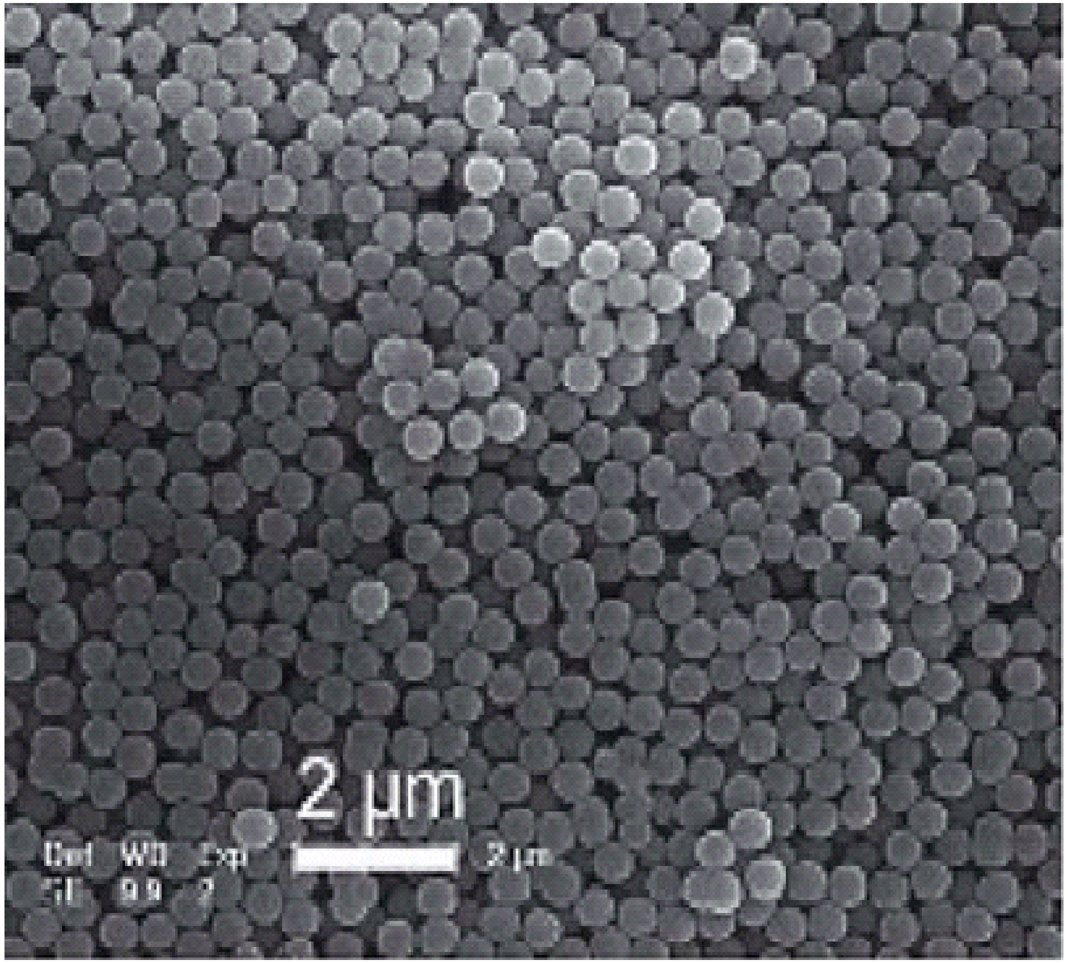


An SEM micrograph of a fractured Cu-4.9 at. % Sn specimen.



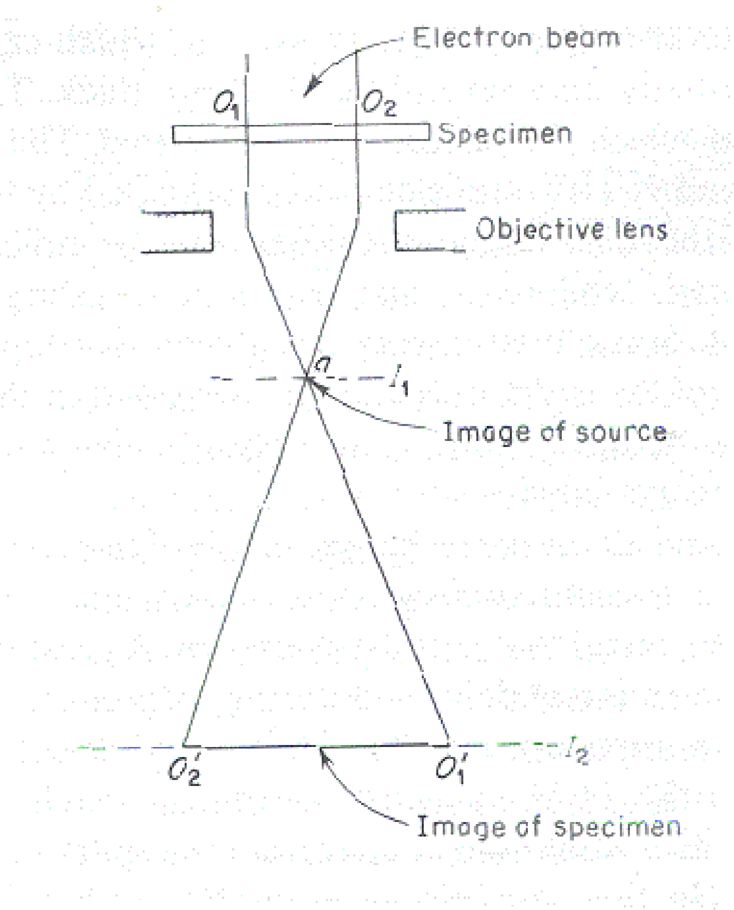
Left side is an image of part of an integrated circuit, right side is an enlargement of the highlighted rectangle on the left: (magnification = ×850 left, ×3300 right, accelerating voltage = 10.0 keV).

# *Field-Emission Scanning Electron Microscopy*

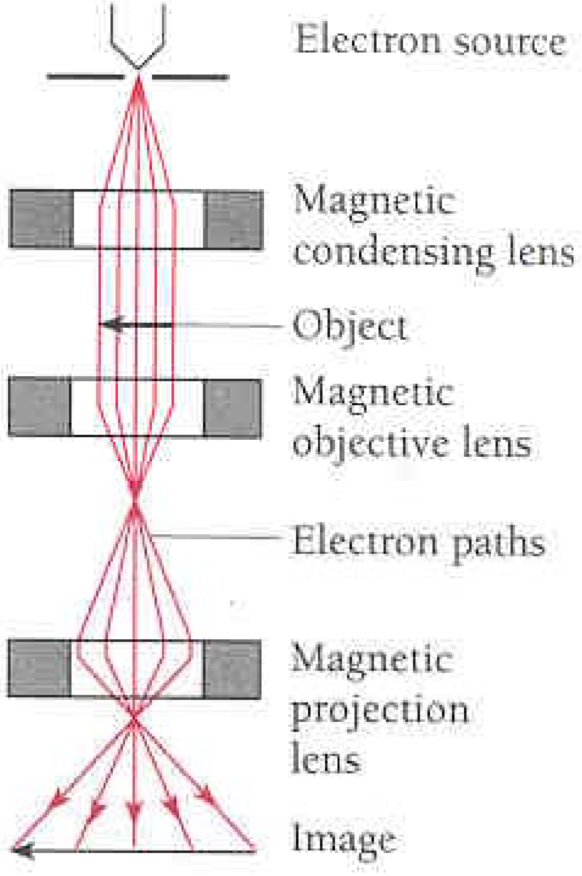


**- $SiO_2$ Spherical Particles, *APL* (2005)**

# *Transmission Electron Microscopy*

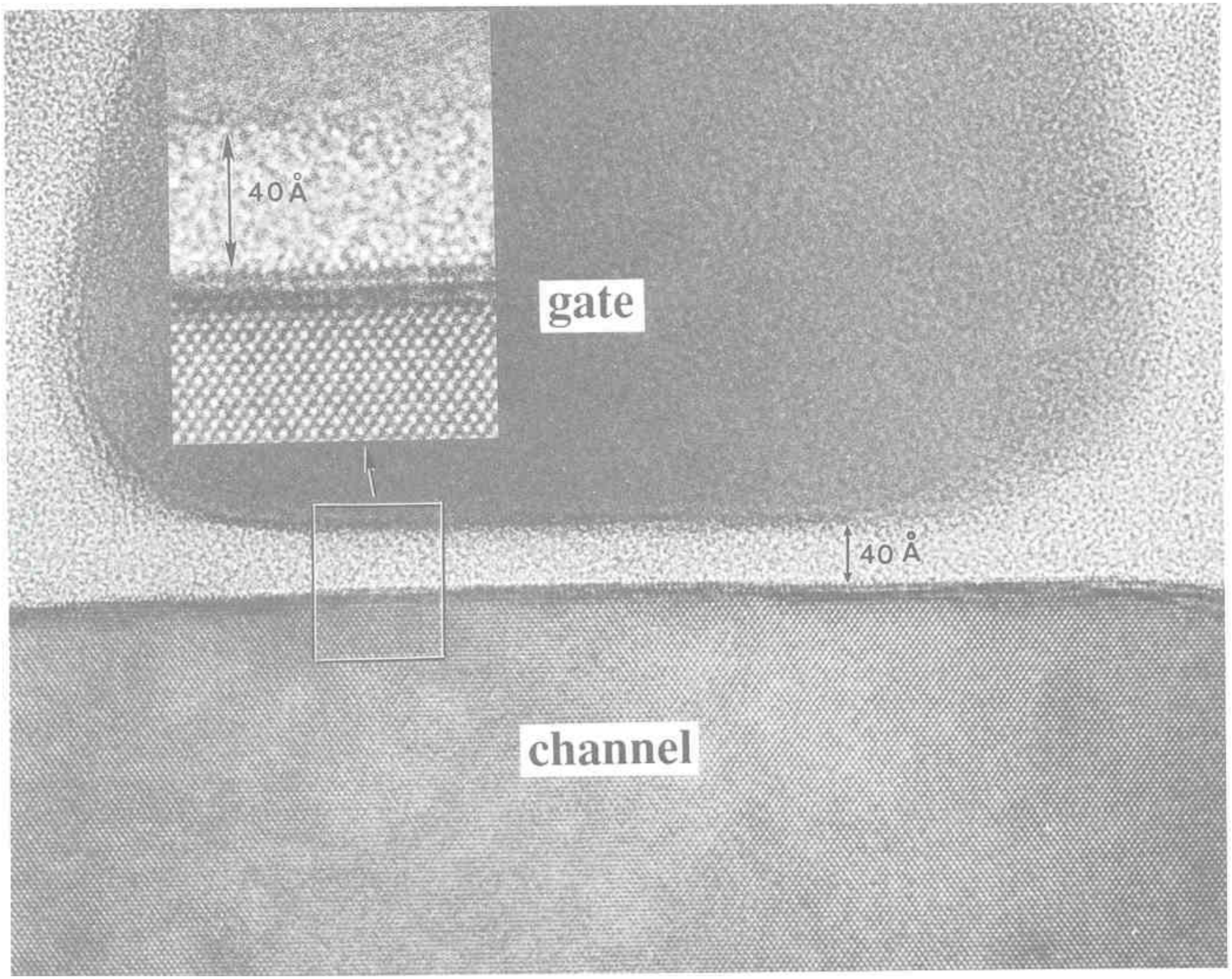


Schematic drawing of a transmission electron microscope.



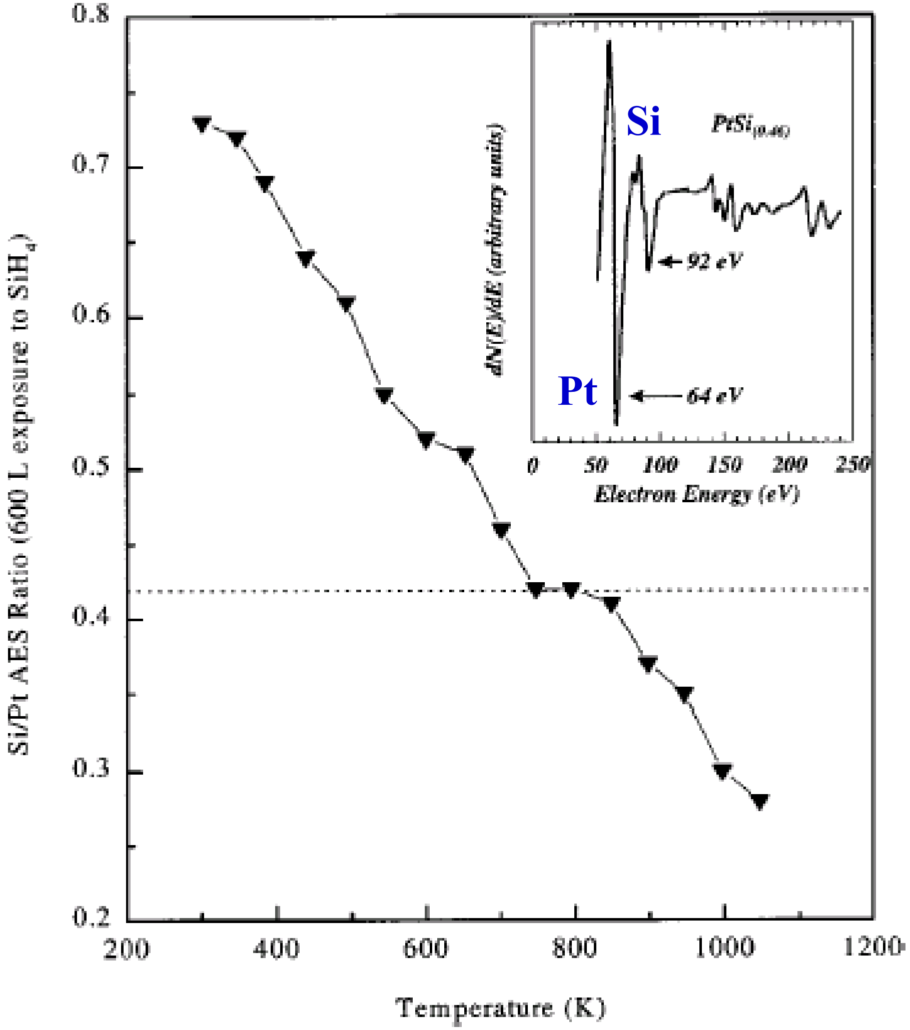
The electron beam in an electron microscope is focused by magnetic fields.

# High-Resolution TEM



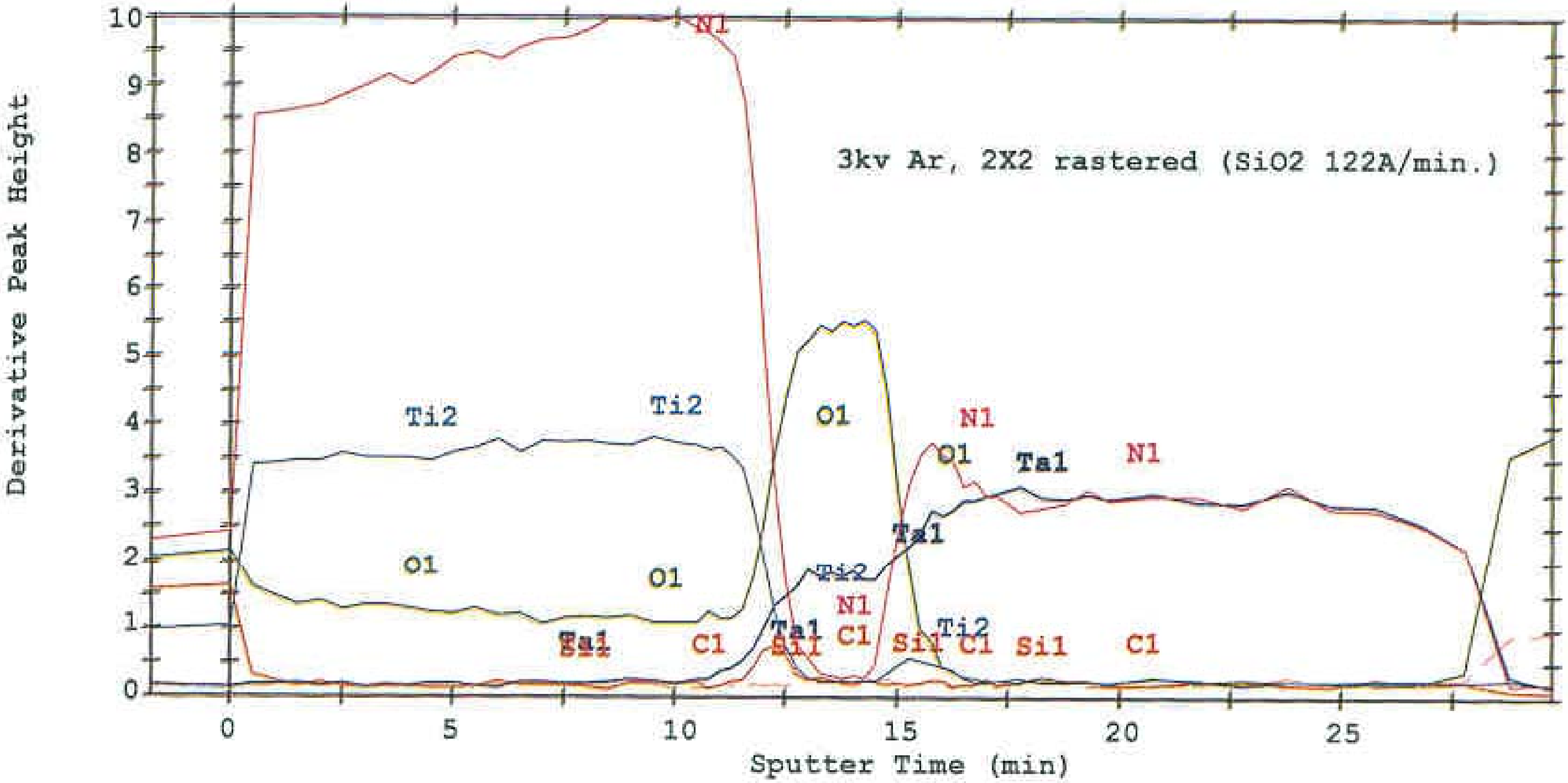
High-resolution cross-sectional TEM, showing an experimental silicon metal-oxide field effect transistor (MOFET). Each white blob represents a pair of atom columns. The gate is only a few hundred atoms long, and the **gate oxide** is 4 nm thick. Such devices, fabricated by a team at AT&T Bell Laboratories,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

# *Auger Electron Spectroscopy*



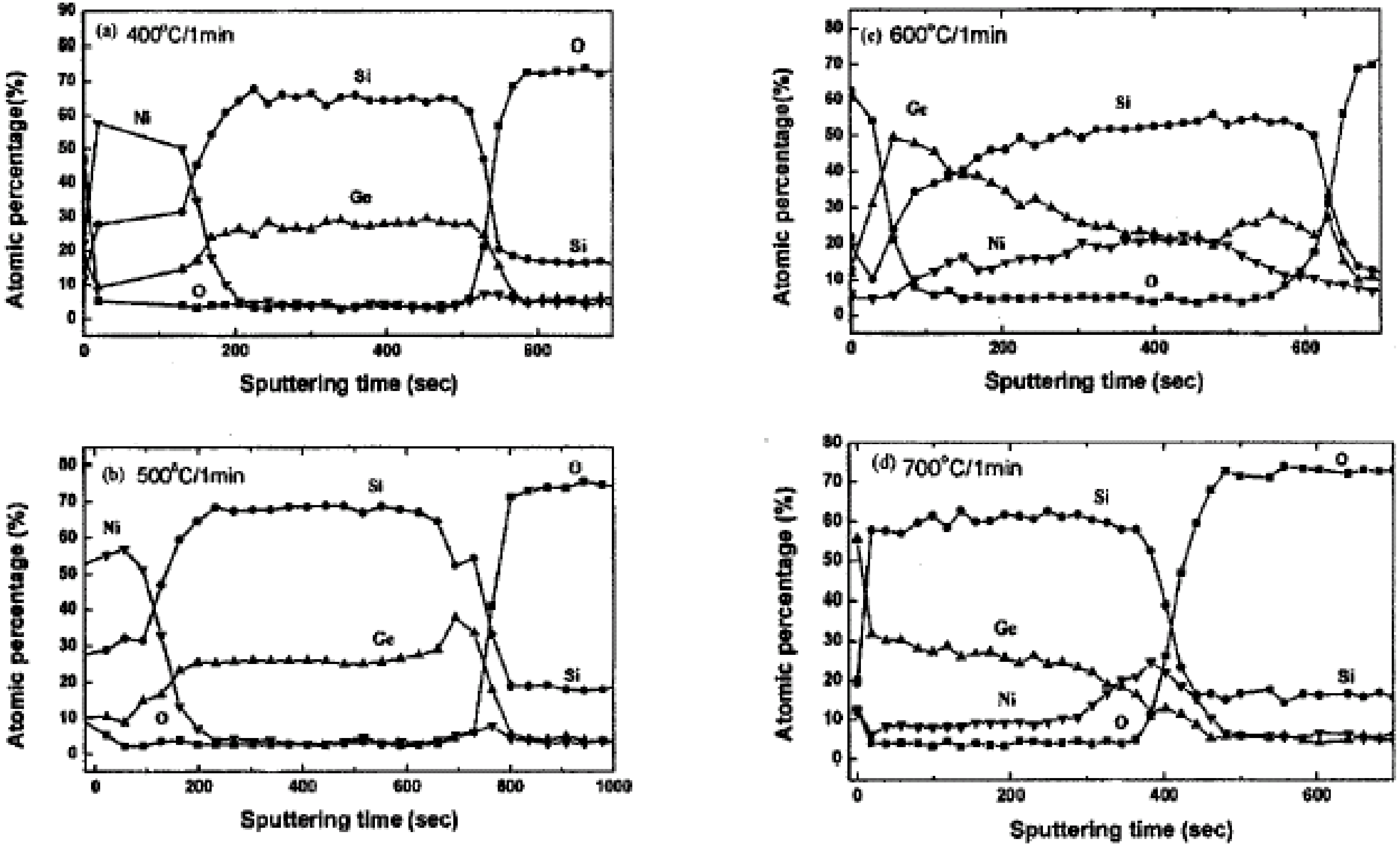
- Si saturated Pt (100) surface, silicide as interconnects in FET, *JACS* (1999)

# *Depth Profile by AES*



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

# *AES Depth Profile*



- Ni (5 nm) / SiGe (100 nm) / $SiO_2$ layer, SiGe as an alternative to poly-Si, *JVST* (2006)

# *Ion Method*

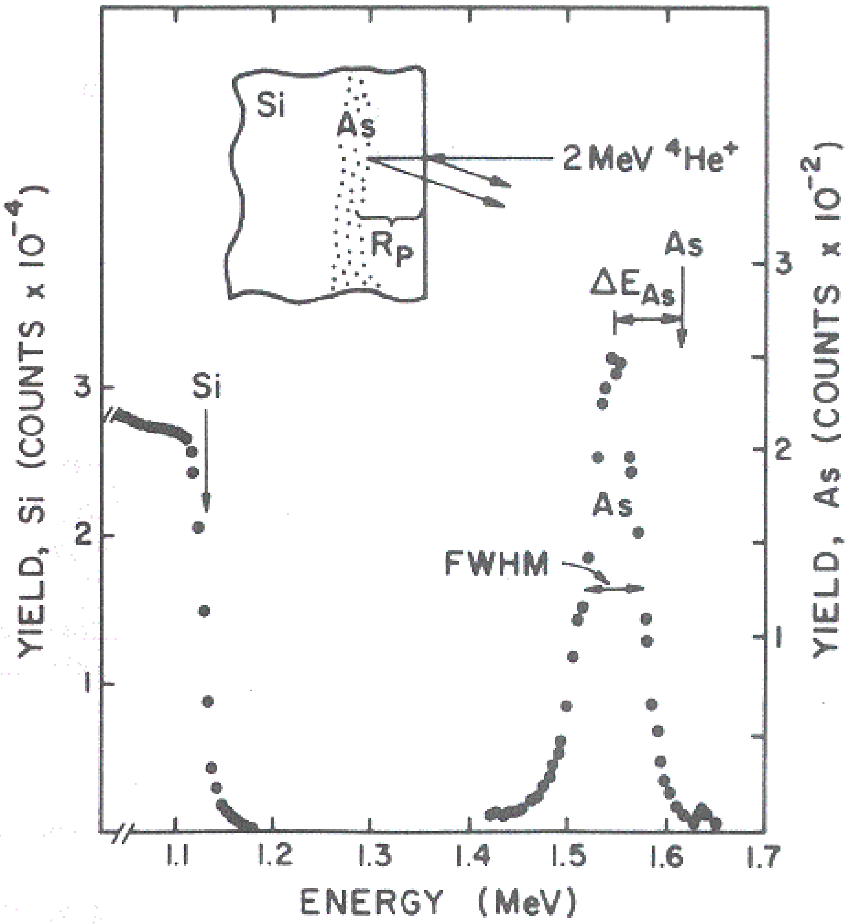
- RBS (Rutherford Backscattering Spectroscopy):
  Through the measurements of intensity and energy of the scattered ions, it is possible to infer the composition and depth of thin films.

- 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 1.2x$10^{15}$ As$^+$/cm$^2$ at 250 keV. The vertical arrows indicate the energies of particles scattered from surface atoms of $^{28}$Si and $^{75}$As.

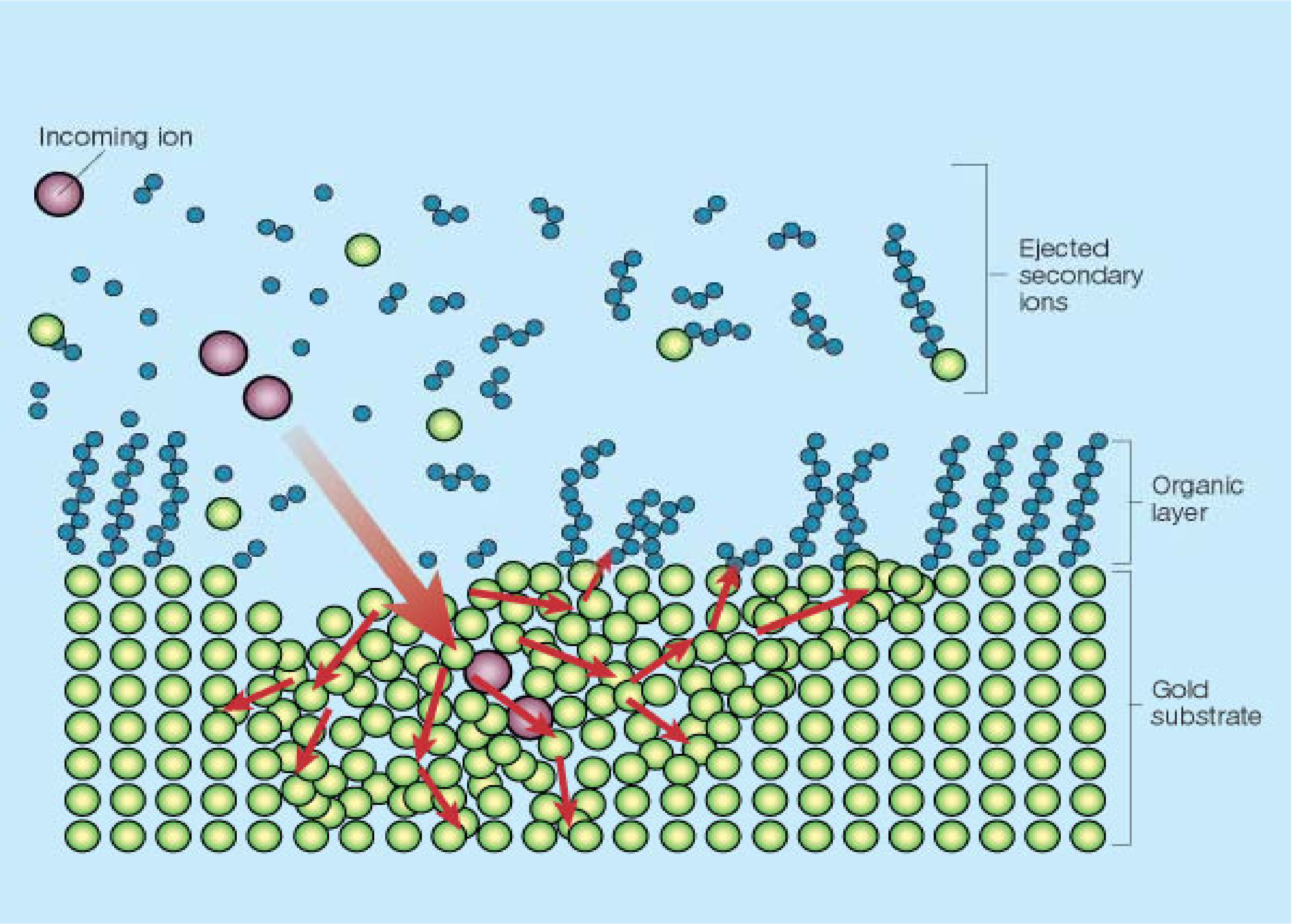
# *Secondary Ion Mass Spectroscopy (SIMS)*

- 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)*

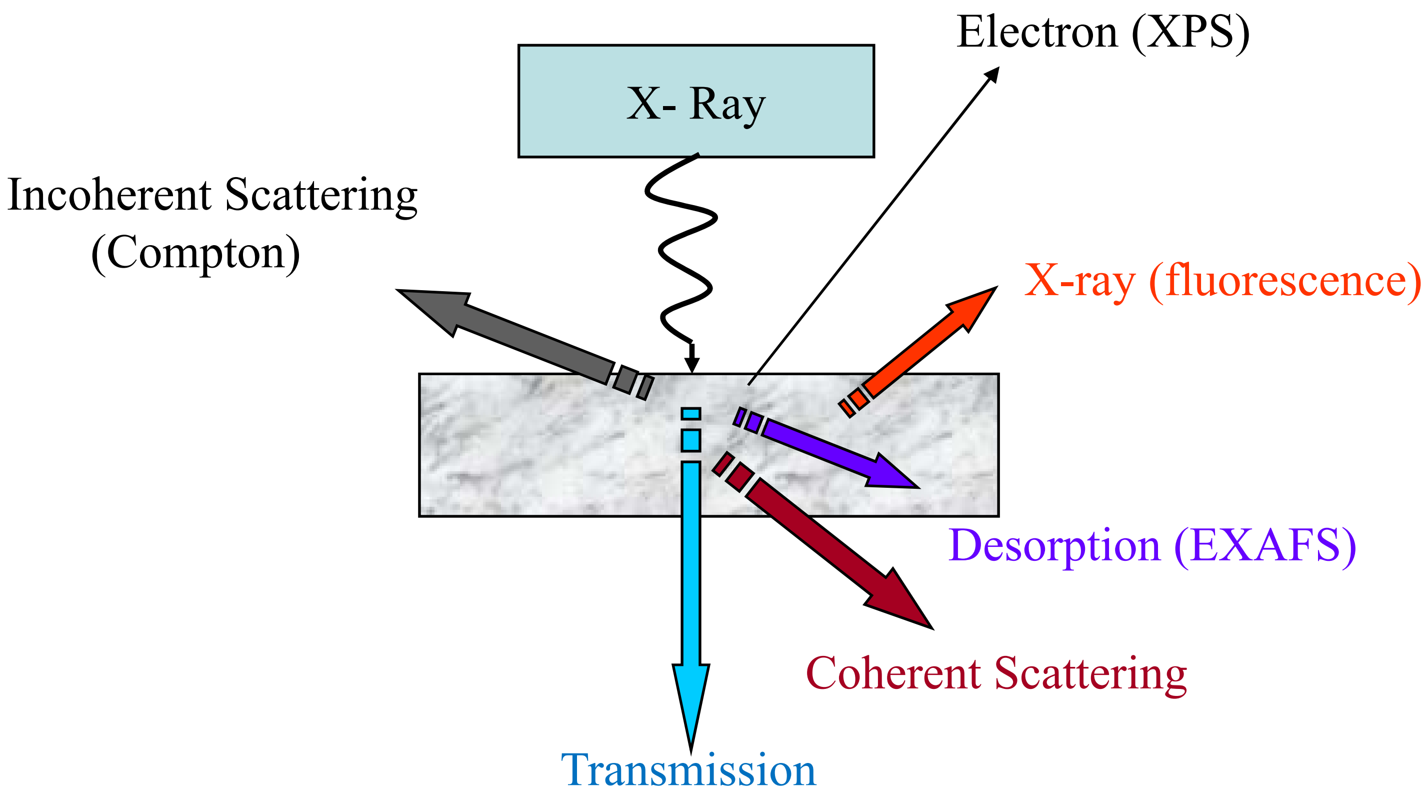


http://www.nature.com/nature/journal/v422/n6928/fig_tab/422129a_F1.html

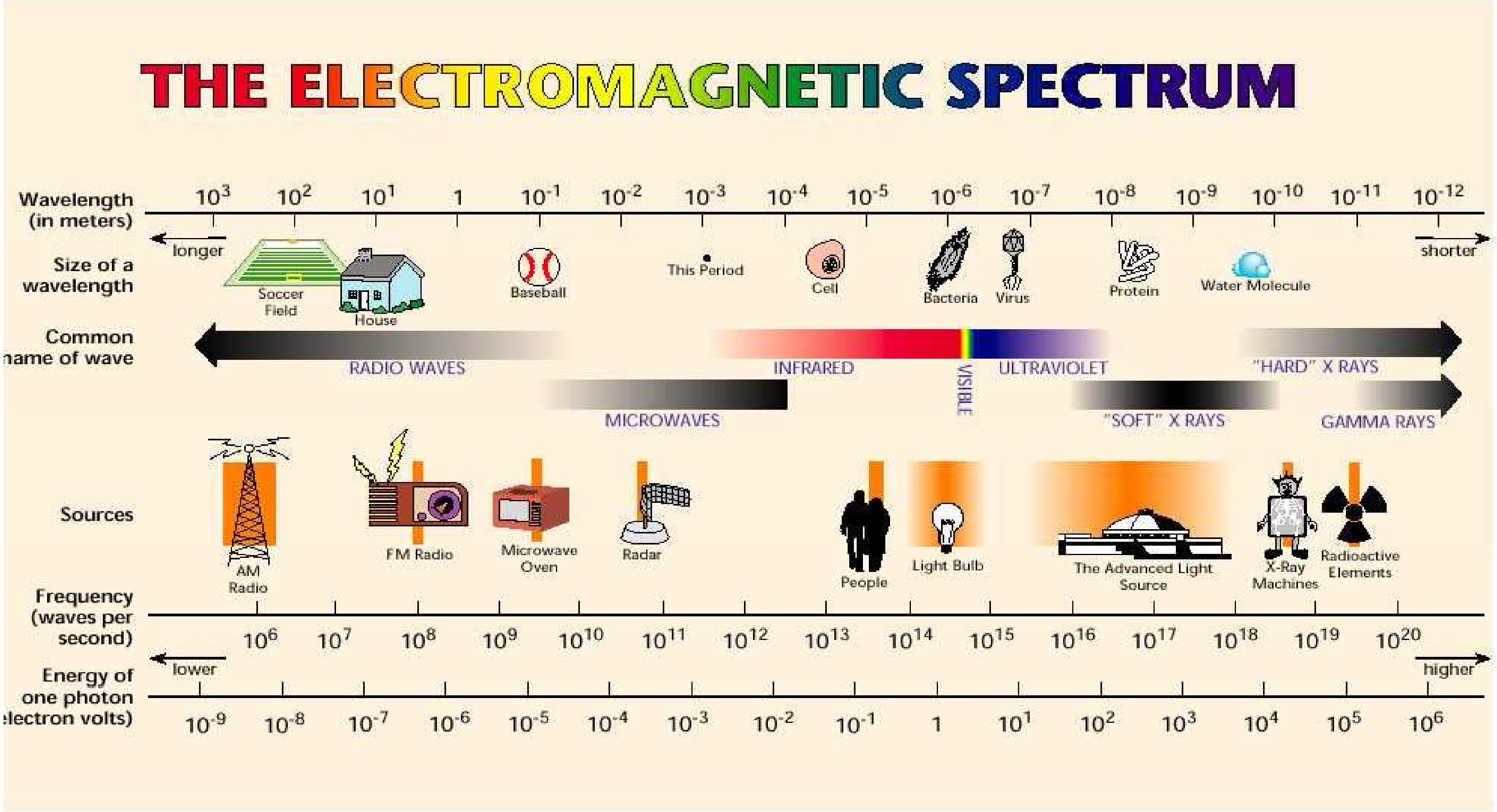
Ions are fired into an organic self-assembled monolayer on a gold substrate. The energy deposited in the surface region from the incoming primary ions produces a collision cascade. This results in the ejection of a wide range of atomic and molecular fragments, of which about **1% are ions**. **Mass analysis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

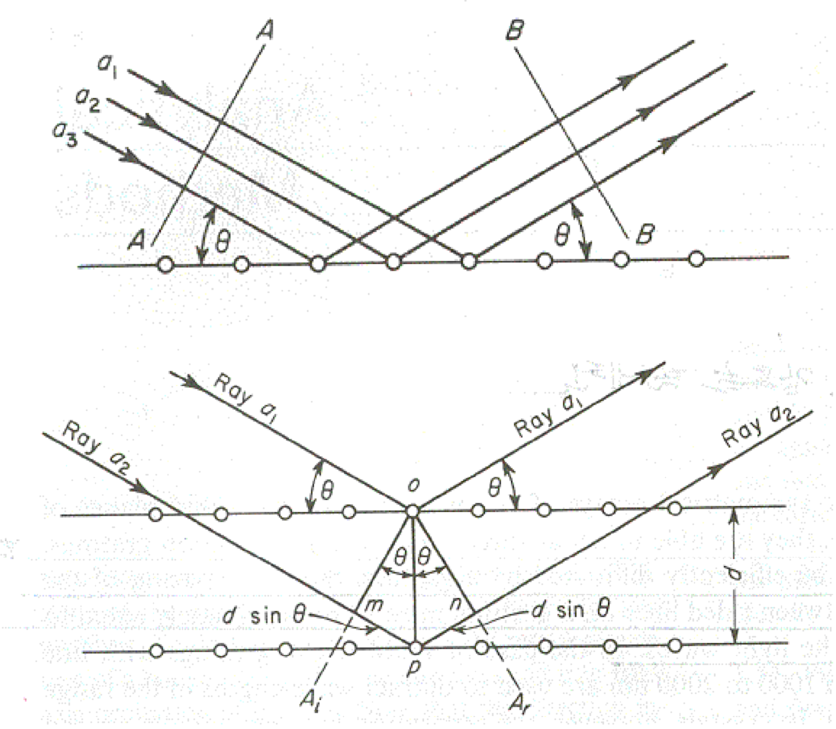
# *X-Ray Method*

- 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**

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

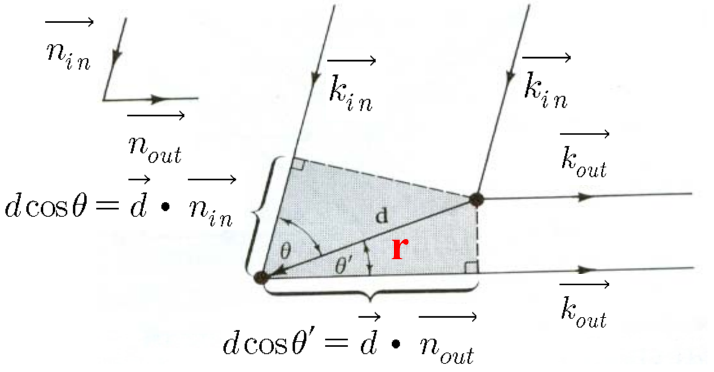
where $n$ = 1, 2, 3…

$\lambda$ = wavelength

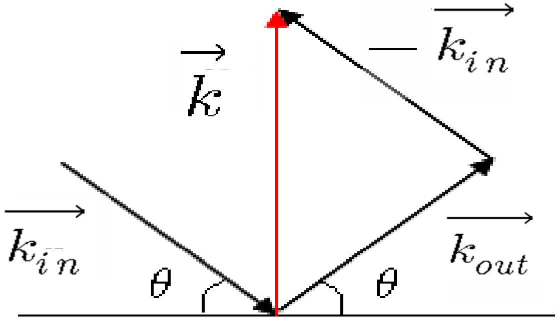
$\theta$ = scattering angle

# General Theory of Diffraction

$$d\cos\theta + d\cos\theta' = \vec{d} \bullet (\overrightarrow{n_{in}} - \overrightarrow{n_{out}})$$ → **Path difference, n is unit vector**

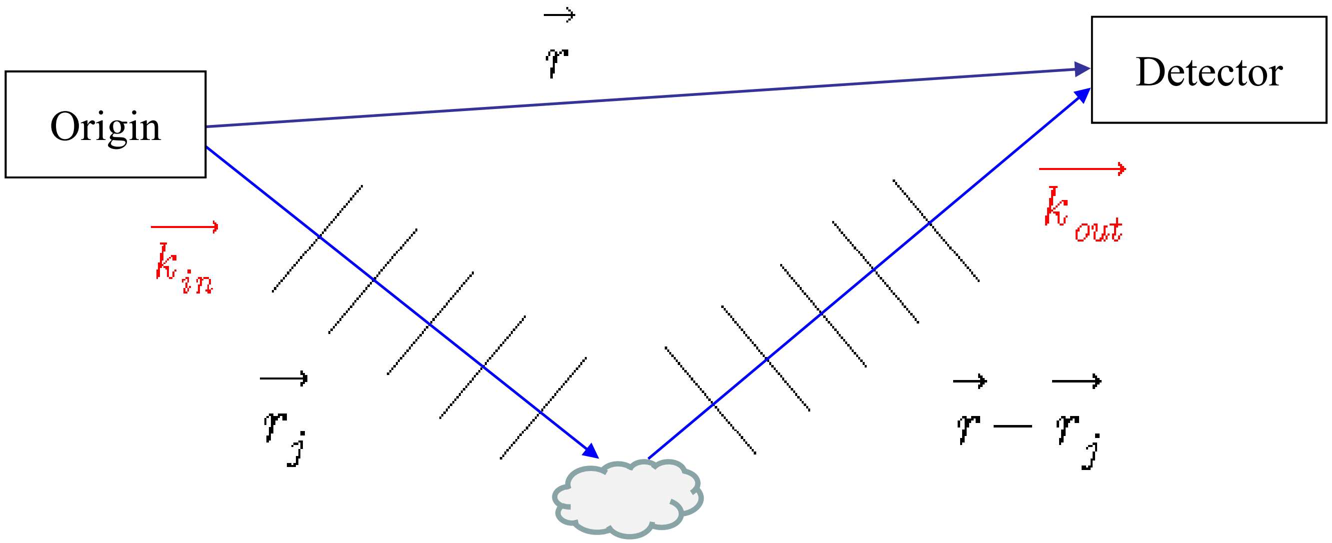


With $\vec{k} = \overrightarrow{k_{out}} - \overrightarrow{k_{in}}$ and $|\overrightarrow{k_{in}}| = |\overrightarrow{k_{out}}| = \dfrac{2\pi}{\lambda}$ → $\vec{k}$ is reciprocal lattice



# Constructive Interference

- Assumption: Incoming plane wave + Scattered plane wave.



$\overrightarrow{k_{in}}$ : incident plane wave vector

$\overrightarrow{k_{out}}$ : scattered plane wave vector

$$|\overrightarrow{k_{in}}| = |\overrightarrow{k_{out}}| = \frac{2\pi}{\lambda}$$

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

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

# *Constructive Interference*

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

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

$f_j(\theta)$ : Atomic form factor

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

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

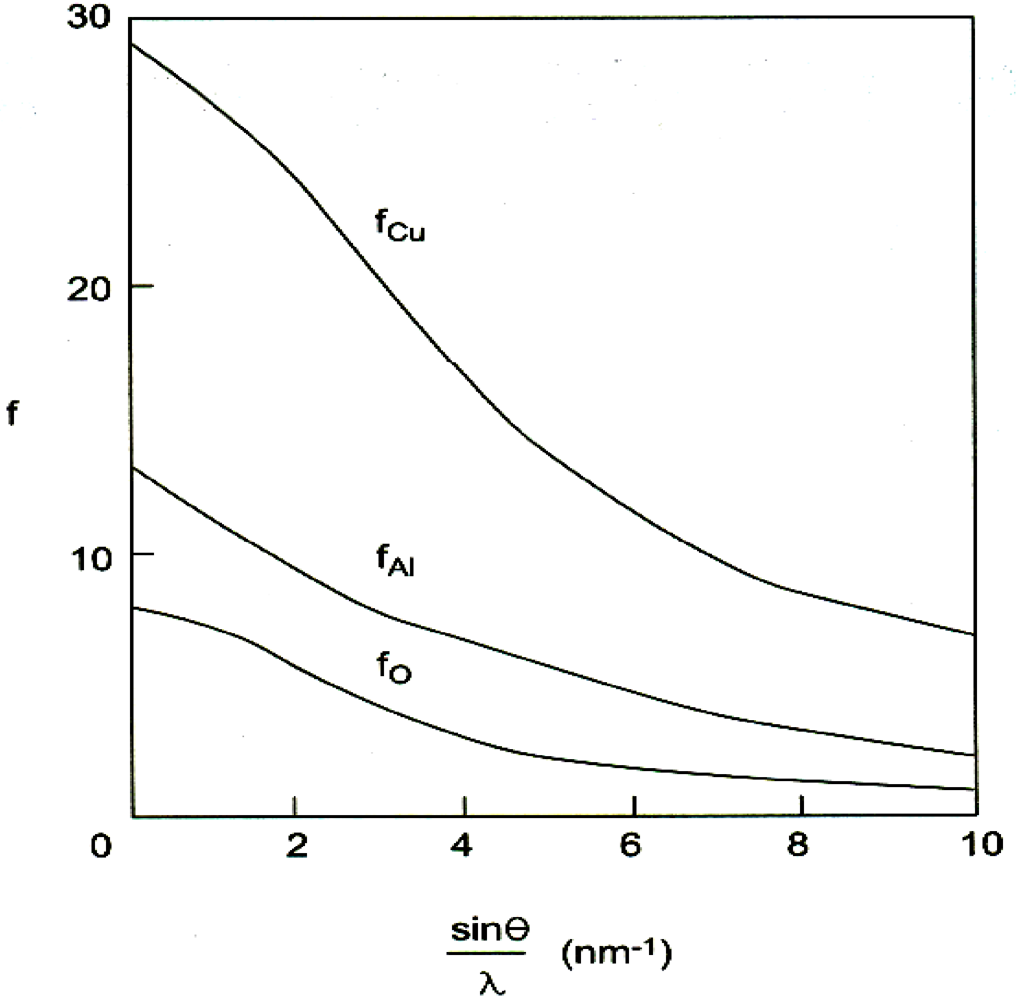
$\vec{k} = \overrightarrow{k_{out}} - \overrightarrow{k_{in}}$ : Reciprocal wave vector (diffraction condition)

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

# Atomic Form Factor

**<Atomic form factor>**

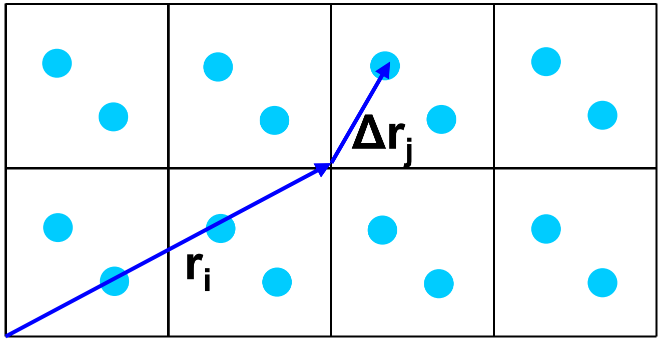
$f(\theta)$ = Amplitude scattered by an atom / Amplitude scattered by a single electron



# *Structure Factor*

**<Structure factor>**

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



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

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

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

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

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

Atomic form factor

Structure factor (= $F_{hkl}$ )

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

**Sorry for the different definition of $k_{in}$ (2π/λ or 1/λ).**

# *Fourier Transformation and Electron Diffraction*

- Recall Kinematical electron diffraction

$$\Psi_{sc} = \sum_{j=1}^{N} f_j(\theta) e^{-2\pi i \vec{K}\cdot\vec{r}_j} \longrightarrow$$

The formula is a Fourier series.

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

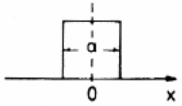
**Diffraction pattern is the Fourier transformation of the real lattice.**

✓ Special Example

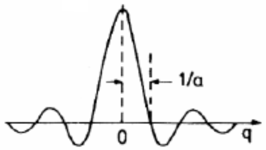
1 a) One-dimensional slit

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

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



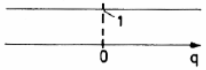
Transformation



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 $1/\lambda$).**

# Convolution

- Convolution Theorem

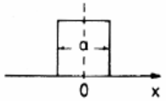
$$C(x) = \int_{-\infty}^{+\infty} f(\xi) g(x-\xi) d\xi = f(x) \otimes g(x)$$

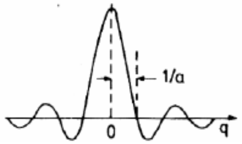
$$F\{f \otimes g\} = F(k) \cdot G(k)$$
$$F\{f \cdot g\} = F(k) \otimes G(k)$$

1 a) One-dimensional slit

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

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

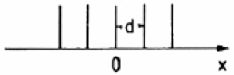


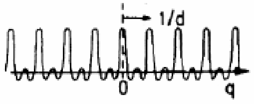


7) One-dimensional point lattice

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

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



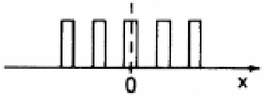


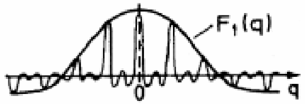
- Convolution Atomic Form Factor $f_1(x)$ $\otimes$ Point array $f_7(x)$

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

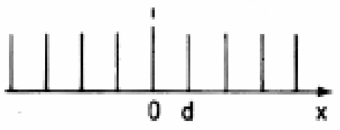
**Sorry for the different definition of $k_{in}$ ($2\pi/\lambda$ or $1/\lambda$).**

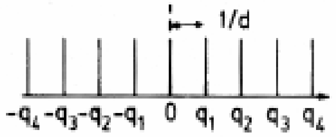
# Convolution

- At the infinite point condition

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

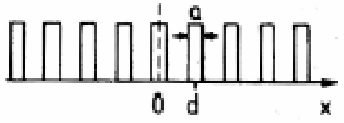
$$f_{11} = \sum_{n=-\infty}^{+\infty} \delta(x - nd) \qquad F_{11}(q) = \sum_{n=-\infty}^{+\infty} \delta\left(q - \frac{n}{d}\right)$$

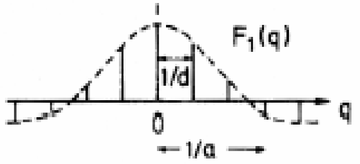




12) Infinite periodic function

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

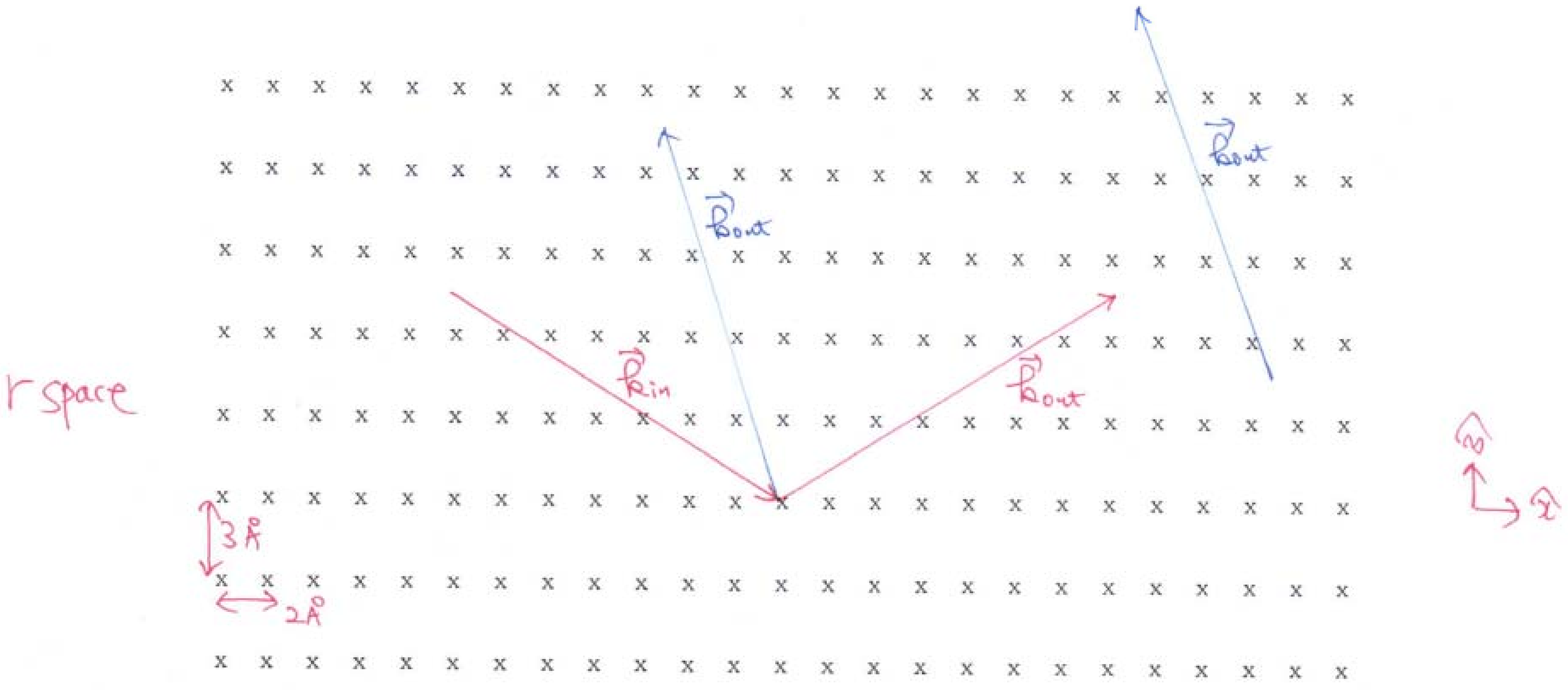




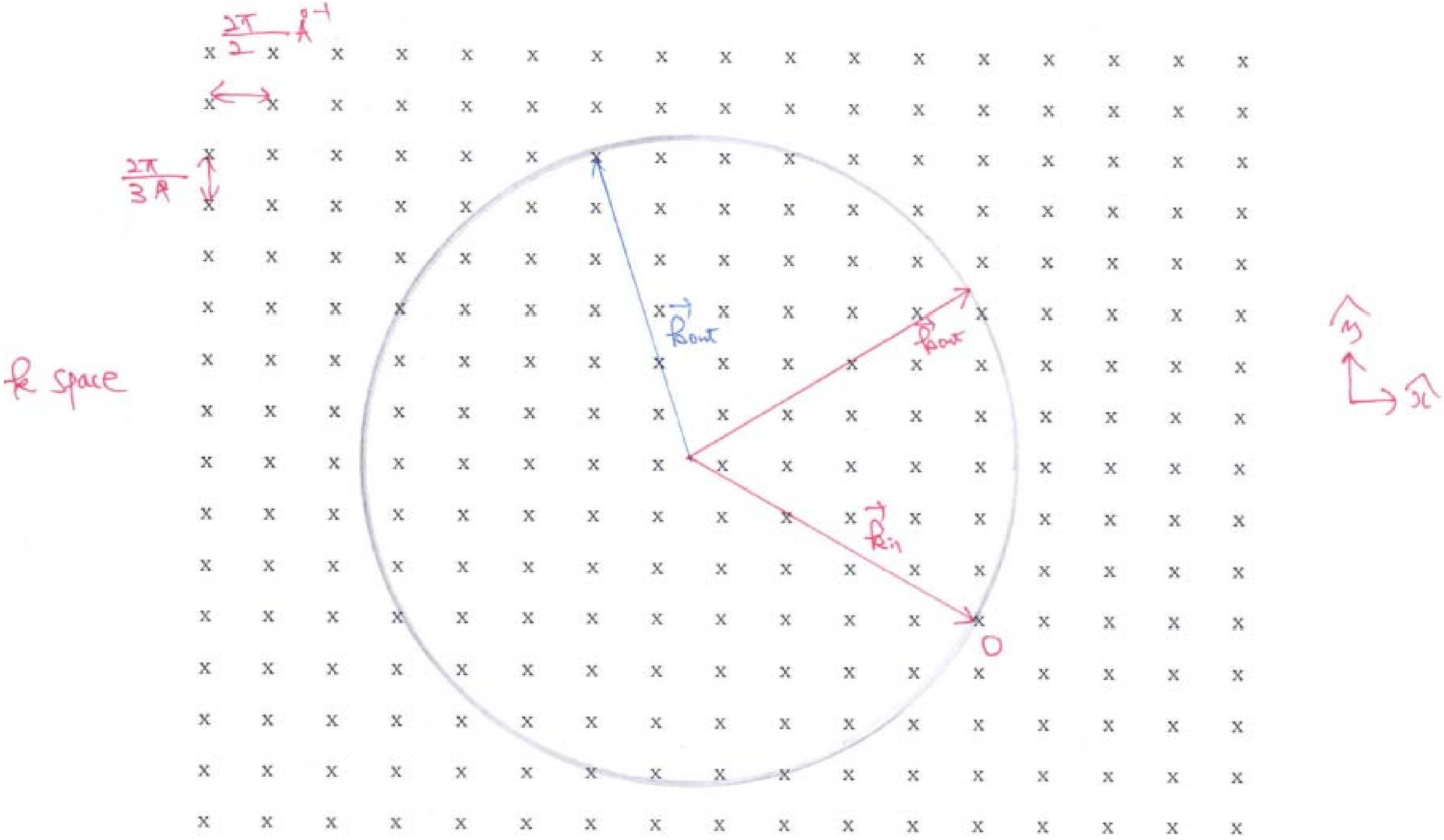
Assumption: $\overrightarrow{k_{in}} = \frac{1}{\lambda}$

**Sorry for the different definition of $k_{in}$ (2π/λ or 1/λ).**

# Real Space

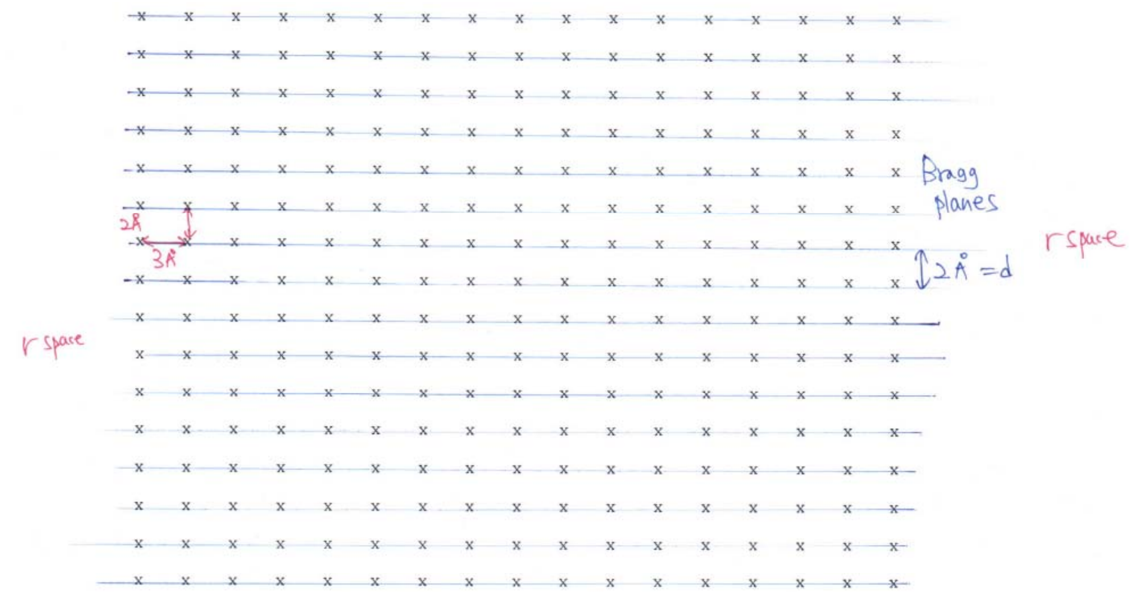


# Ewald Sphere

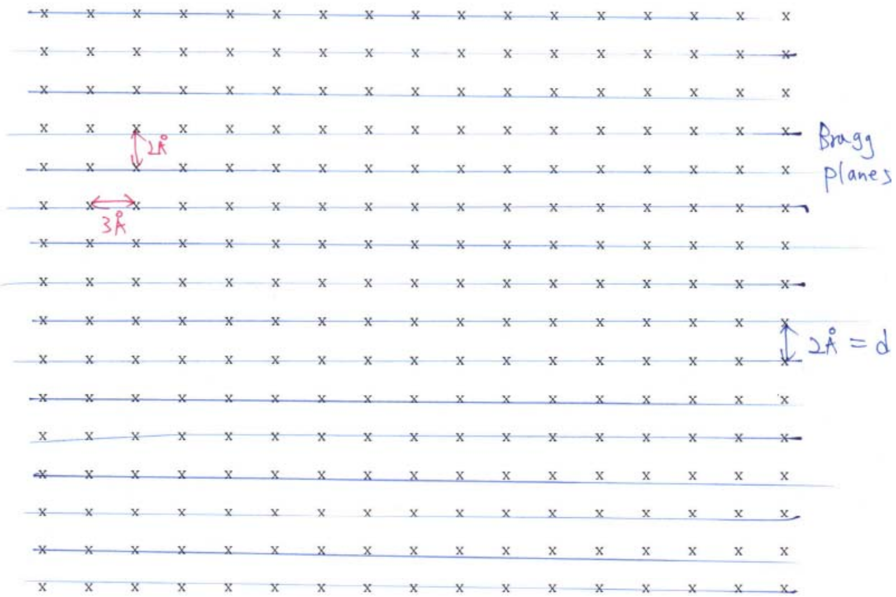


$$\vec{k}_{out} - \vec{k}_{in} = \vec{k}$$

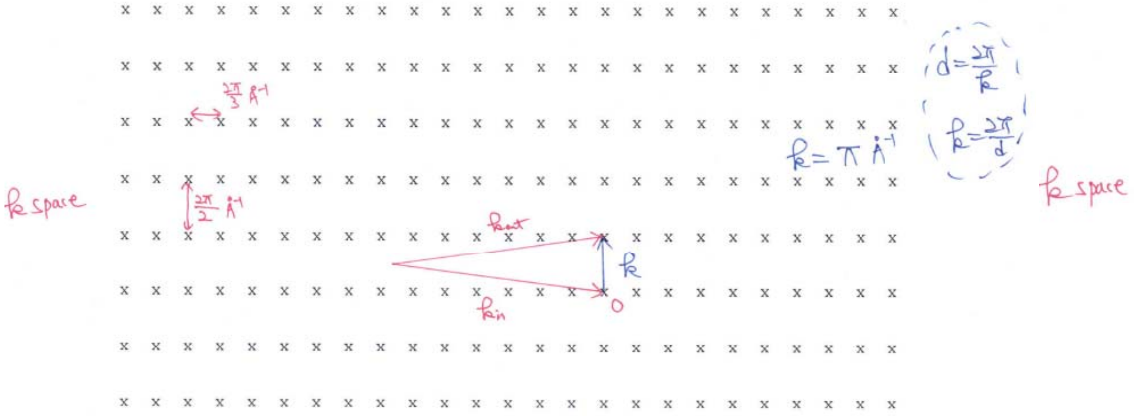
# Laue Condition



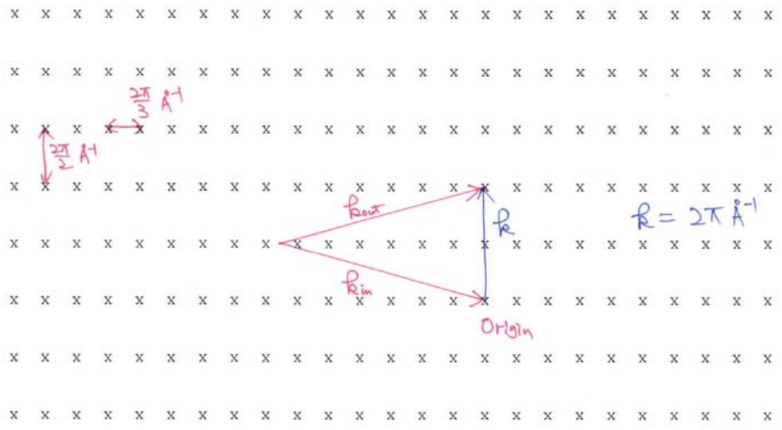
$2d \sin\theta = \lambda$



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

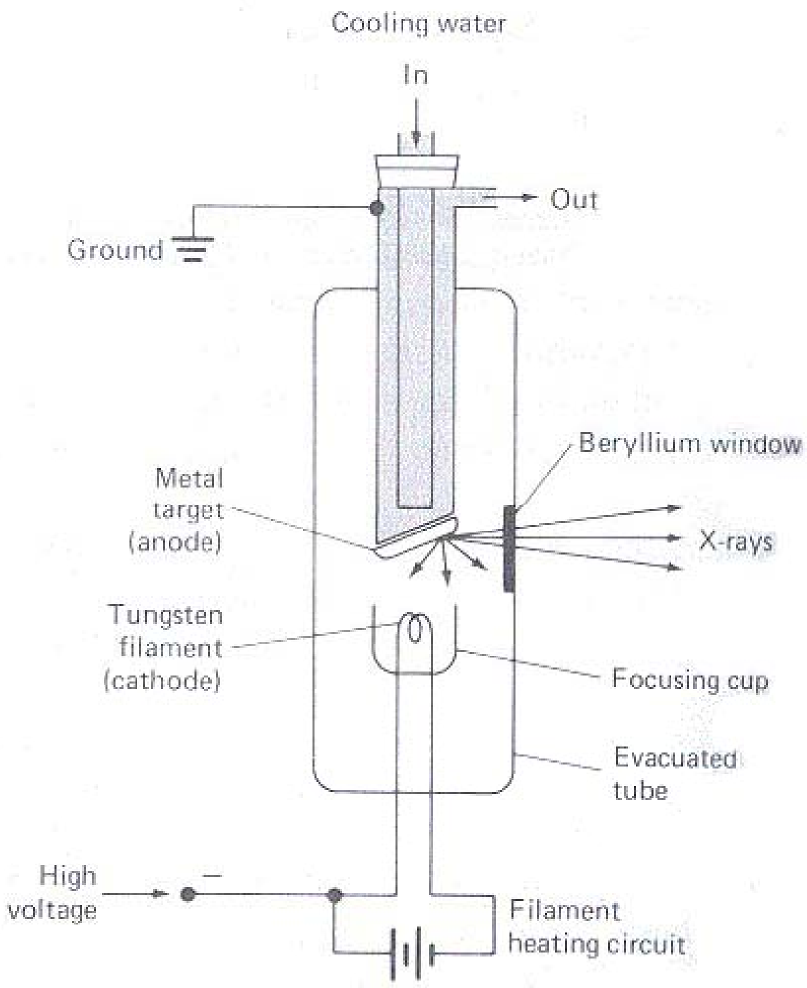


$k_{in} = 4\pi$ Å$^{-1}$ $= \frac{2\pi}{\lambda}$ So $\lambda = 0.5$ Å

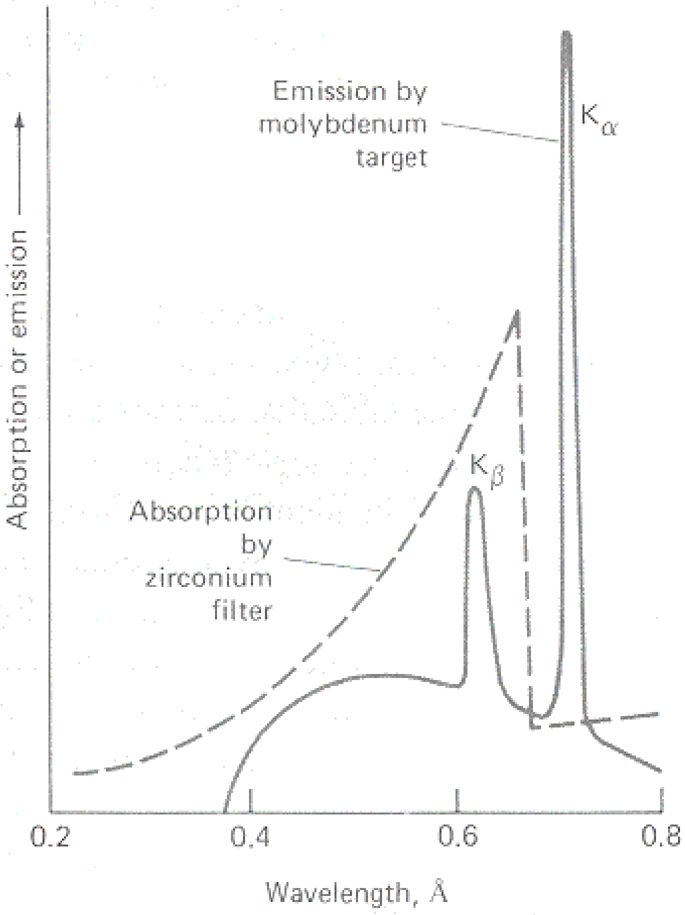


$k_{in} = 4\pi$ Å$^{-1}$ $\lambda = 0.5$ Å

# X-Ray Source

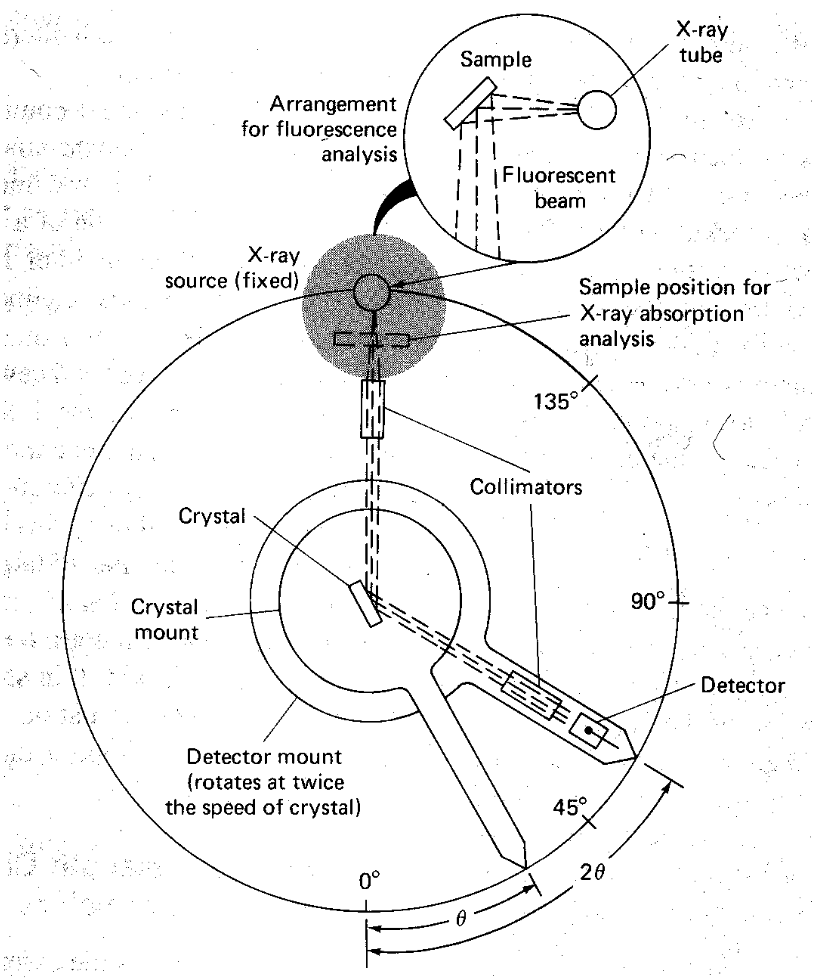


Schematic of an x-ray tube



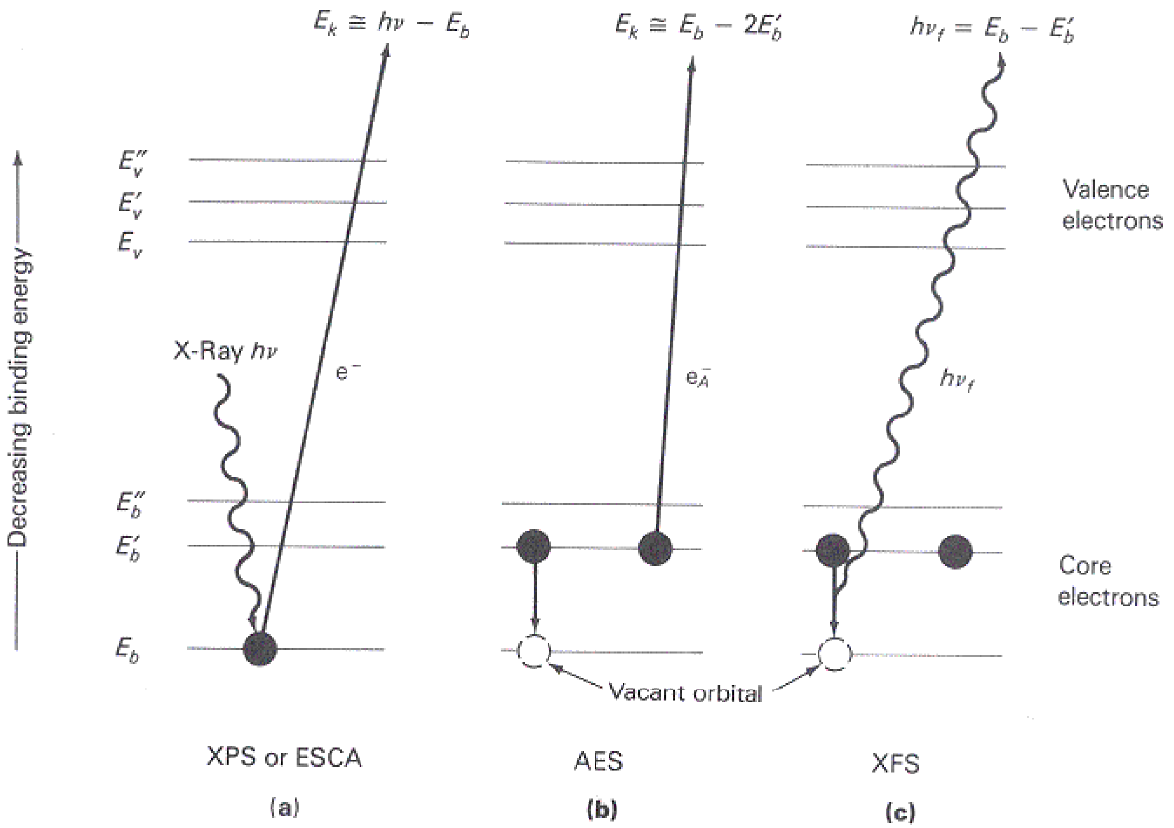
Filter to produce monochromatic radiation

# *Θ-2θ Diffraction*



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

# *Principles of Electron Spectroscopy*

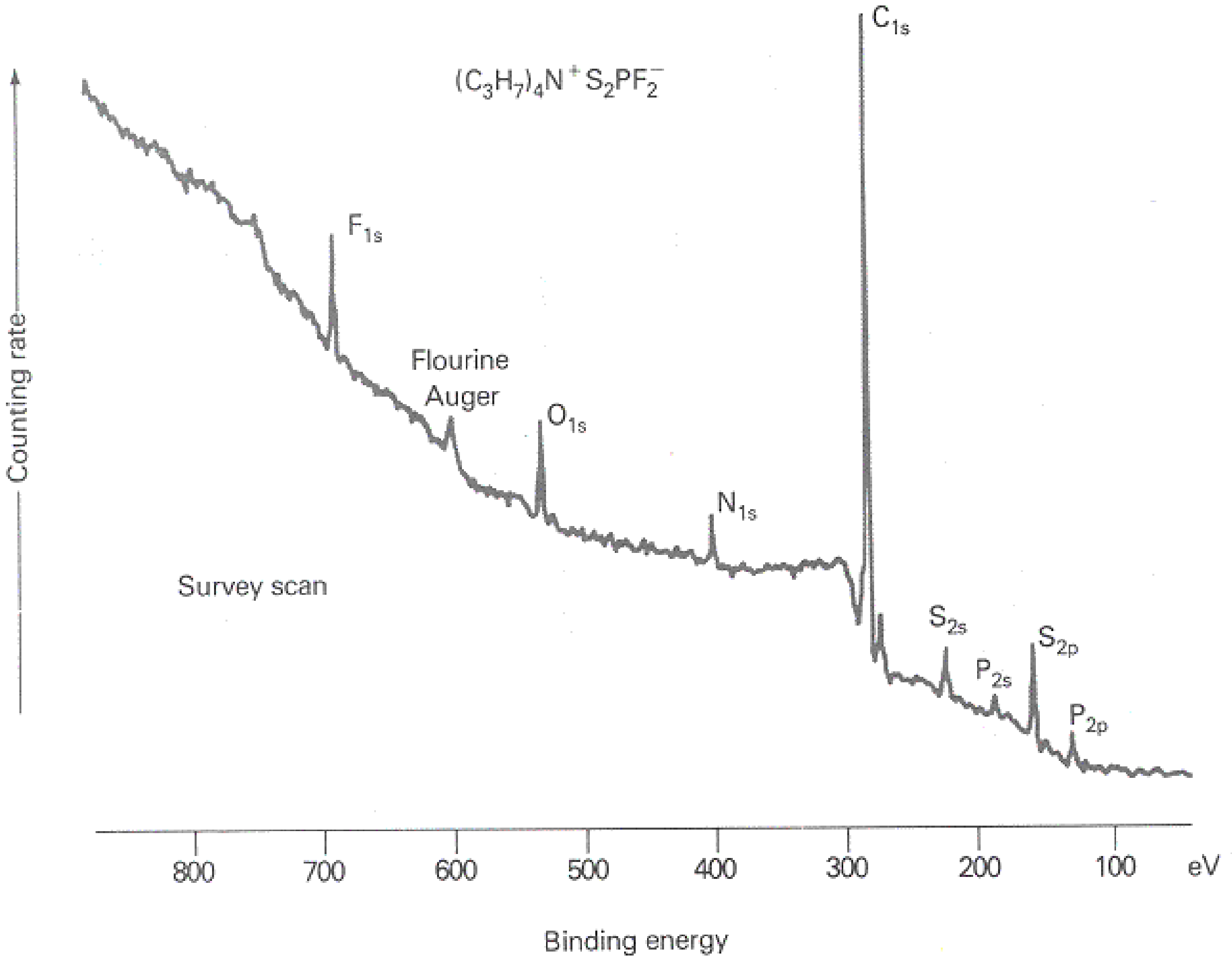


**XPS, ESCA** **AES** **X-Ray Fluorescence (EDS, EPMA)**

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.

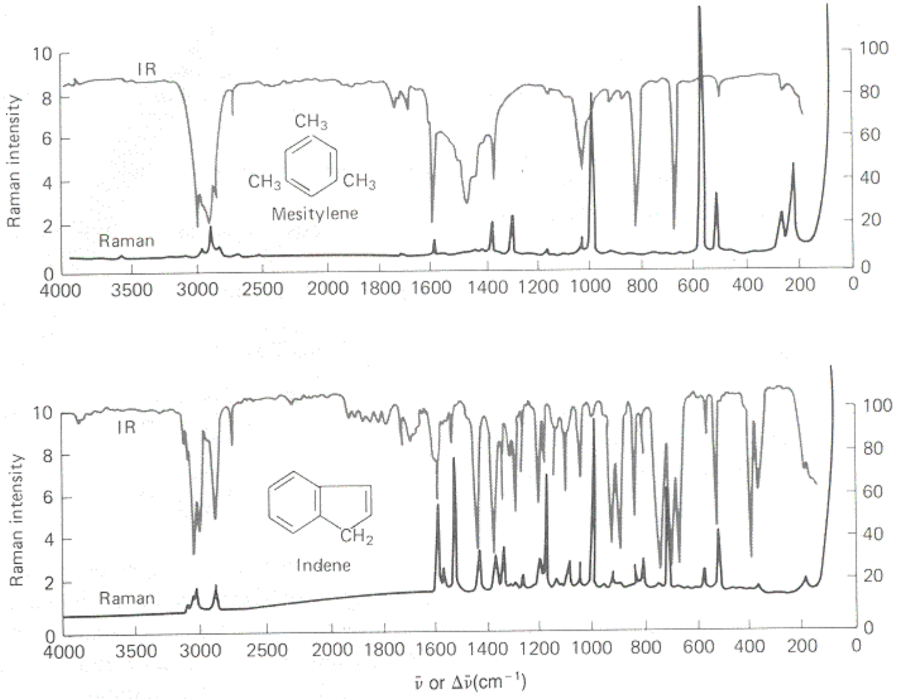
# *X-Ray Photoelectron Spectrum*



XPS of tetra-propyl-ammonium-di-fluoride-thio-phosphate.

# *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.

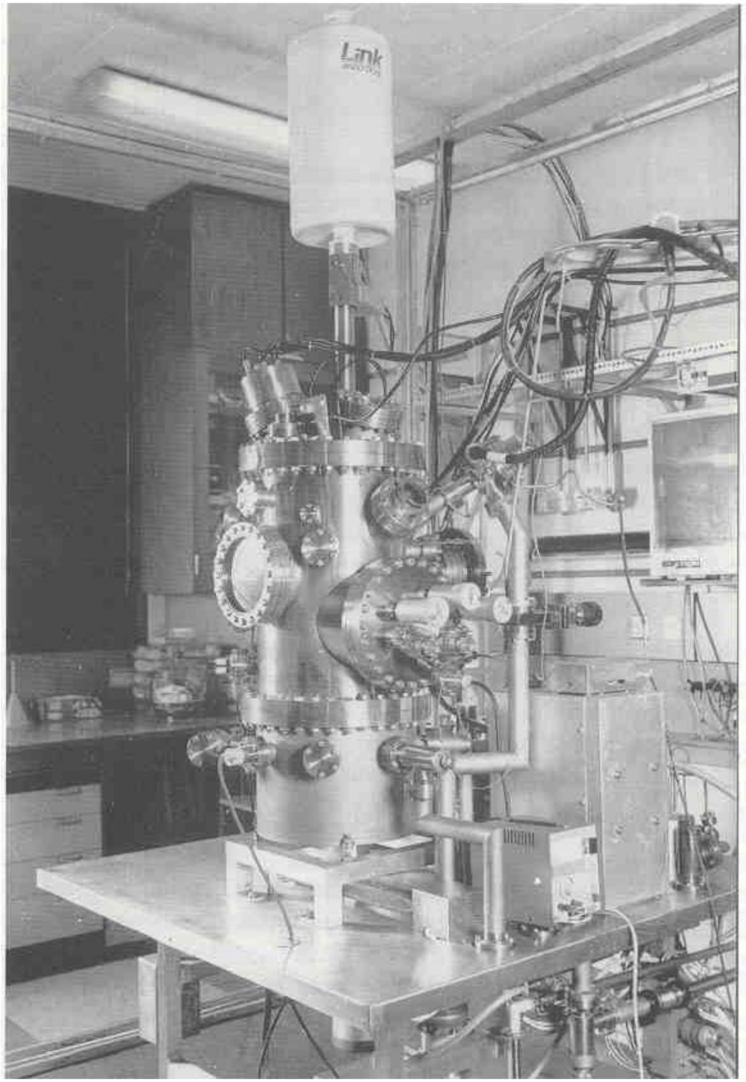


Comparison between Raman and FTIR

# *Fourier Transform Infrared Absorption Spectroscopy (FTIR)*

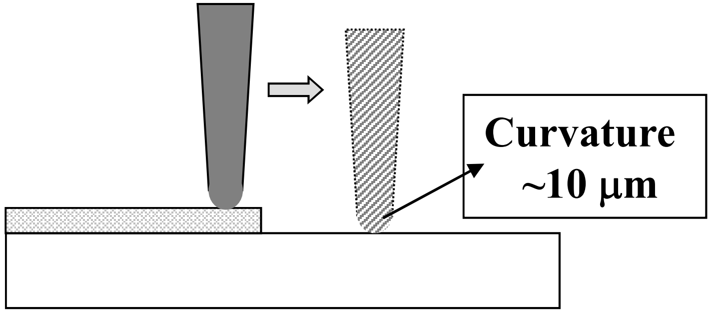
- Resolution: 0.026 $cm^{-1}$
- Spectral range: 5 - 4500 $cm^{-1}$
- IR source:
  - Mercury (원적외선)
  - Globar (중적외선)
  - Quarts-Halogen (근적외선 및 가시광선)
- Detector:
  - MCT detector (450 - 4500 $cm^{-1}$) : operating at 77 K
  - DTGS detector (350 - 7000 $cm^{-1}$) : operating at R.T.
  - Si:B detector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

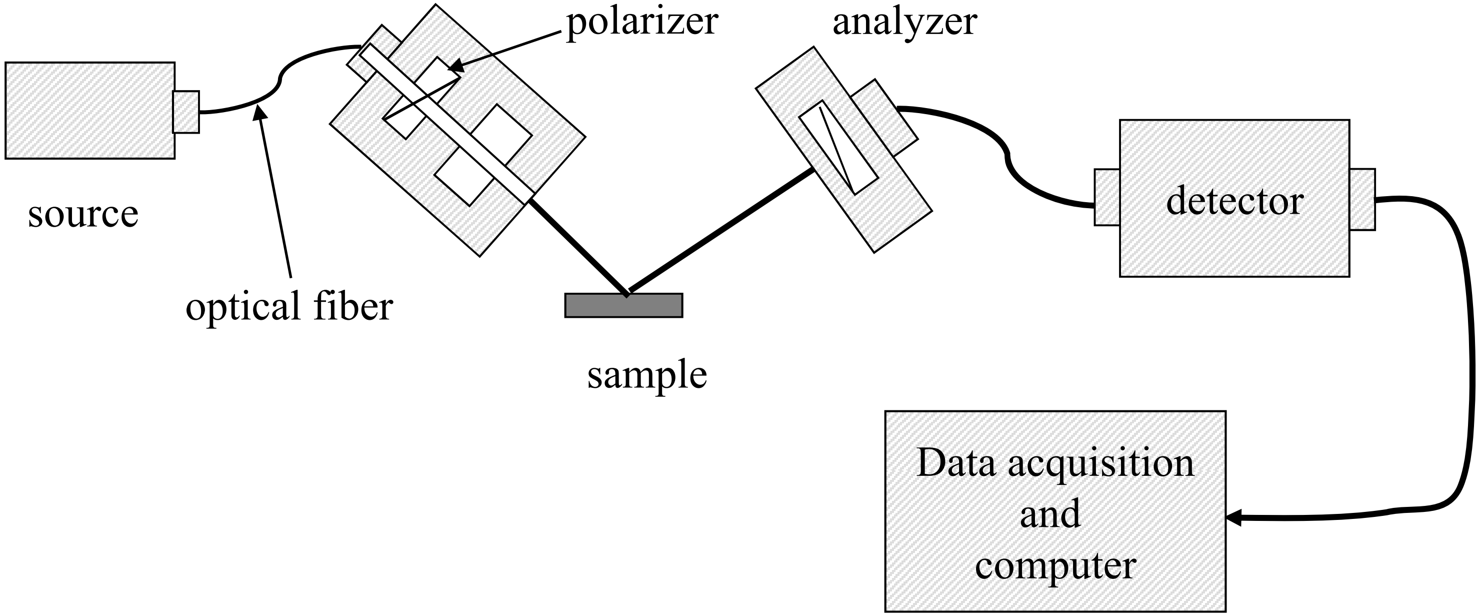
# *α-step (Thickness Measurement)*



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

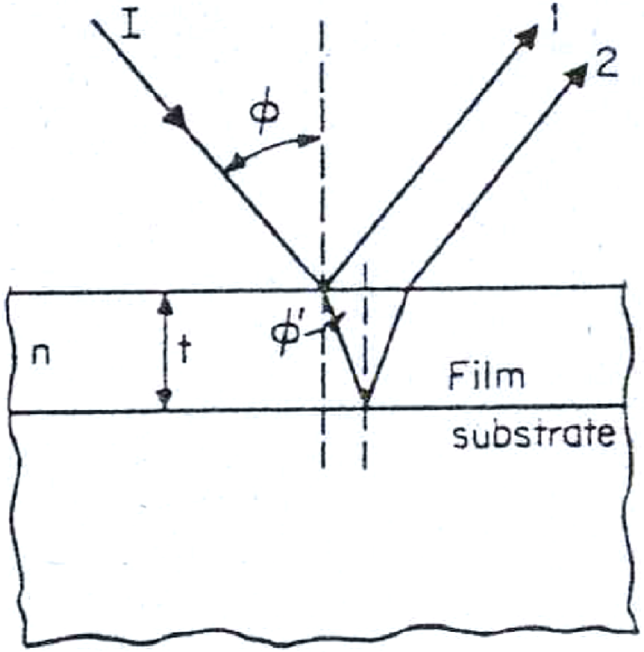
# *Ellipsometry (Thickness Measurement)*

- 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 |

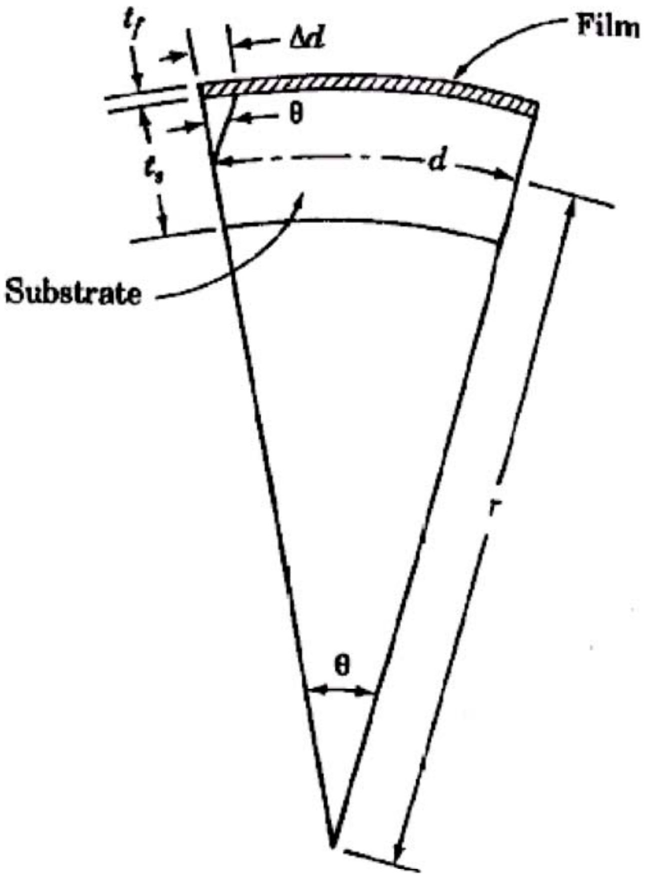


Color chart for thermal dioxide (refractive index of 1.48) and silicon nitride (1.97)

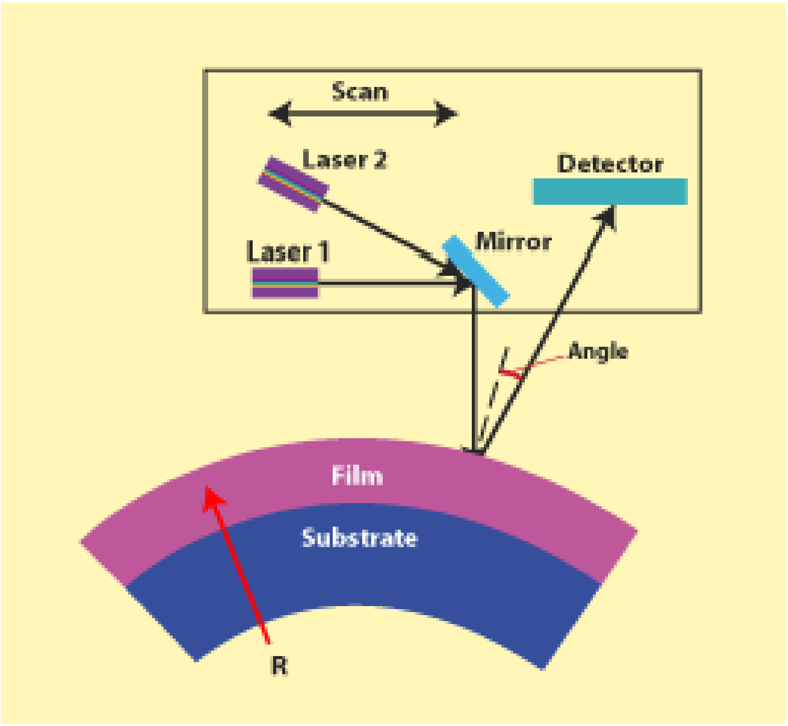
*From Stephen A. Campell, The Science and Engineering of Microelectronic Fabrication, Oxford University Press, 1996*

# *Film Stress*

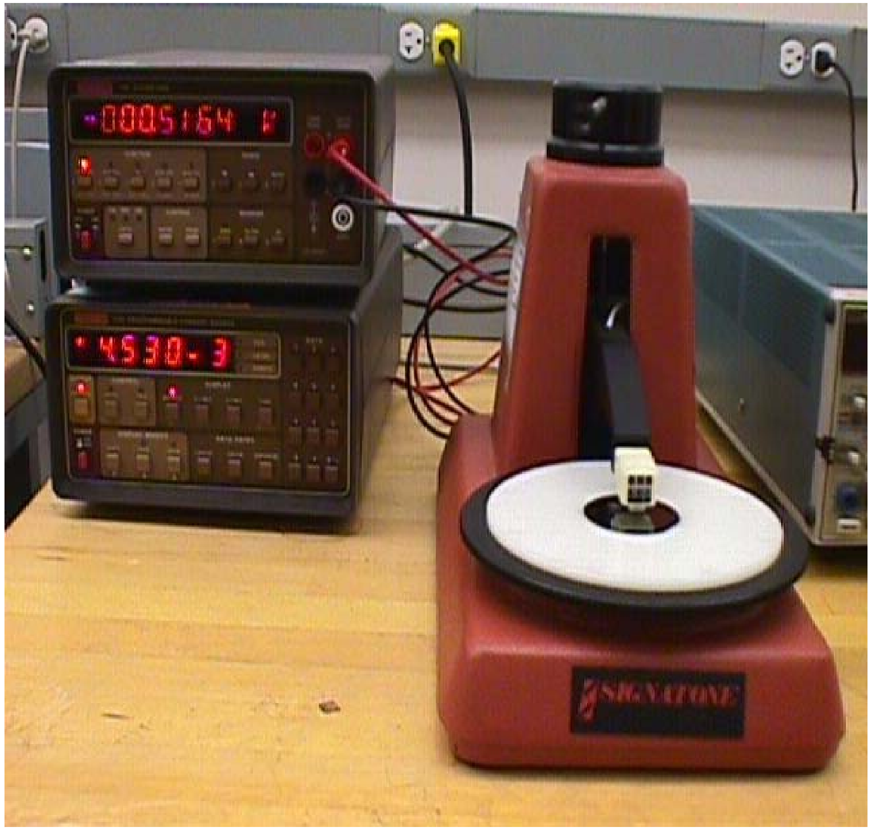
### ❖ Deflected Substrate & Film

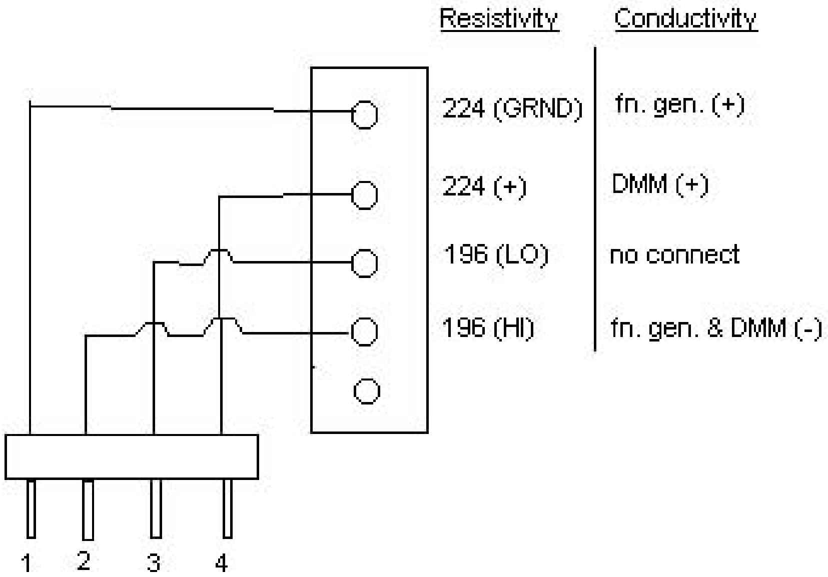


### ❖ Laser Scanning Measurement



# 4 Point Probe (Conductivity Measurement)

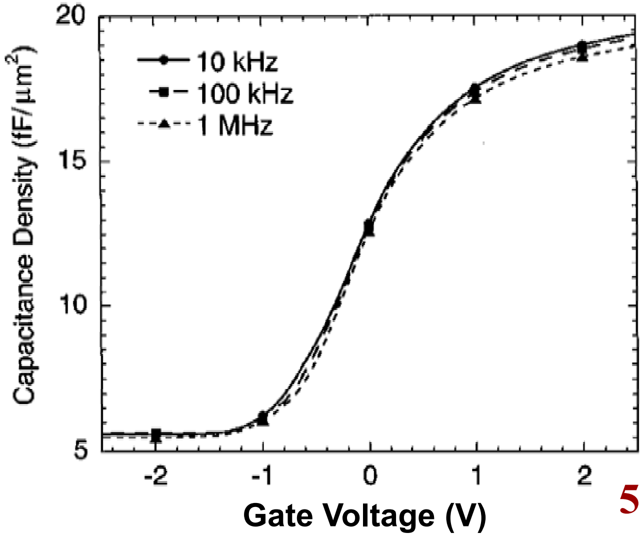




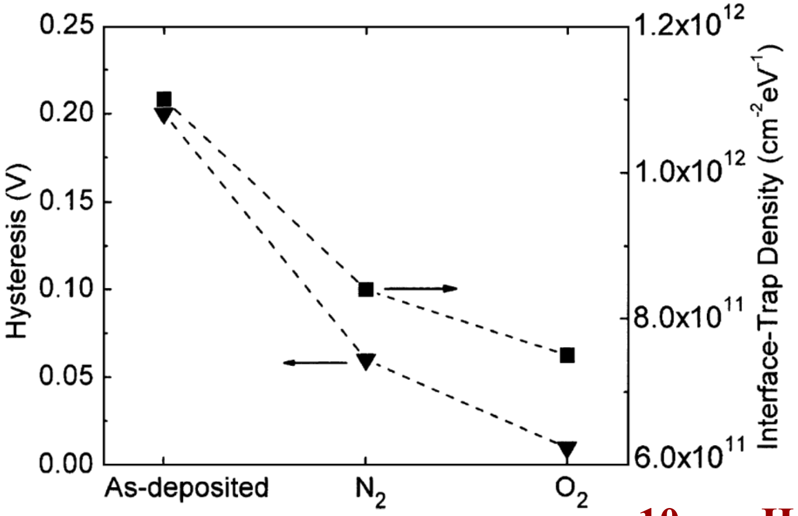
| Resistivity | Conductivity |
|---|---|
| 224 (GRND) | fn. gen. (+) |
| 224 (+) | DMM (+) |
| 196 (LO) | no connect |
| 196 (HI) | fn. gen. & DMM (-) |

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

# *Capacitance-Voltage Measurements*

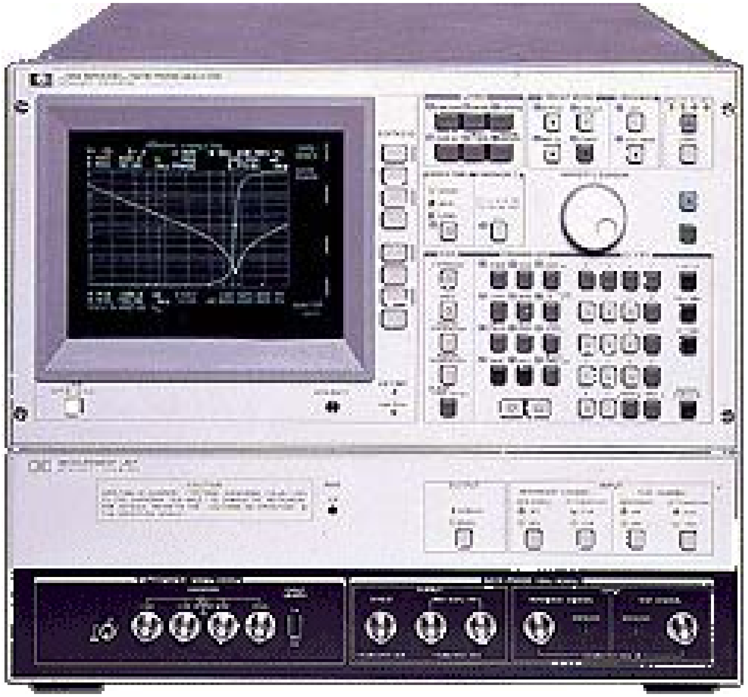


**5 nm $HfSi_xO_y$** *APL* (1999)

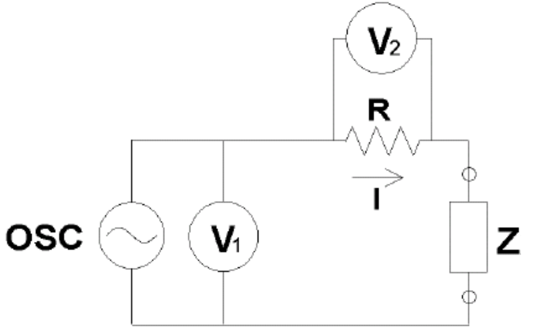


**10 nm $HfO_2$** *APL* (2005)

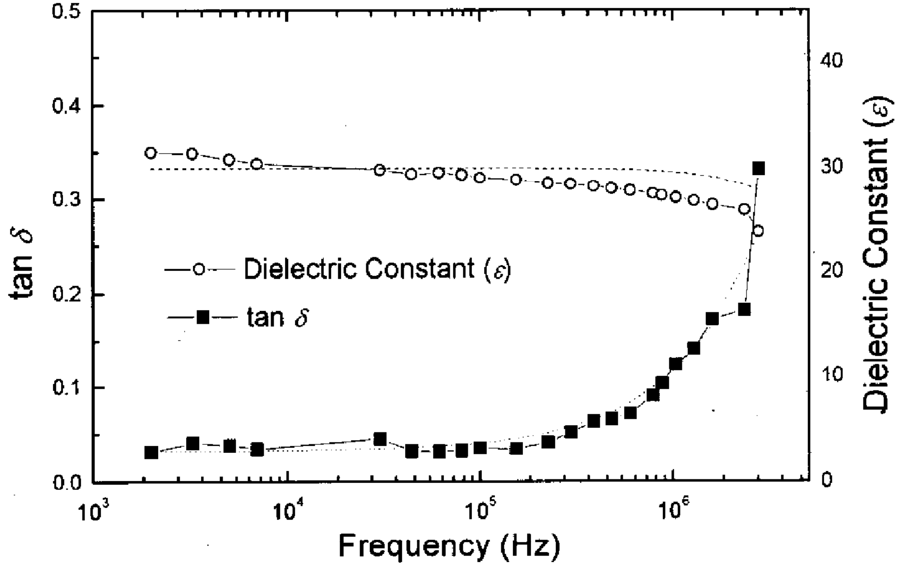
# *Impedance Analyzer*



I-V method

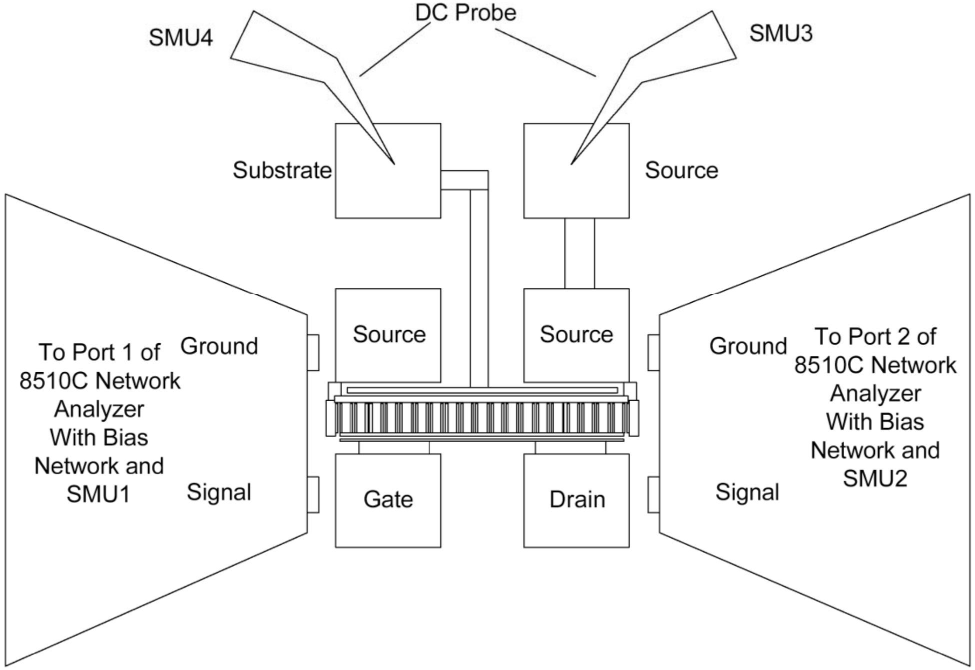


$$Z = \frac{V_1}{I} = \frac{V_1}{V_2} R$$

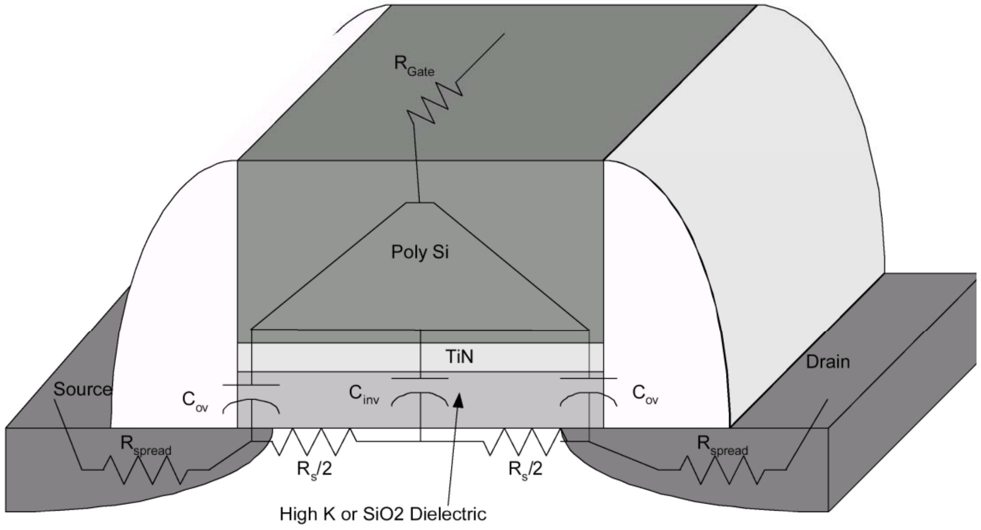


- *APL* (2000)

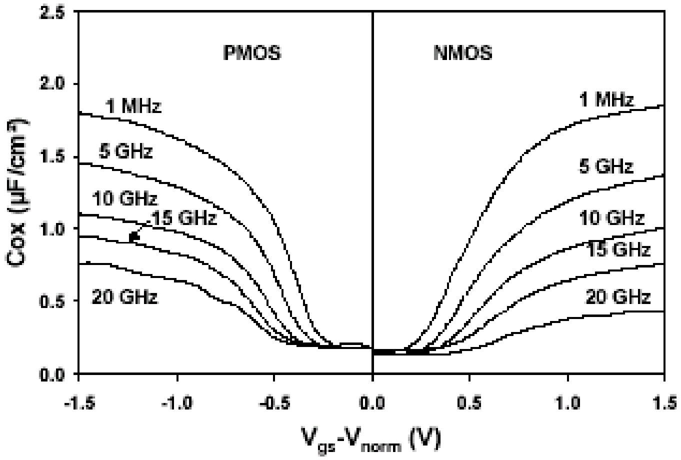
# Network Analyzer

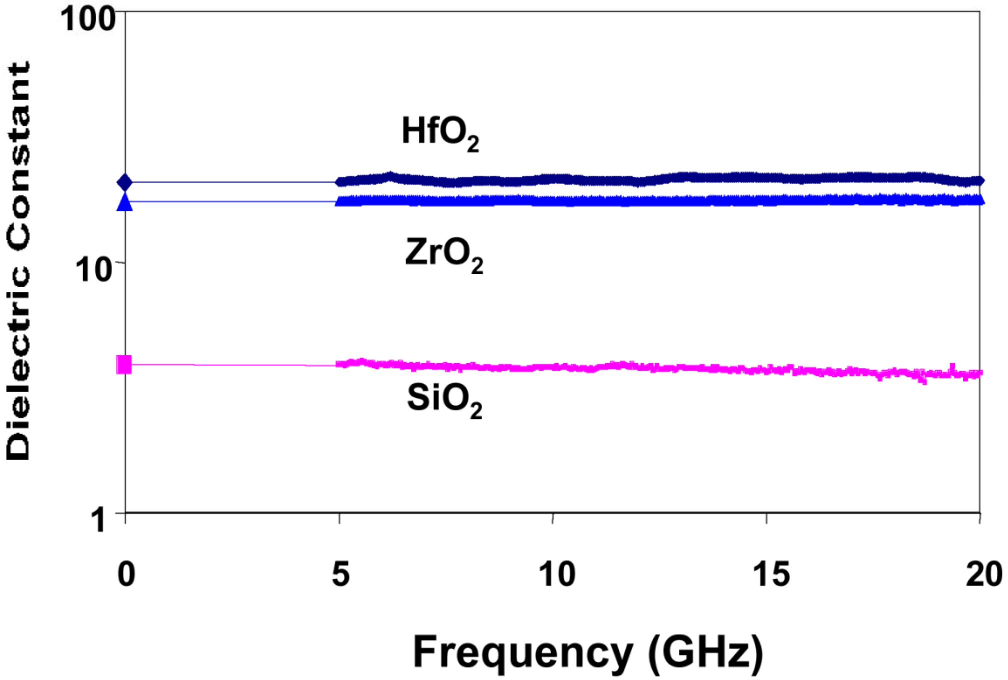


# *Network Analyzer*



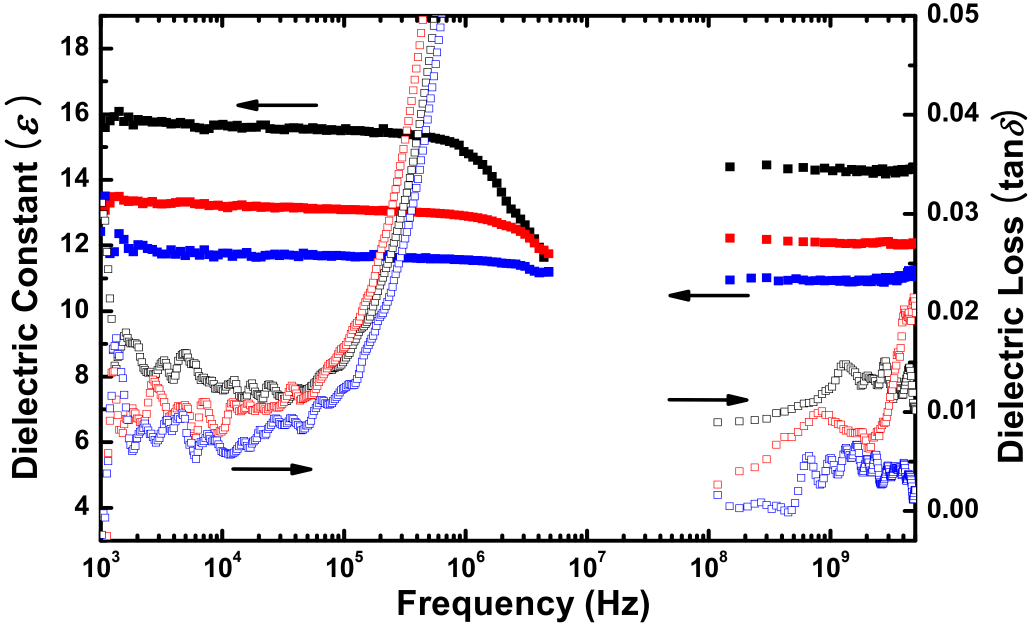
$R_{spread} < R_{gate} < R_s/2$

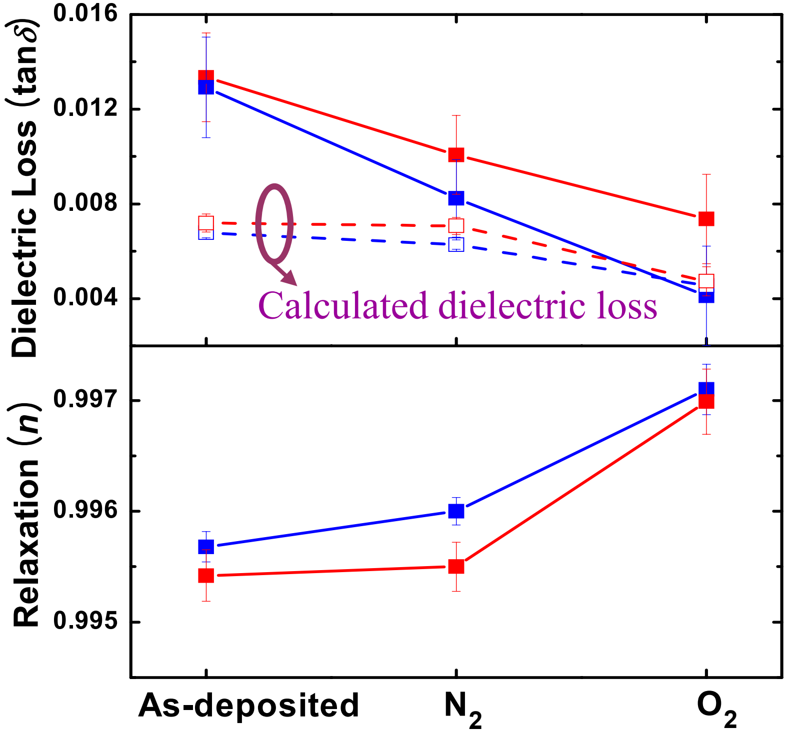




- Intel, *IEEE* (2001)

# ALD $HfO_2$ Thin Film-Dielectric Relaxation

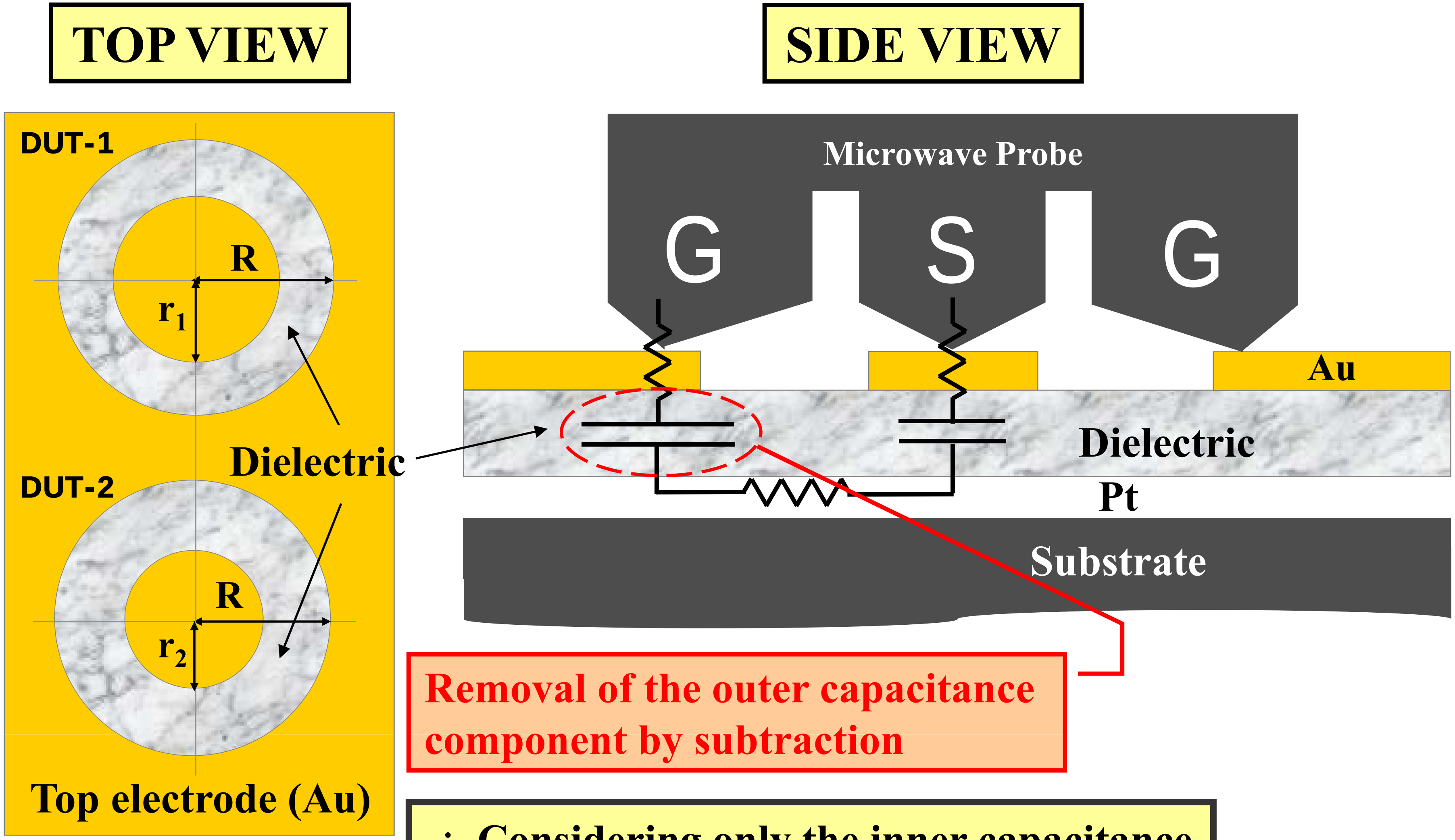




- Curie-von Schweidler relaxation from 1 kHz to 5 GHz.
- Dielectric relaxation depends on the annealing condition.
- Various defects in the $HfO_2$ layer and/or interface.

➤B. Lee, T. Moon, T.-G. Kim,
D.-K. Choi, and B. Park
<u>Appl. Phys. Lett.</u> **87**, 012901 (2005).

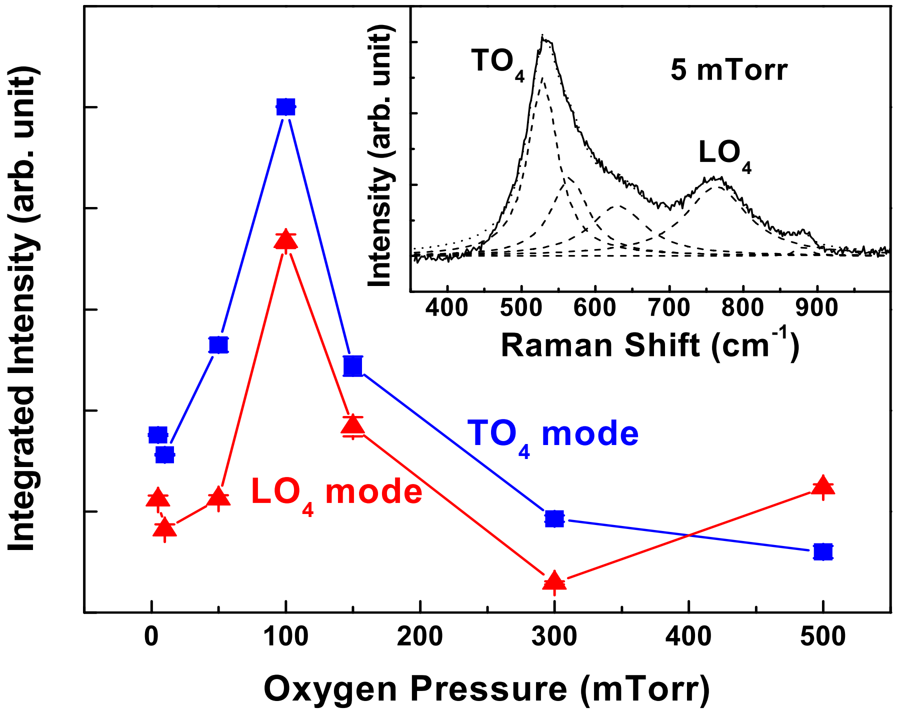
# *Measurement Technique at GHz-Frequency Ranges*

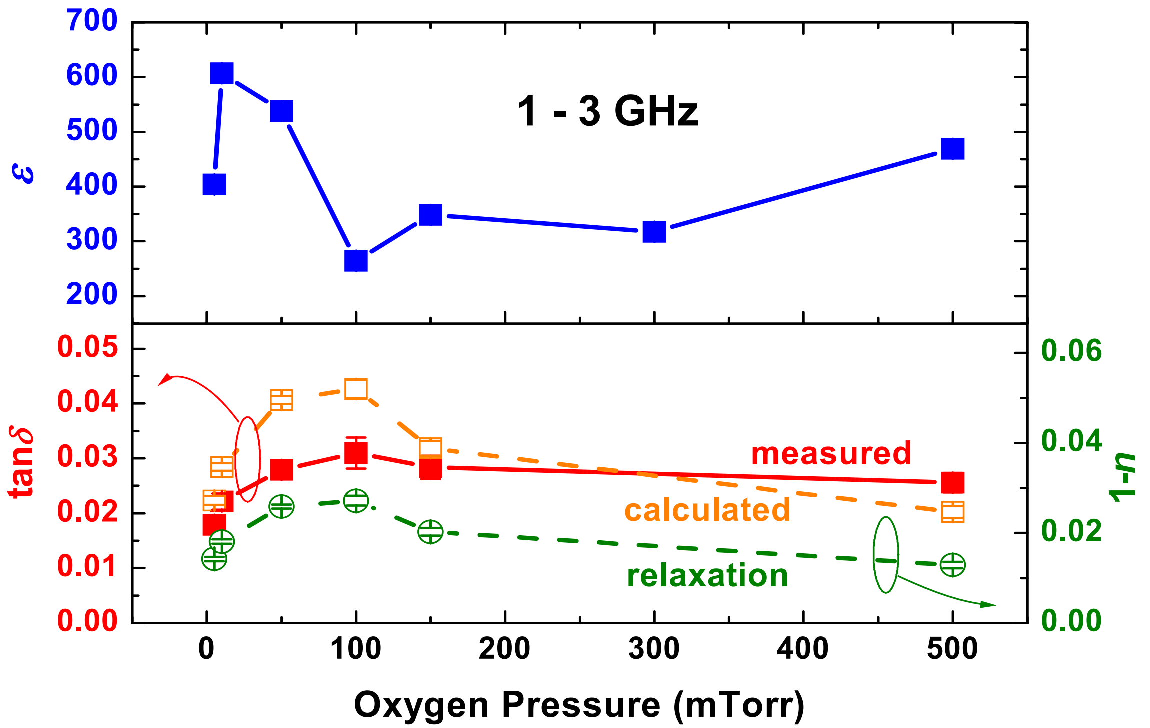


**Removal of the outer capacitance component by subtraction**

**∴ Considering only the inner capacitance**

# (Ba,Sr)TiO$_3$ Thin Film: Microwave Dielectric Relaxation





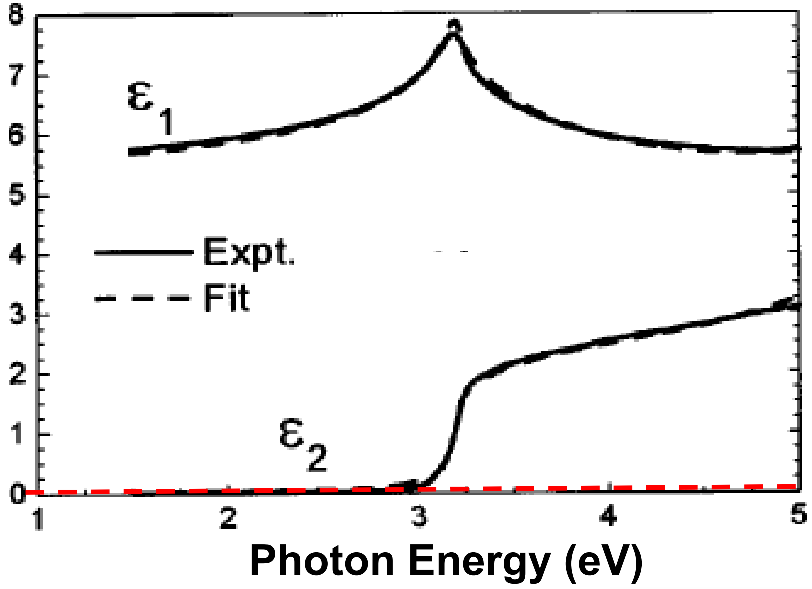
- Ferroelectric fluctuation
- Nanopolar reorientation
- Defect dipole related oxygen vacancy (Vo¨)

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

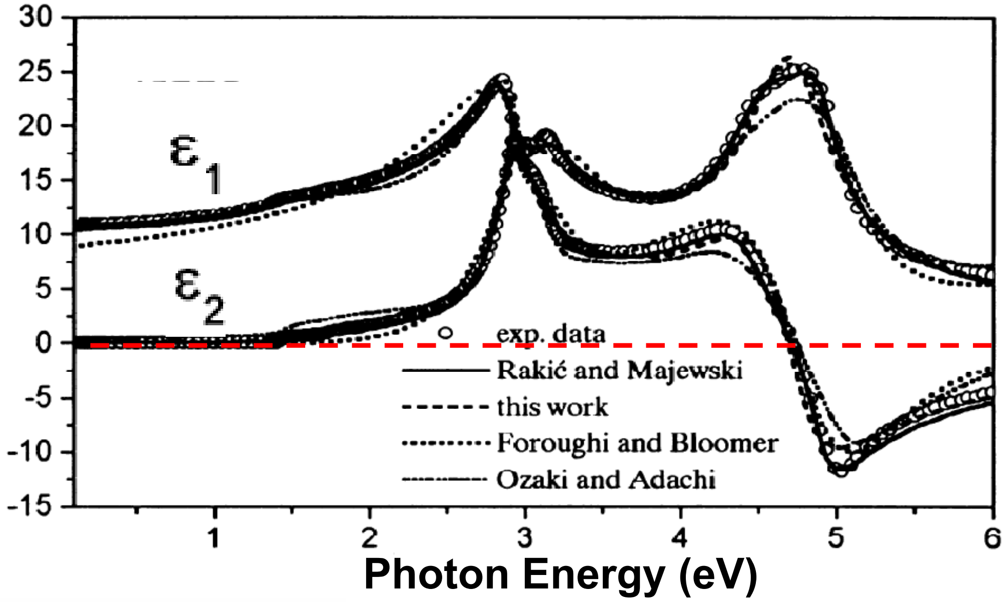
# *Dielectric Constant vs. Photon Energy*

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

**c-GaN**



**c-GaAs**



***$E_g$* ~3.2 eV**

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

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

with a complex refractive index

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

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

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

***$E_g$* ~1.4 eV**

Djurisic's Group
*Thin Solid Films* (2000)