# Optical Properties of Solids
## Lecture 1

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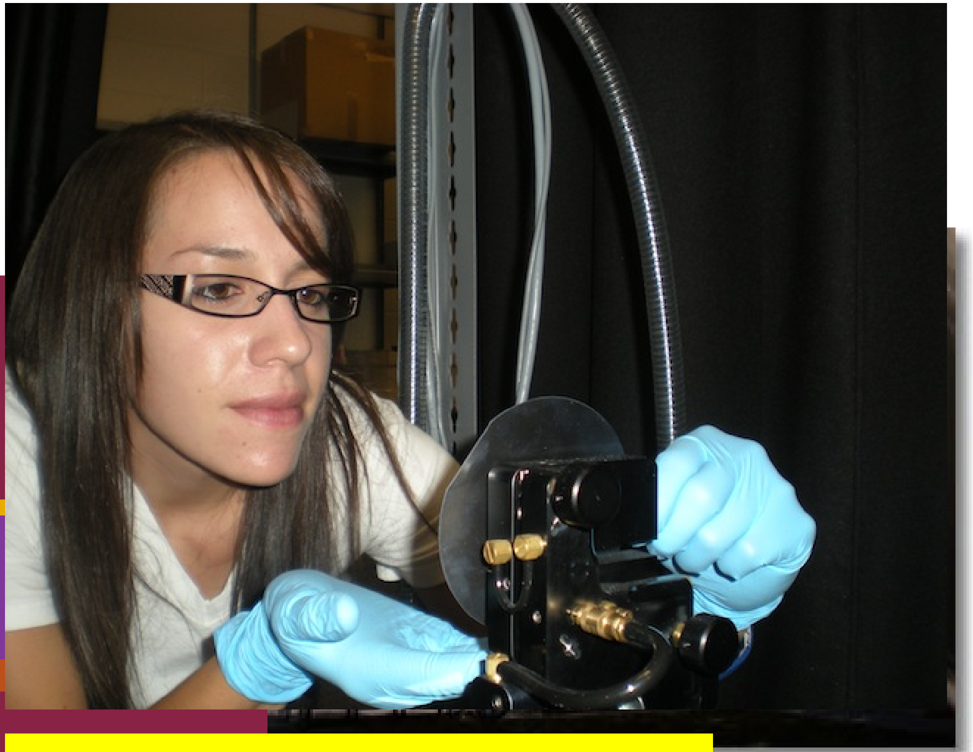

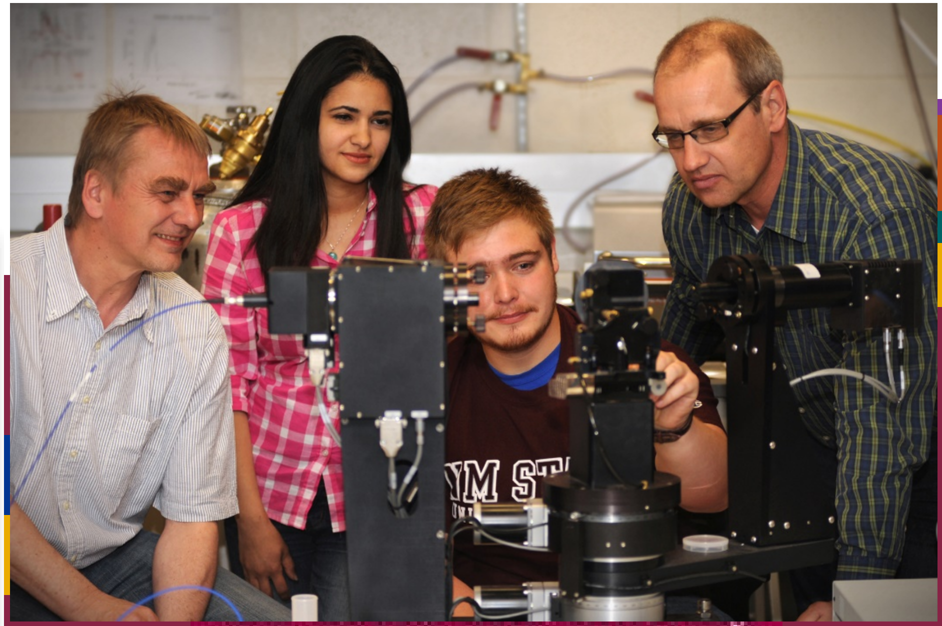

http://ellipsometry.nmsu.edu

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# Acknowledgements

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EUROPEAN UNION
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MINISTRY OF EDUCATION,
YOUTH AND SPORTS

# Contributions by Czech researchers

Jan Tauc
Brown University
a-Si:H (solar cells)

Karel Kunc
Sorbonne (Paris)
lattice dynamics

Josef Humlicek
Masaryk U
ellipsometry

Bedrich Velicky
FZU
Ge, excitons, KK

**Others:**

Frantisek Lukes, E. Schmidt (Masaryk University, Brno)
Libuse Pajasova, A. Abraham, E. Antoncic, B. Velicky: Reflectance on Ge and $GeO_2$
E. Antoncic: Temperature dependence of band gaps

**Czechoslovak Journal of Physics (1952-2006, Springer online)**
**1960 ICPS-5 Conference held in Prague**

# Optical Properties of Solids: Lecture 1

- Introductions: Why are we here?
- Lecture series overview
- Spectroscopy: what is that?
- Experimental spectroscopy techniques
- Optical constants:
  - Complex refractive index
  - Complex dielectric function
  - Absorption coefficient, extinction coefficient
  - Normal-incidence reflectance
- Solid-State Physics:
  What can we learn from optical properties?

# Where is Las Cruces, NM?

# Biography

Regensburg/Stuttgart
Germany

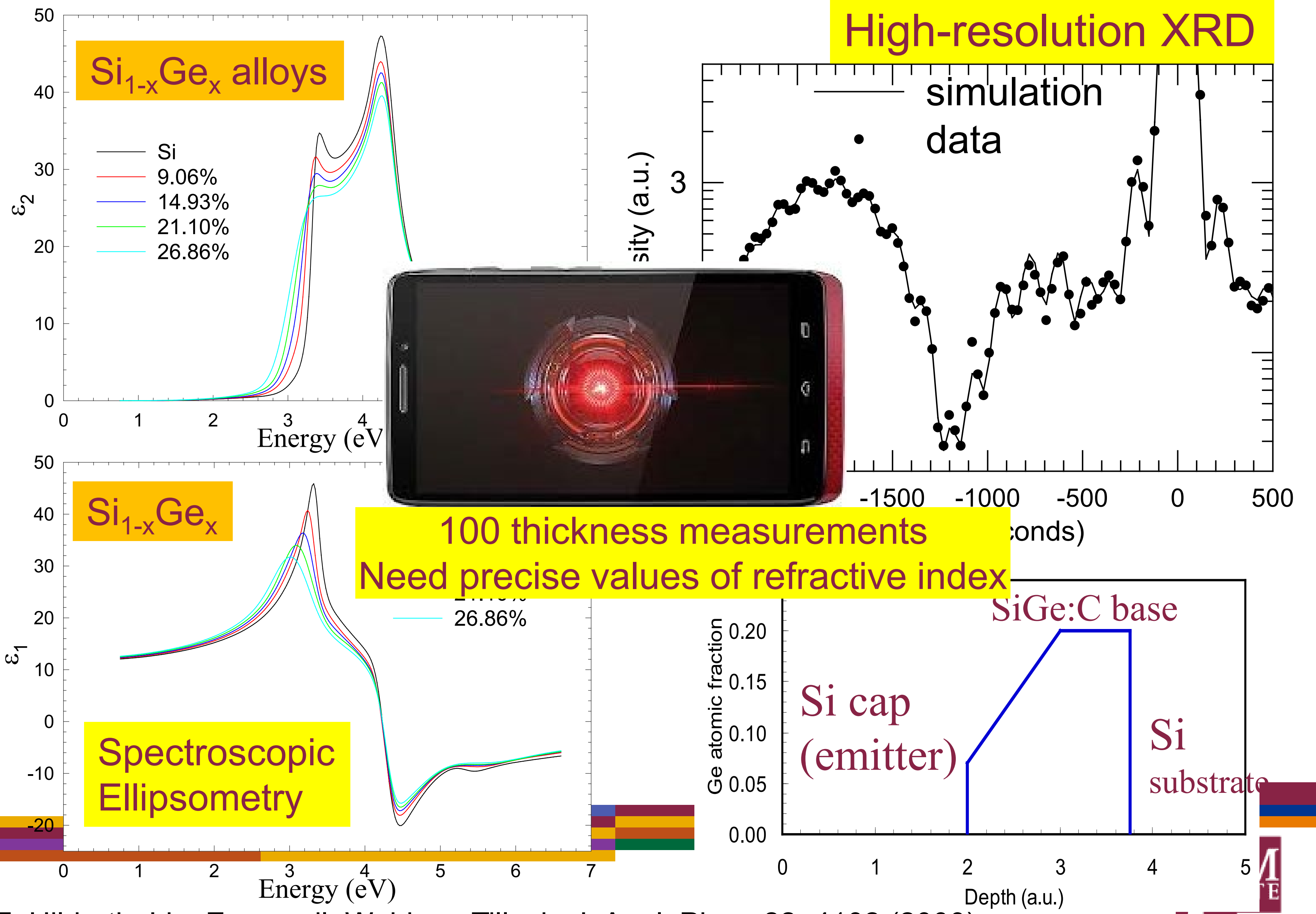
Motorola (Mesa, Tempe)
Arizona, 1997-2005

Freescale, IBM
New York, 91-92;07-10

Motorola, Freescale
Texas, 2005-2007

Las Cruces, NM
Since 2010

# SiGe:C Metrology: How thick is my film?



$Si_{1-x}Ge_x$ alloys

$Si_{1-x}Ge_x$

Spectroscopic Ellipsometry

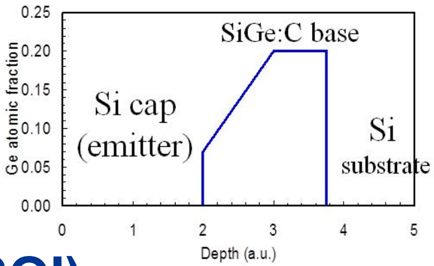
High-resolution XRD

100 thickness measurements
Need precise values of refractive index

SZ, Hildreth, Liu, Zaumseil, Weidner, Tillack, J. Appl. Phys. **88**, 4102 (2000)

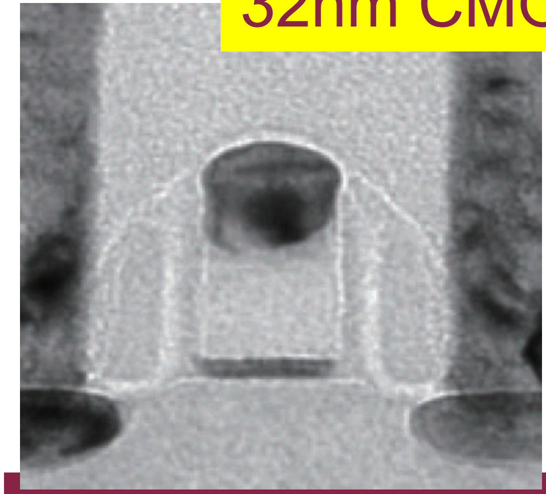
# Key HW accomplishments for 3G smart phones

1. **Power amplifier:**
   InGaP Heterojunction bipolar transistor (HBT)
2. **Low-noise amplifier:**
   Silicon-germanium-carbon HBT

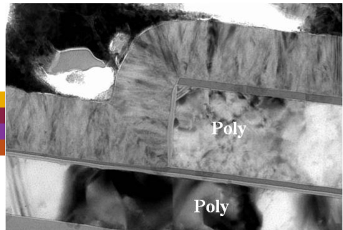


3. **New CMOS materials:**
   Advanced substrate materials (SOI)
   High-k (complex metal oxide) gate dielectrics
   Metal gate
   Si-Ge-C source-drain stressors
   Laser annealing (>100 citations)
   Nickel silicide Ohmic contacts
   Copper interconnects
   Low-k interlayer dielectrics

32nm CMOS on SOI



4. **Power, analog, passives**



Double-poly capacitor

**Grad. Students:** Nuwanjula Samarasingha, Farzin Abadizaman, Carola Emminger, Rigo Carrasco

**Undergraduate Students:** Pablo Paradis,Cesy Zamarripa, Zachary Yoder

**Collaborators:** Jose Menendez (Arizona State), Sudeshna Chattopadhyay (IIT Indore)

**Samples:** Arnold Kiefer (AFRL), Jim Kolodzey (Delaware), John Kouvetakis (Arizona State), Alex Demkov (UT Austin)

Flat, clean, & uniform films, at least 5 by 5 $\text{mm}^2$, 190 nm to 40 $\mu$m, 10-800 K
low surface roughness, layers on single-side polished substrate

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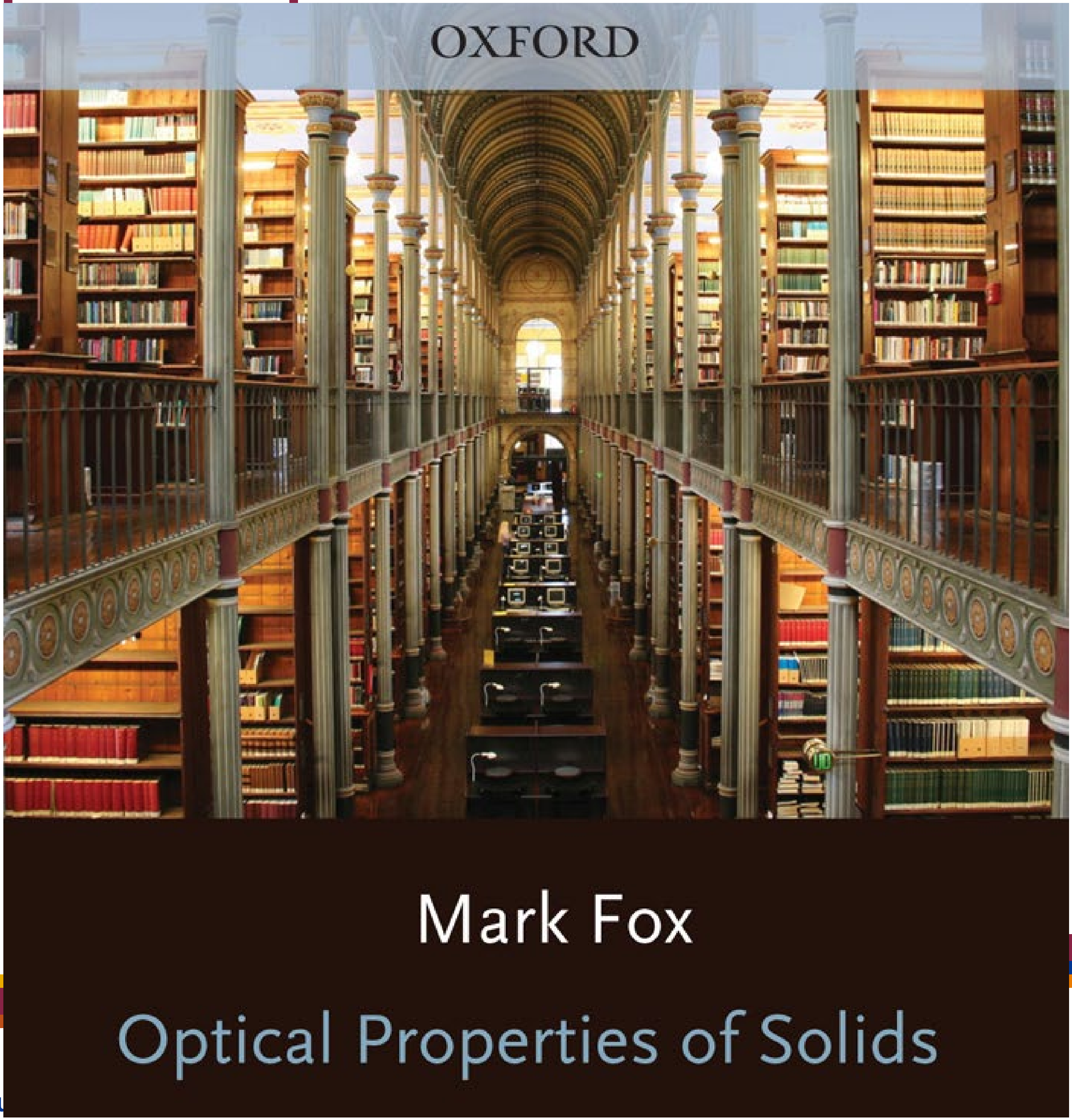
http://ellipsometry.nmsu.edu

# Introductions: Why are we here?

# Optical Properties of Solids: Overview

1. **Overview: spectroscopy, optical constants, and solid-state physics**
2. Crystal structures, Wyckoff positions, point and space groups, classification of optical vibrations
3. Maxwell’s equations in vacuum, plane waves, polarized light
4. Maxwell’s equations in continuous media, dielectric function, Lorentz and Drude model, Sellmeier, poles, Cauchy
5. Analytical properties of the dielectric function, KK relations
6. Application of Lorentz and Drude models to insulators and metals
7. Electronic band structure, direct and indirect gap absorption
8. Free electrons, effective masses in semiconductors, excitons
9. Interband transitions, van Hove singularities, critical points
10. Photoluminescence, Einstein coefficients, quantum confinement
11. Applications: Anisotropic materials
12. Applications: Thin films, stress/strain, deformation potentials

# Optical Properties of Solids: Text Book

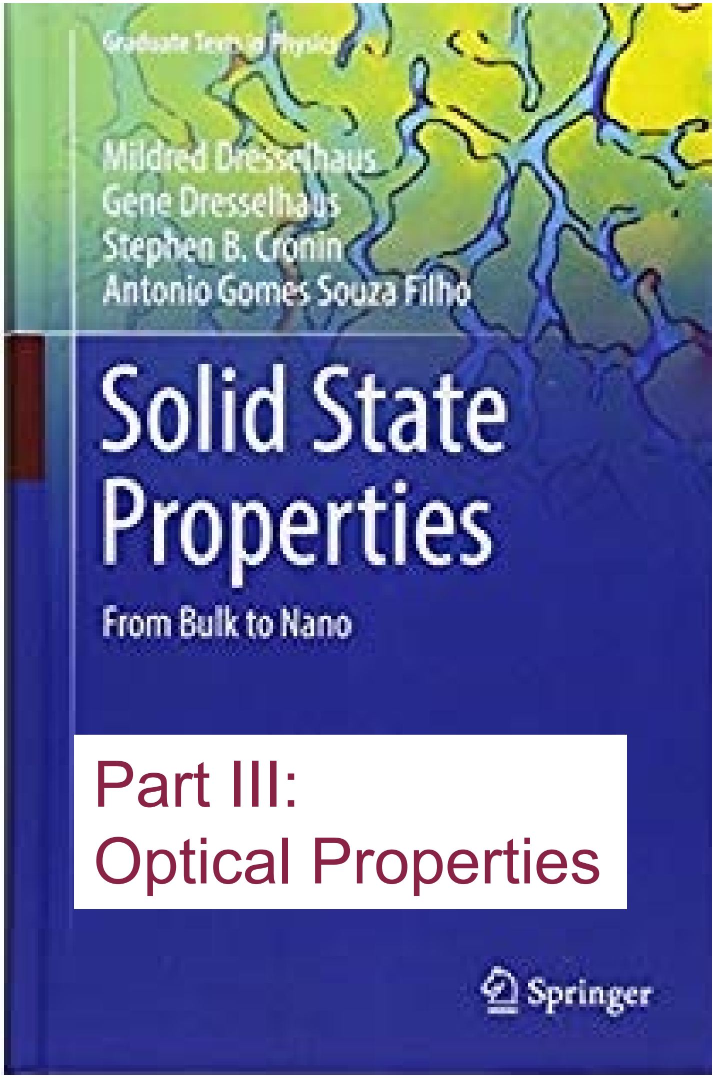


OXFORD

Mark Fox

Optical Properties of Solids

# Optical Properties of Solids: Other Text Books


Graduate Texts in Physics

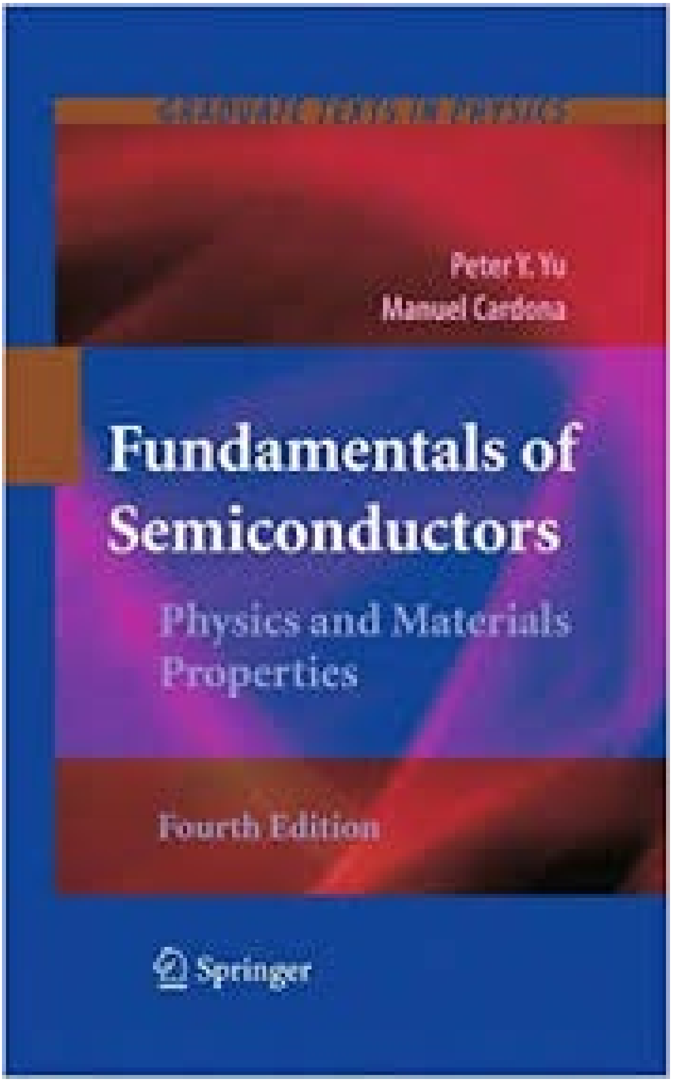
Mildred Dresselhaus
Gene Dresselhaus
Stephen B. Cronin
Antonio Gomes Souza Filho

Solid State Properties

From Bulk to Nano

Springer

Part III:
Optical Properties


GRADUATE TEXTS IN PHYSICS

Peter Y. Yu
Manuel Cardona

Fundamentals of Semiconductors

Physics and Materials Properties

Fourth Edition

Springer

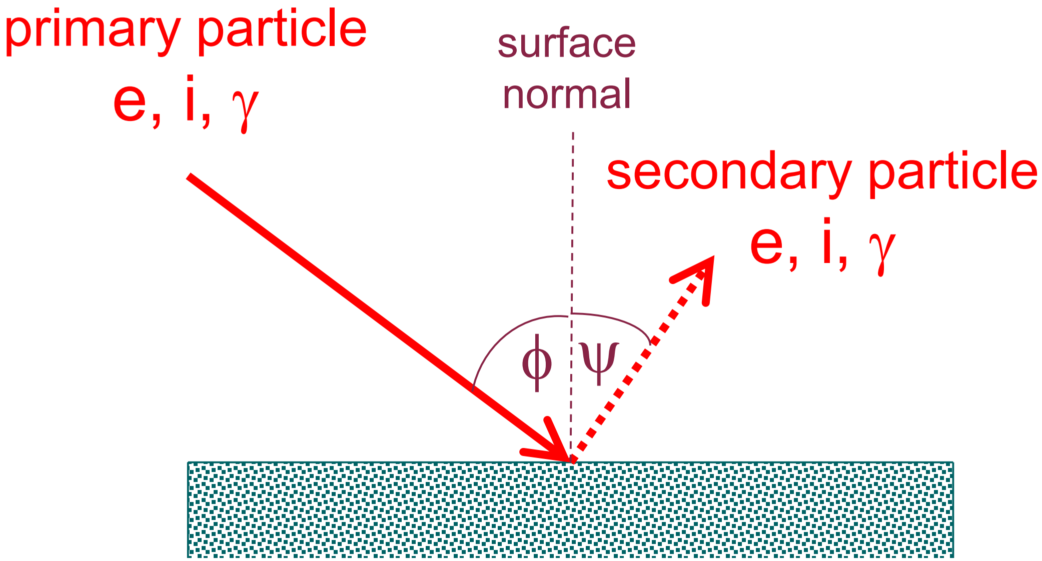
M.L. Cohen &
J. Chelikowsy:
Electronic Structure &
Optical Properties

Tanner (U FL): notes

C. Klingshirn:
Semiconductor Optics

**Ellipsometry:**
Fujiwara
Tompkins/Hilfiker
Fujiwara/Collins
Palik I, II, III
Azzam/Bashara

# Classification Schemes for Surface Spectroscopy I



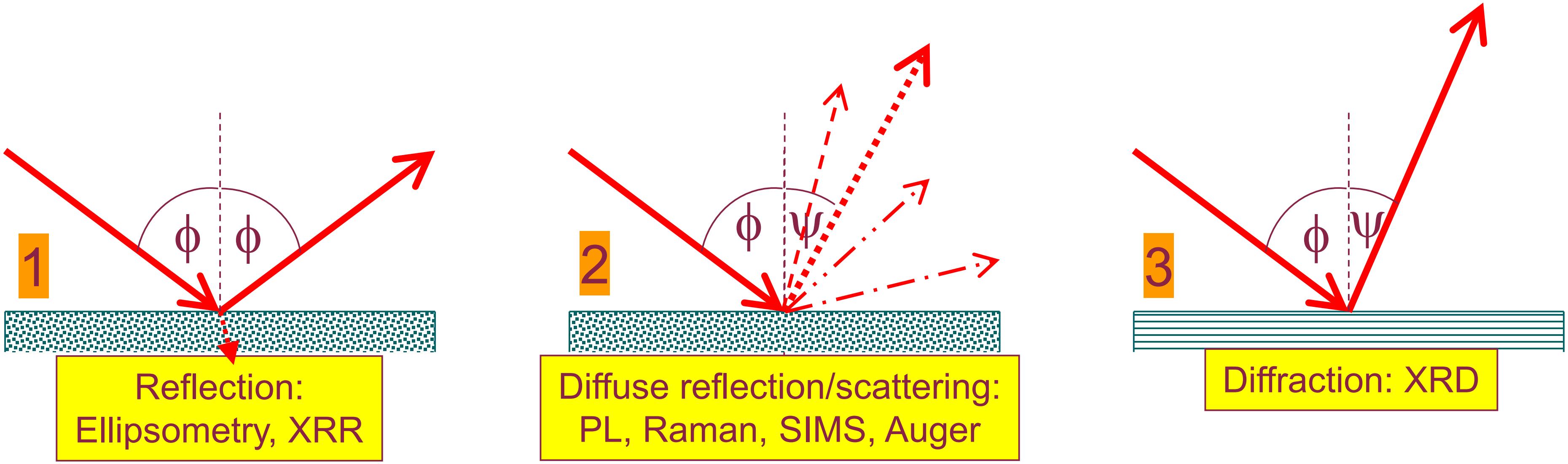
**Particles:** Electron (e), ion (i), or photon (γ)

The term **spectroscopy** implies that we prepare, vary, or measure the **energy (wavelength)** and/or **momentum** of the primary and/or secondary particle.

For **photons**, we can also measure the **polarization** of the primary and/or secondary photon.

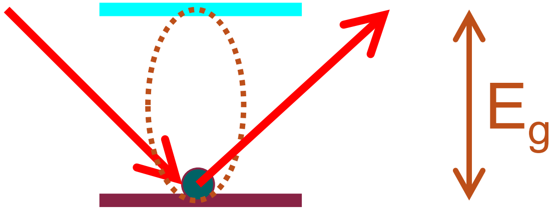
The **interaction depth** for thin films depends on the **penetration depth** of the primary particle and the **escape depth** of the secondary particle. (This can be nanometers to micrometers, depends on each technique.)

# Classification Schemes for Surface Spectroscopy II

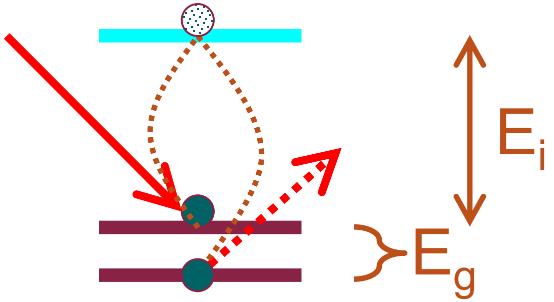


1. **Specular reflection:** The angle of reflection is equal to the angle of incidence. For some spectroscopies, the angles are measured relative to the surface (XRR), for others relative to the surface normal (SE).
2. **Diffuse reflection or scattering:** There is no well-defined direction, in which the secondary particle exits. The scattering probability may depend on the angles.
3. **Diffraction:** Requires a periodic (crystalline) layer. There is a well-defined angular relationship between the spacing of the diffraction (Bragg) planes and the momentum of the incident/diffracted beams.

# Classification Schemes for Surface Spectroscopy III



Elastic: The intensity of the reflected (relative to the refracted beam) depends on the excited states of the system (band gaps).



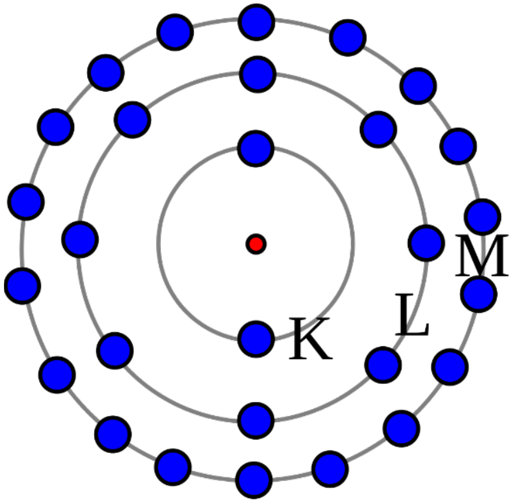
Inelastic: The energy difference (gain or loss) provides information about vibrational (Raman) or electronic (Auger) energy states. The strength of the scattering process depends on the interaction with an intermediate state.

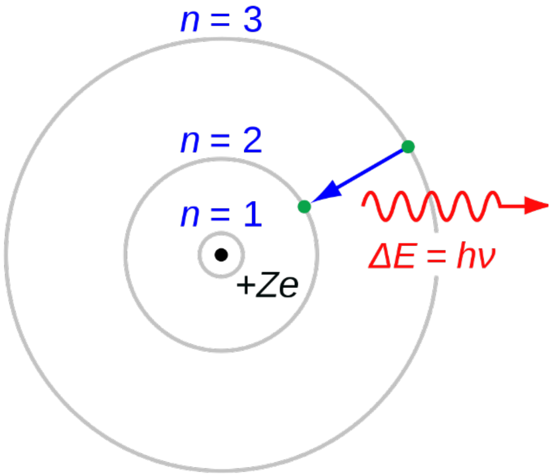
- **Elastic scattering:** The energy of the incident particle equals that of the scattered particle.
- **Inelastic scattering:** The two energies are different, depending on the energy gained or lost by the interaction with the thin film.
- Both can yield information about the energy states in the film.

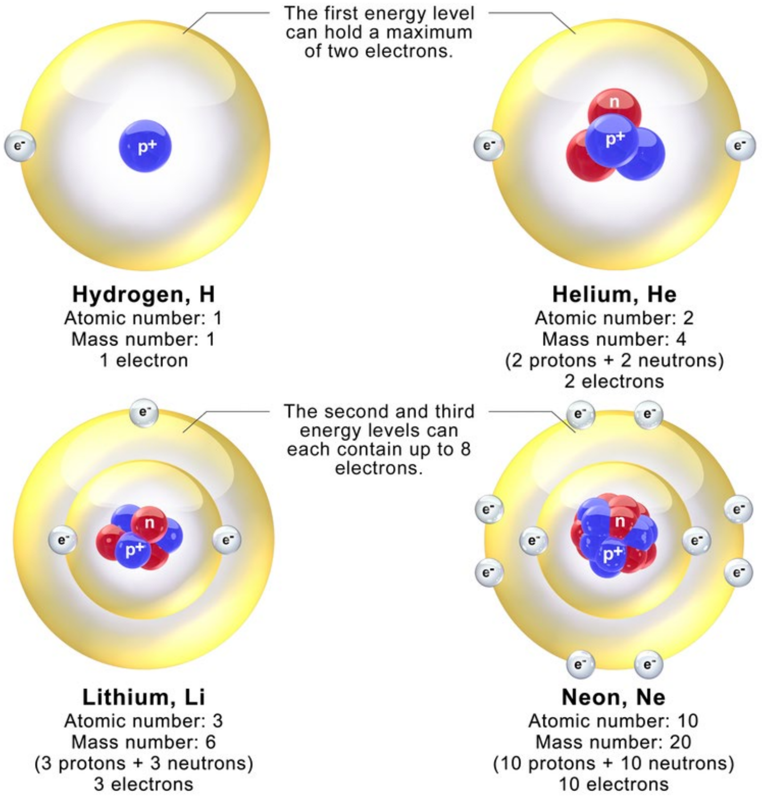
# Classification Schemes for Surface Spectroscopy IV

- Spectroscopic Ellipsometry: Elastic, specular, $\gamma \rightarrow \gamma$
  Thickness, Energy (band gap), refractive index, composition
- X-ray reflectivity: Elastic, specular, $\gamma \rightarrow \gamma$
  Thickness, density, surface/interface roughness
- X-ray diffraction: Elastic, diffracted, $\gamma \rightarrow \gamma$
  Lattice constant, stress/strain, composition
- UV Raman Spectroscopy: Inelastic, scattered, $\gamma \rightarrow \gamma$
  Vibrational (phonon) energy, composition, stress/strain
- Secondary Ion Mass Spectrometry: Inelastic, scattered, $i \rightarrow i$
  Composition, depth profile (sputtering), doping
- Auger Electron Spectrometry: Inelastic, scattered, $e \rightarrow e$
  Composition, depth profile (sputtering)
- Rutherford backscattering: Inelastic, scattered, $\alpha \rightarrow \alpha$
  Composition, some depth information, primary standard

# Bohr Model for the Hydrogen Atom






The first energy level can hold a maximum of two electrons.

**Hydrogen, H**
Atomic number: 1
Mass number: 1
1 electron

**Helium, He**
Atomic number: 2
Mass number: 4
(2 protons + 2 neutrons)
2 electrons

The second and third energy levels can each contain up to 8 electrons.

**Lithium, Li**
Atomic number: 3
Mass number: 6
(3 protons + 3 neutrons)
3 electrons

**Neon, Ne**
Atomic number: 10
Mass number: 20
(10 protons + 10 neutrons)
10 electrons

## Quantum Numbers:

| | |
|---|---|
| n | 1,2,3,… |
| l | 0,…,n-1 |
| m | –l,…,l |
| s | +/– 1/2 |

$E(n) = -R/n^2$

R=13.6 eV

## Relativistic corrections:

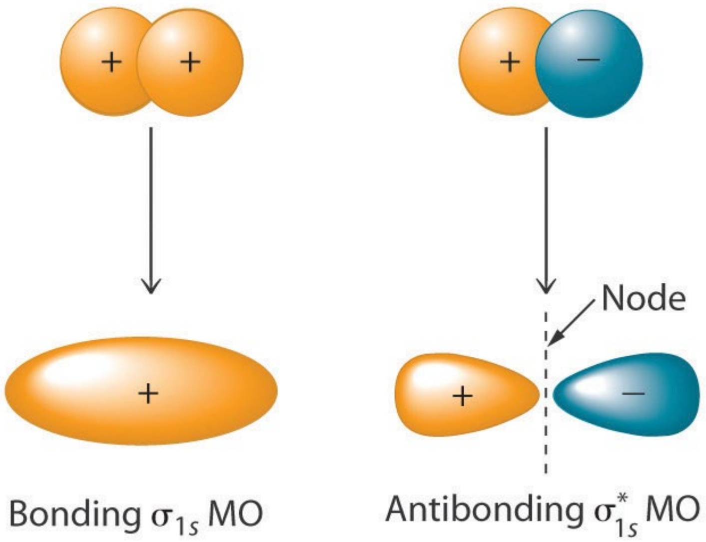
s electrons (l=0) close to the core

**J=L+S** total angular momentum

Spin-orbit coupling **L·S**

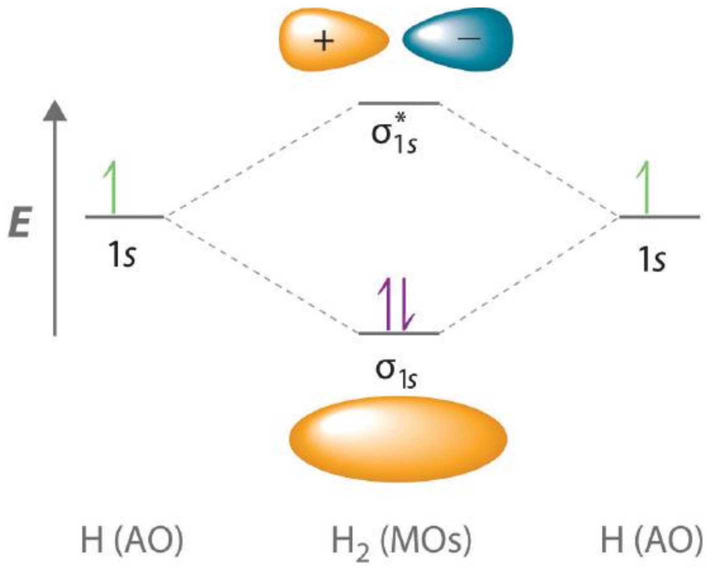
L=1, S=1/2 J=1/2 or 3/2

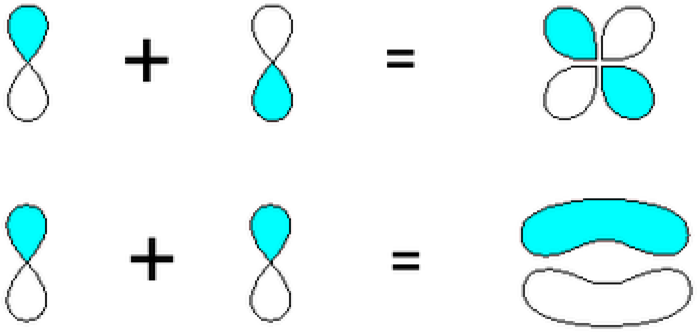
# Bonding and Anti-Bonding Orbitals



s: $\Psi=\psi_1+\psi_2$

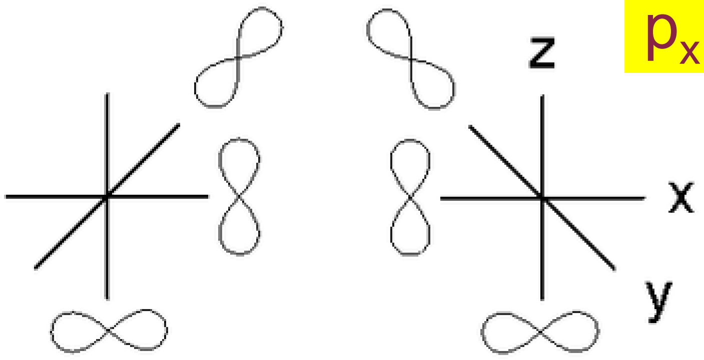
s*: $\Psi=\psi_1-\psi_2$





p*

p

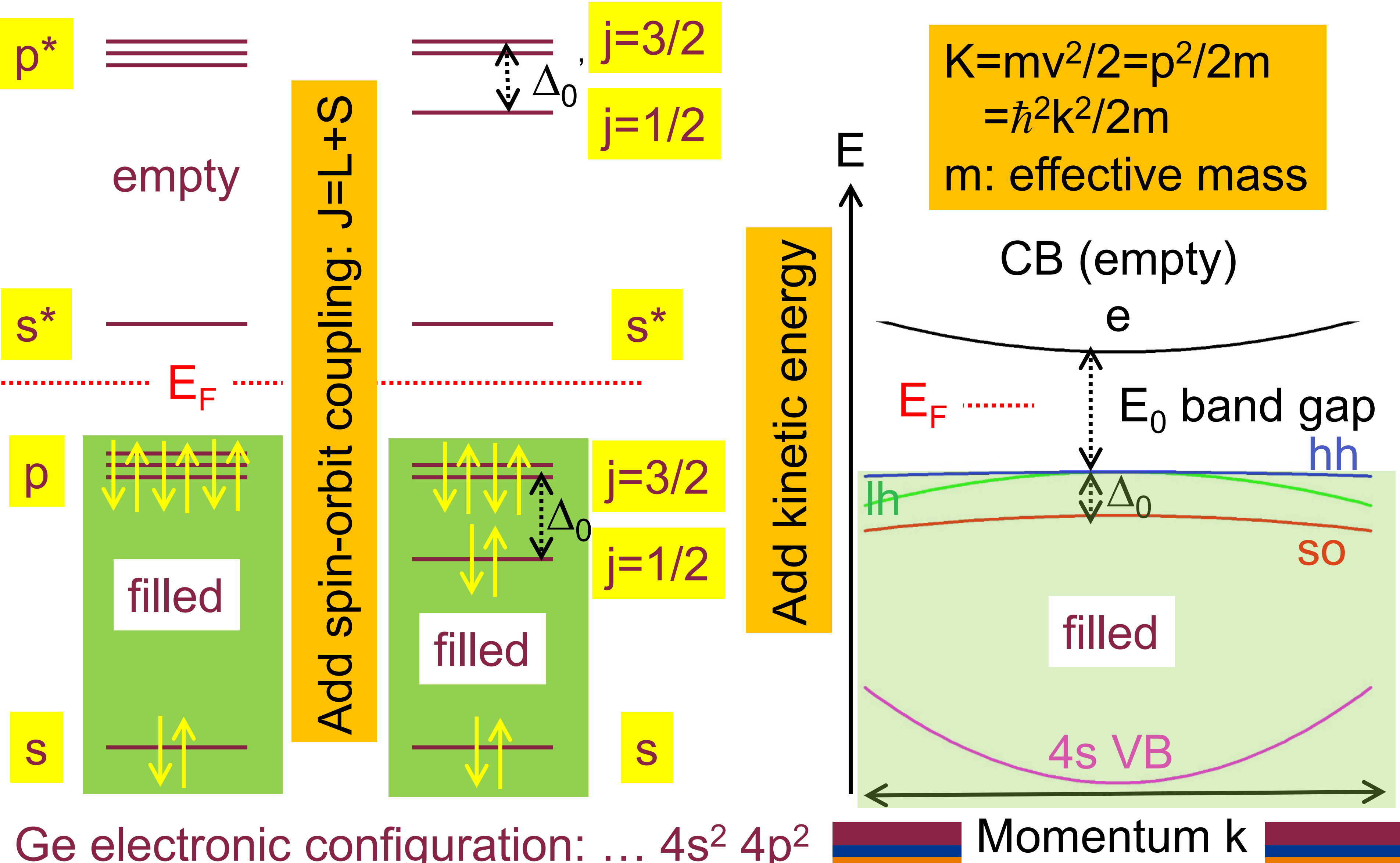


$p_x$, $p_y$, $p_z$

C electronic configuration: $1s^2\ 2s^2\ 2p^2$

L shell forms $sp^3$ hybrid: $1s^2\ 2s^1\ 2p^3$

# A simple band structure for Germanium

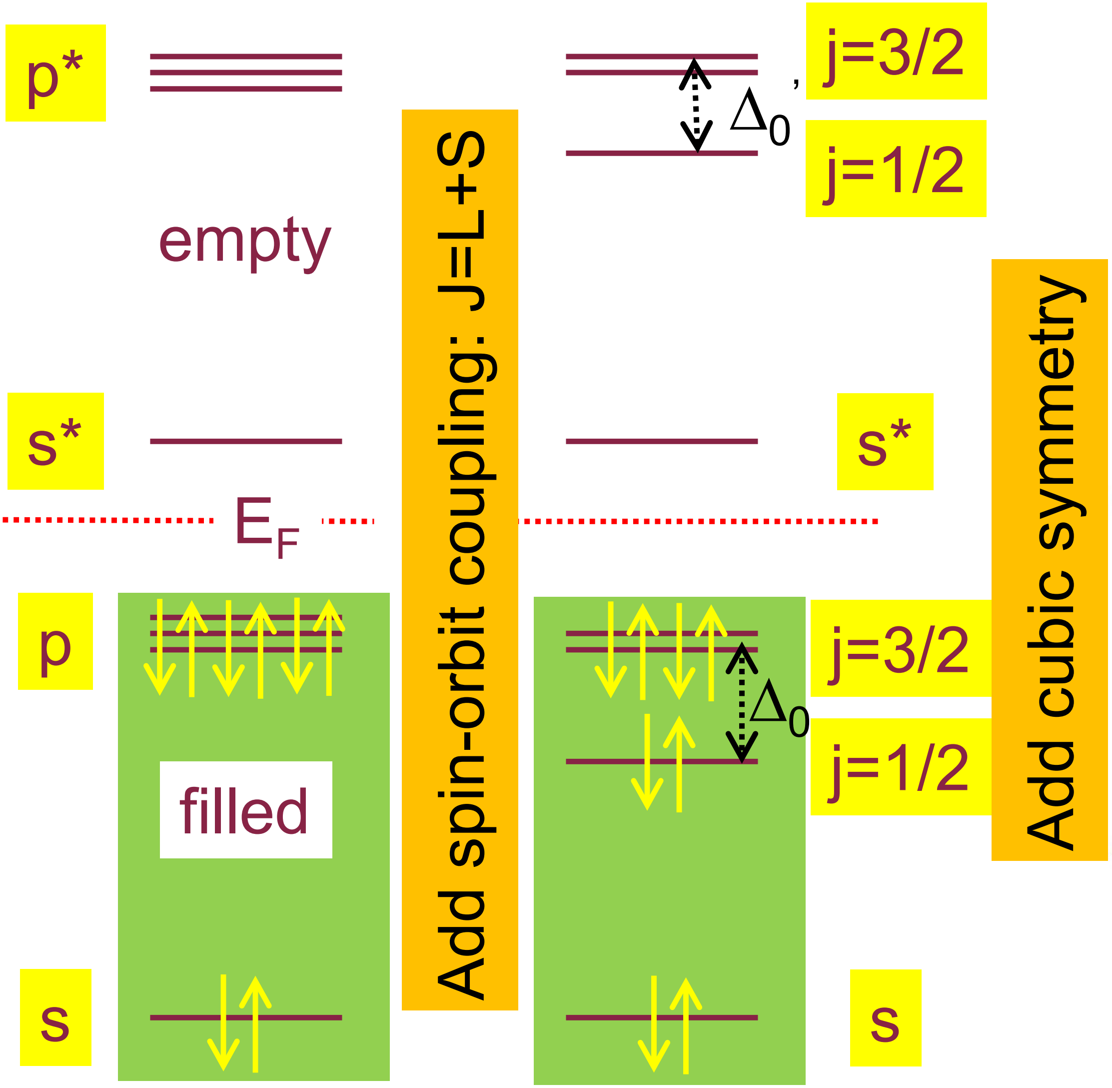


$K = mv^2/2 = p^2/2m$
$= \hbar^2k^2/2m$
m: effective mass

Ge electronic configuration: … $4s^2\ 4p^2$

N shell forms $sp^3$ hybrid: … $4s^1\ 4p^3$

# A simple band structure for Germanium



p*

empty

s*

$E_F$

p

filled

s

Add spin-orbit coupling: J=L+S

j=3/2

$\Delta_0$

j=1/2

s*

j=3/2

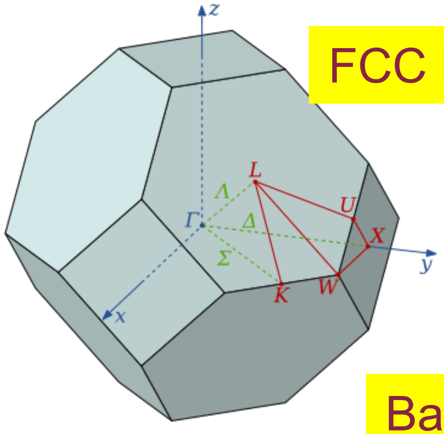
$\Delta_0$

j=1/2

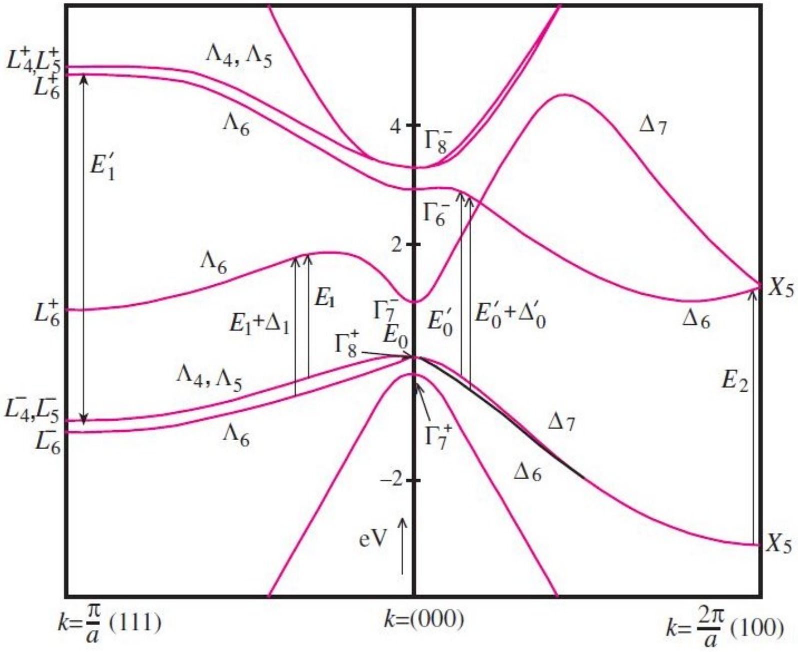
s

Add cubic symmetry

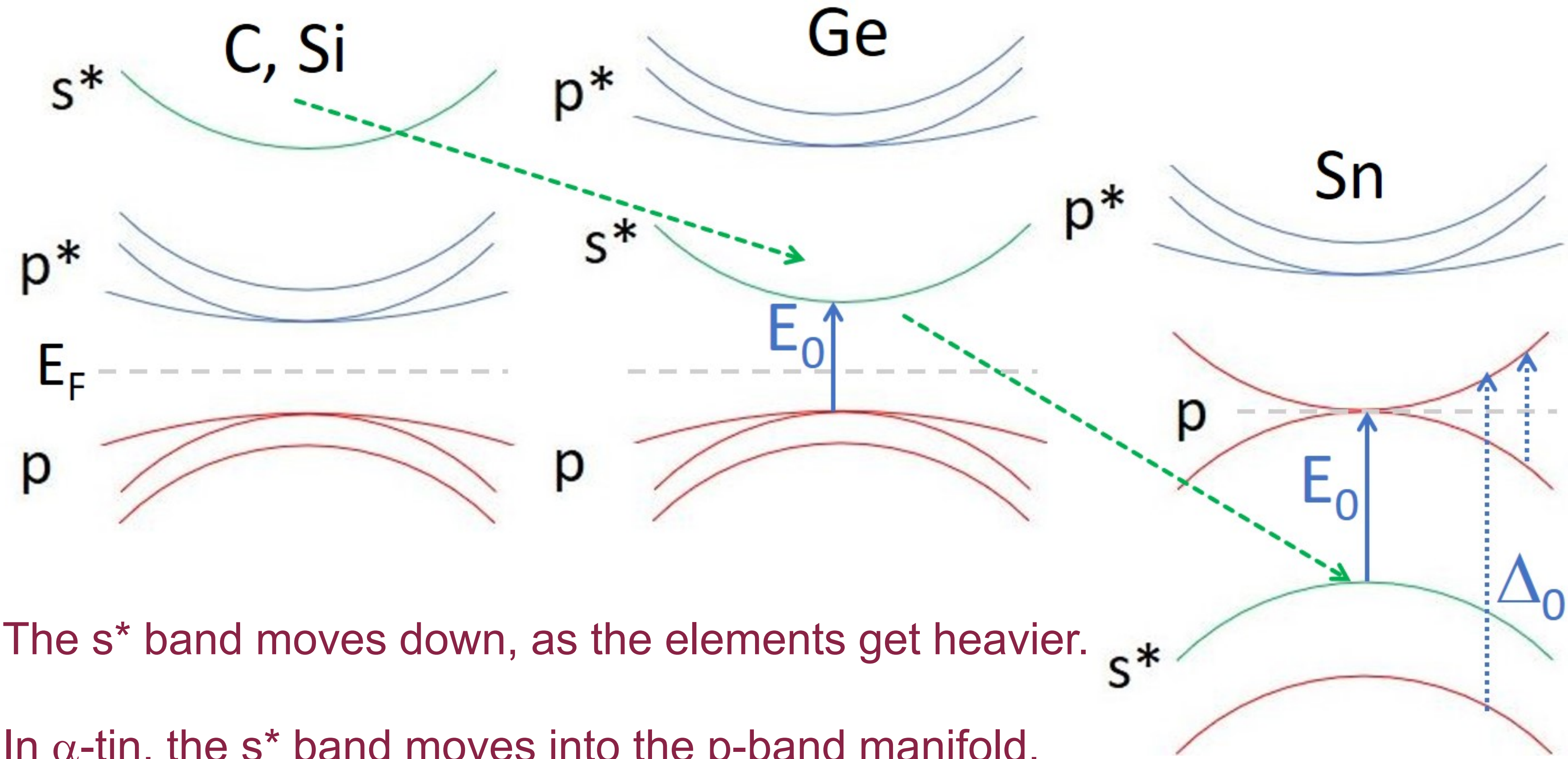
FCC Brillouin zone



Band structure



# Carbon, Silicon, Germanium, Tin



The s* band moves down, as the elements get heavier.

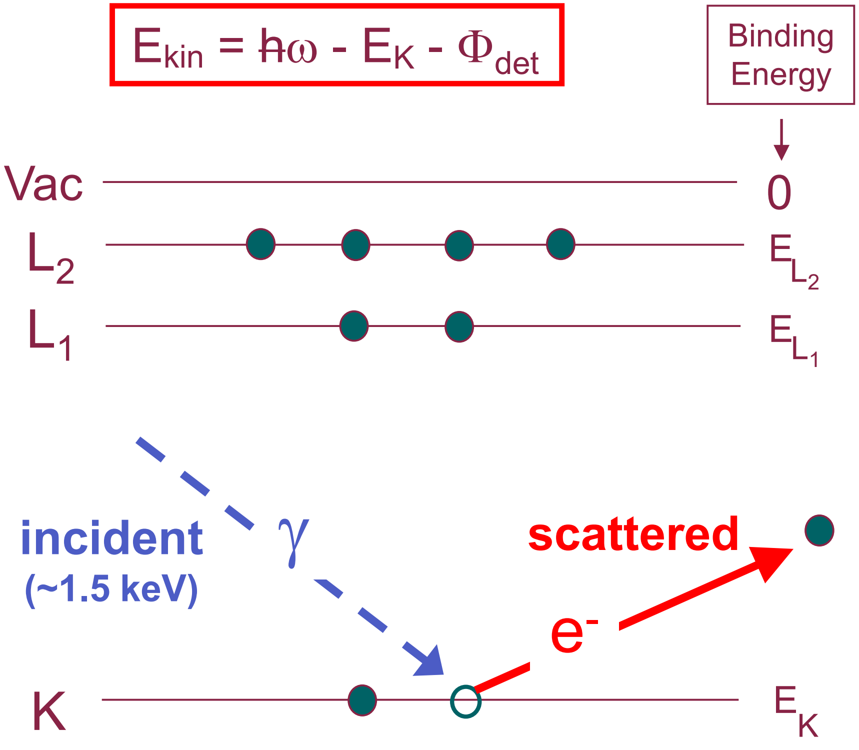
In α-tin, the s* band moves into the p-band manifold, between the j=1/2 and j=3/2 states.
This makes α-tin a zero-gap semiconductor.

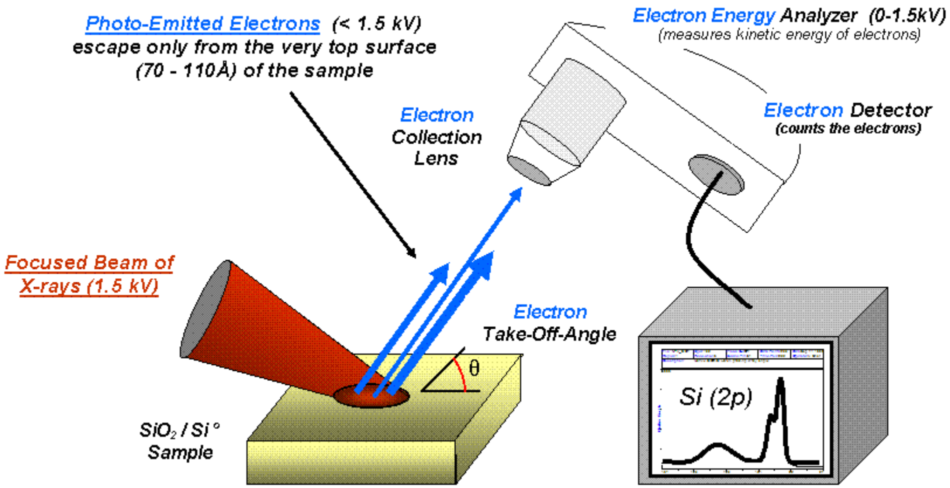
# Classification Schemes for Surface Spectroscopy IV

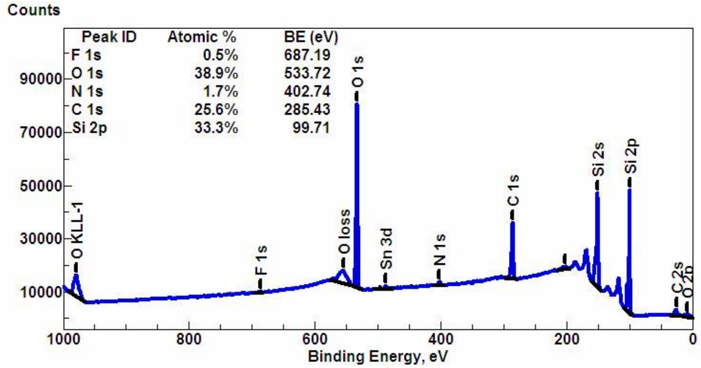
- Spectroscopic Ellipsometry: Elastic, specular, $\gamma \rightarrow \gamma$
  Thickness, Energy (band gap), refractive index, composition
- X-ray reflectivity: Elastic, specular, $\gamma \rightarrow \gamma$
  Thickness, density, surface/interface roughness
- X-ray diffraction: Elastic, diffracted, $\gamma \rightarrow \gamma$
  Lattice constant, stress/strain, composition
- UV Raman Spectroscopy: Inelastic, scattered, $\gamma \rightarrow \gamma$
  Vibrational (phonon) energy, composition, stress/strain
- Secondary Ion Mass Spectrometry: Inelastic, scattered, i → i
  Composition, depth profile (sputtering), doping
- Auger Electron Spectrometry: Inelastic, scattered, e → e
  Composition, depth profile (sputtering)
- Rutherford backscattering: Inelastic, scattered, $\alpha \rightarrow \alpha$
  Composition, some depth information, primary standard

# Example: X-ray Photoelectron Spectroscopy: $\gamma \rightarrow e$

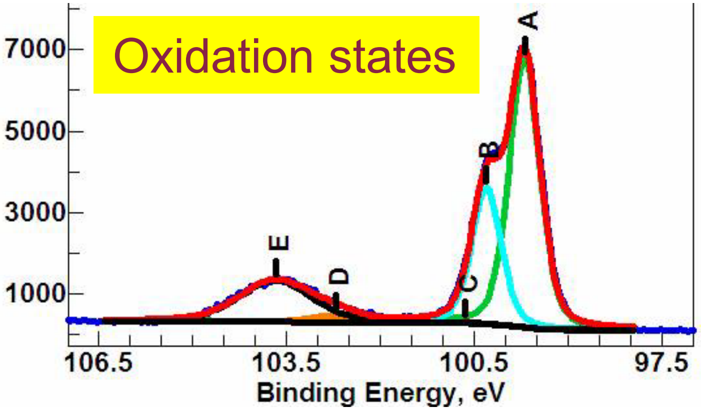
$E_{kin} = \hbar\omega - E_K - \Phi_{det}$





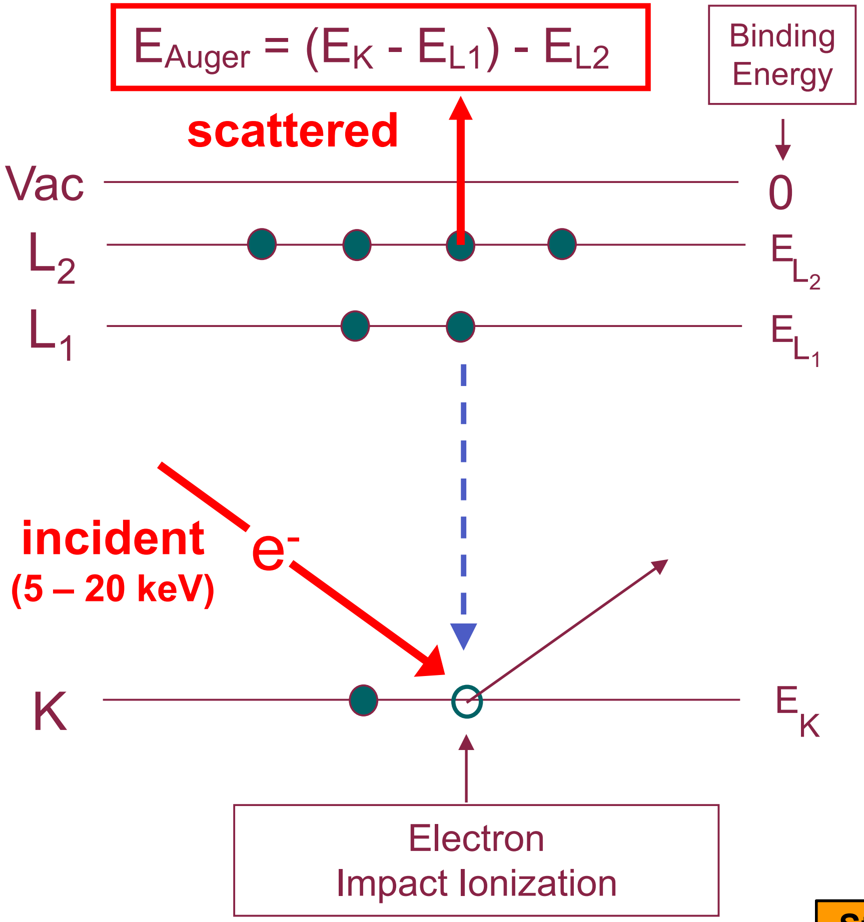


| Peak ID | Atomic % | BE (eV) |
|---|---|---|
| F 1s | 0.5% | 687.19 |
| O 1s | 38.9% | 533.72 |
| N 1s | 1.7% | 402.74 |
| C 1s | 25.6% | 285.43 |
| Si 2p | 33.3% | 99.71 |

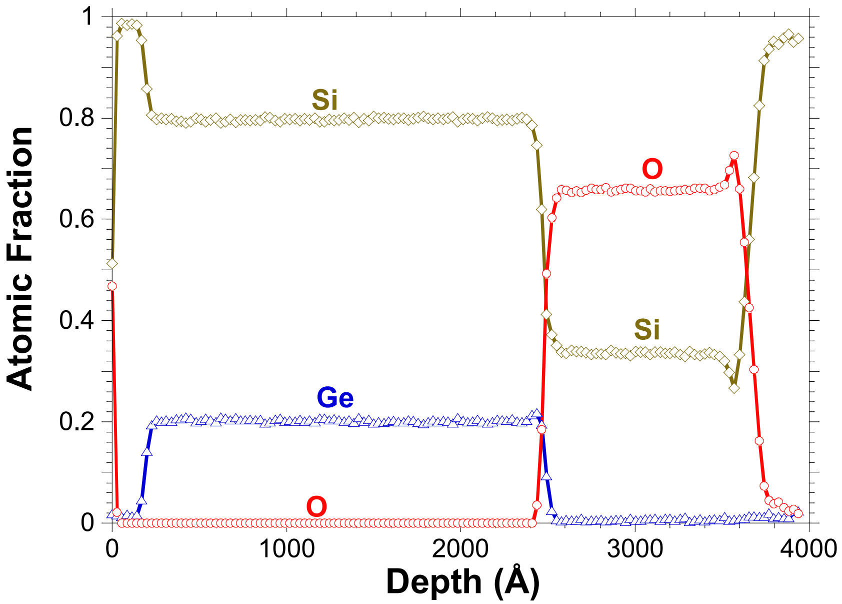


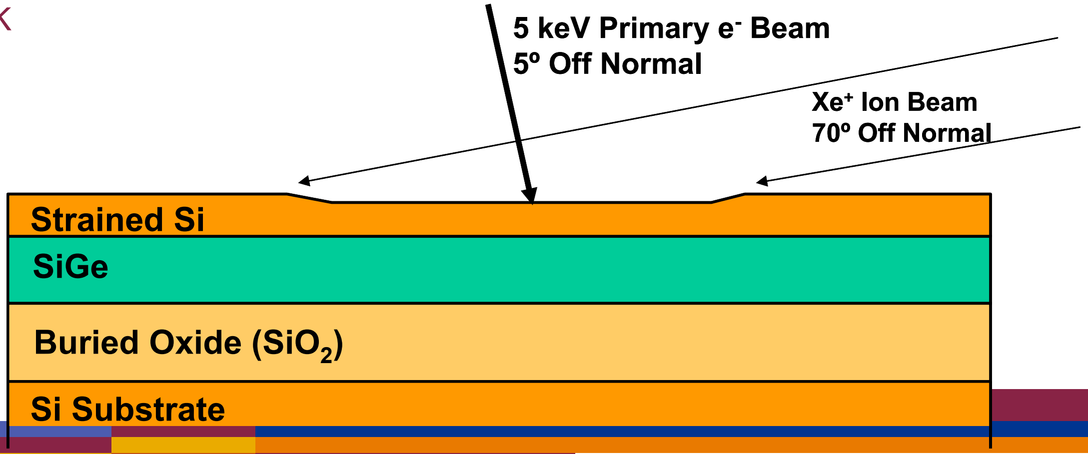
Quantification using RBS standards
High depth resolution
(small escape depth of photoelectrons)

# Example: Auger Electron Spectroscopy: e → e



$$\boxed{E_{Auger} = (E_K - E_{L1}) - E_{L2}}$$

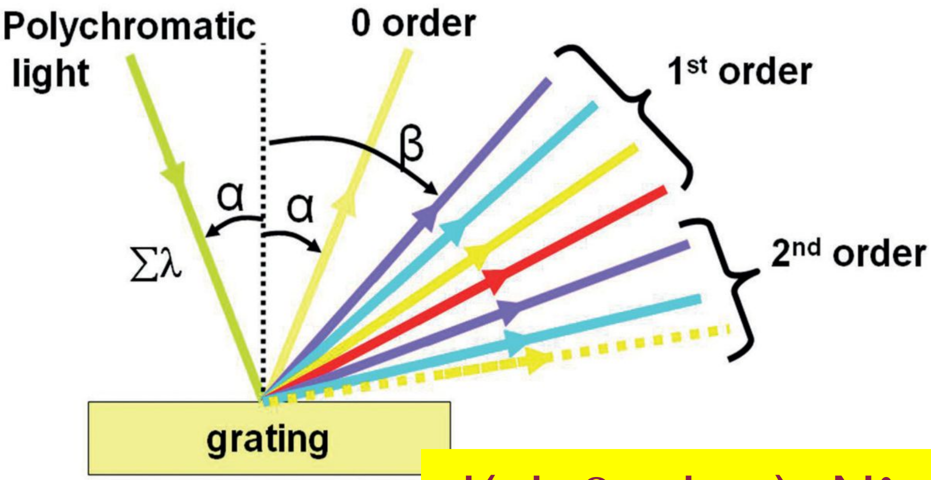




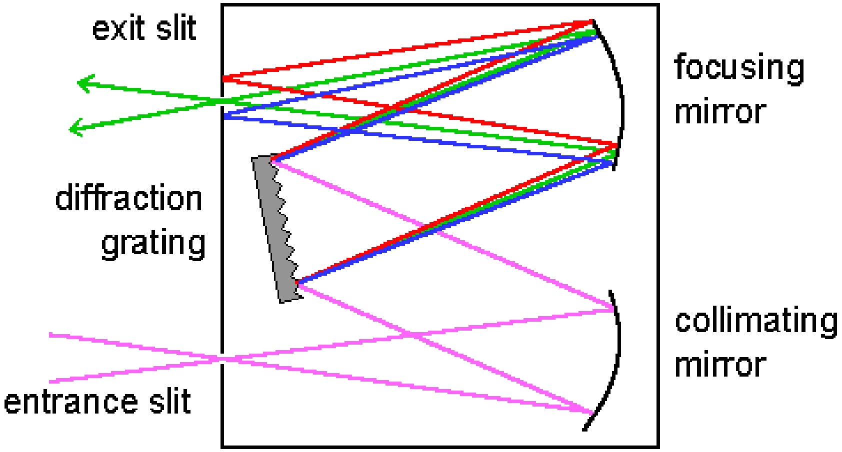
Quantification using RBS standards

High depth resolution
  (small escape depth of L electrons)

# Grating Monochromator

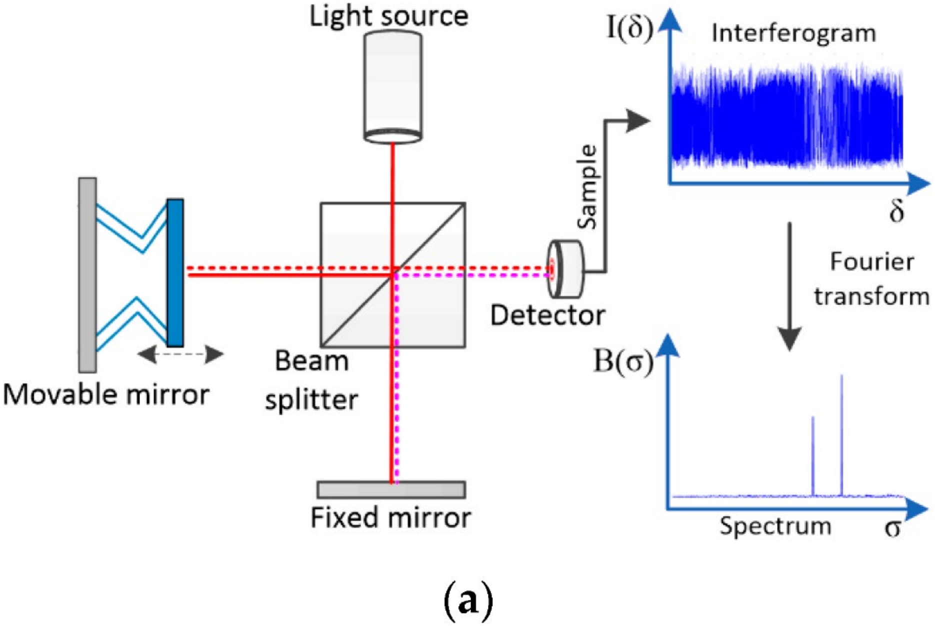


$d(\sin\beta - \sin\alpha) = N\lambda$



Diffracted intensity depends on angle and polarization.

# Fourier-Transform Spectrometer



Constructive interference: $\Delta x = N\lambda$
Destructive interference: $\Delta x = (2N+1)\lambda/2$

Common for mid-infrared spectroscopy (50-500 meV).

# Macroscopic Optical Constants

Why not $n-ik$?
Wave goes like $\exp[i(kx-\omega t)]$

$n$: refractive index, $n=c/v$
$k$: extinction coefficient
$n+ik$: complex refractive index

$R$: reflectance at normal incidence ($I_{refl}/I_0$)
$T$: transmittance ($I_{trans}/I_0$)
$R+T+A+S=1$

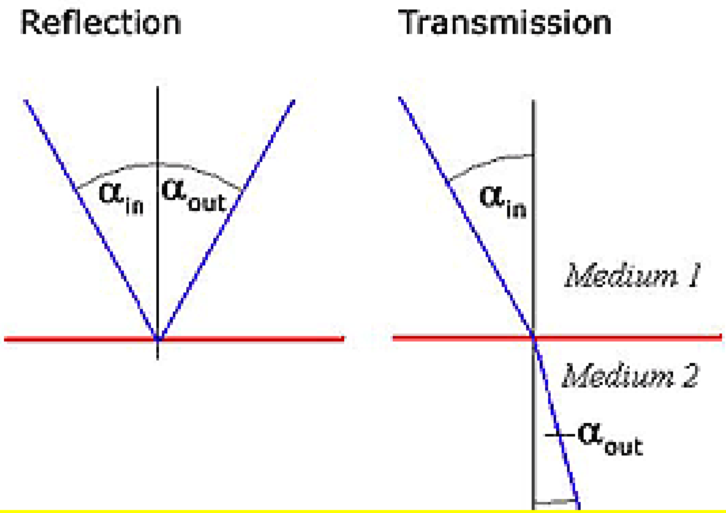
$\alpha$: absorption coefficient
$\alpha=4\pi k/\lambda$

$\varepsilon$: complex dielectric function
$\varepsilon=\varepsilon_1+i\varepsilon_2=(n+ik)^2$

All are connected through
Maxwell's equations (Lectures 3/4).

# Reflection and Transmission

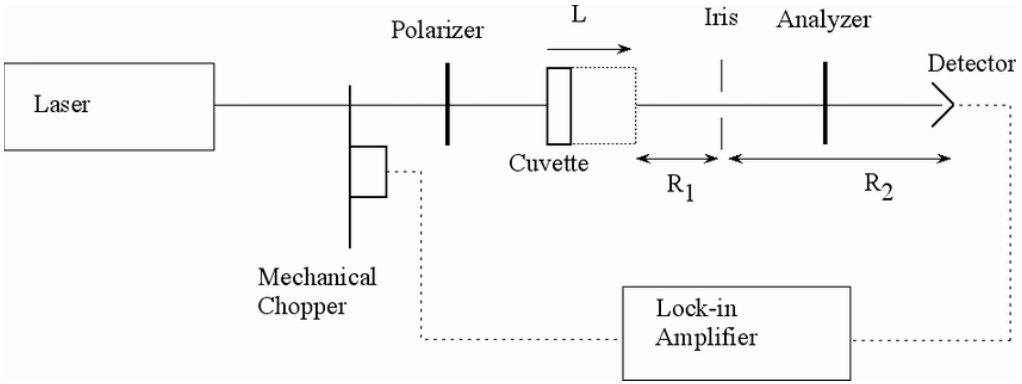
Also have diffuse scattering.



Law of reflection: $\alpha_{in}=\alpha_{out}$
Snell's Law: $n_1 \sin\alpha_{in}=n_2 \sin\alpha_{out}$
n: Refractive Index

$$R=\left(\frac{n-1}{n+1}\right)^2$$

Beer's Law: $I(L)=I_0\exp(-\alpha L)$

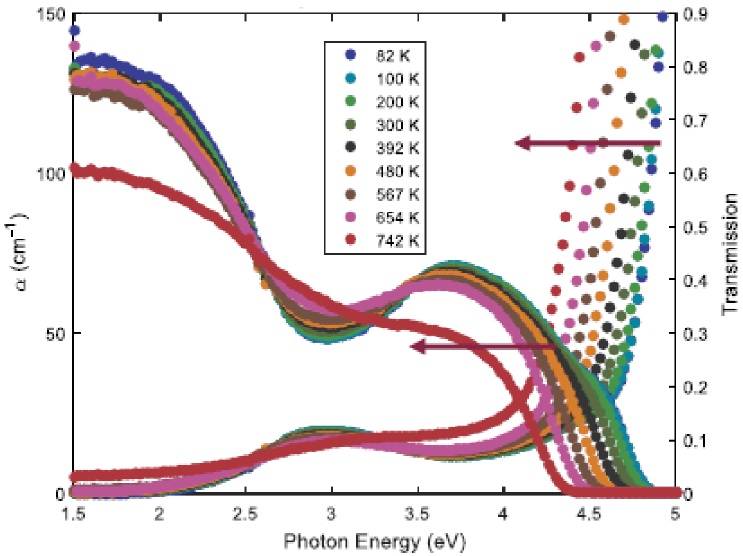


Absorption coefficient $\alpha$ ($cm^{-1}$)
Consider reflection losses

$$\exp(-\alpha L)\approx\frac{T}{(1-R)^2}$$

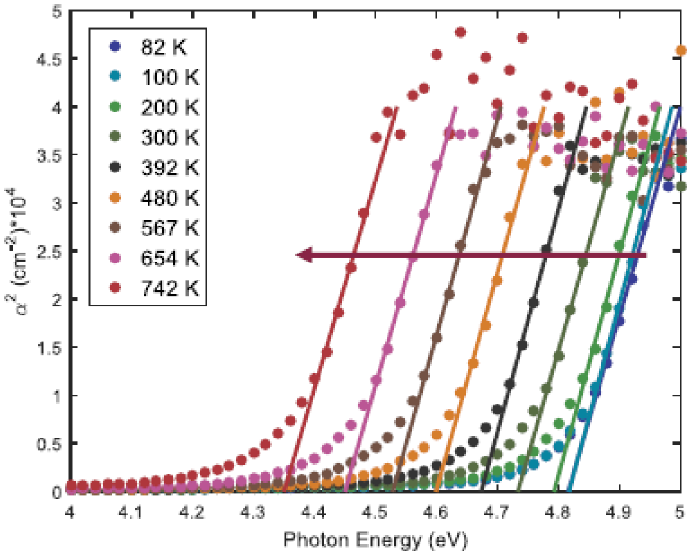
# Transmission: LSAT or $(LaAlO_3)_{0.3}(SrAlTaO_6)_{0.35}$

## Absorption Coefficient and Transmission Data

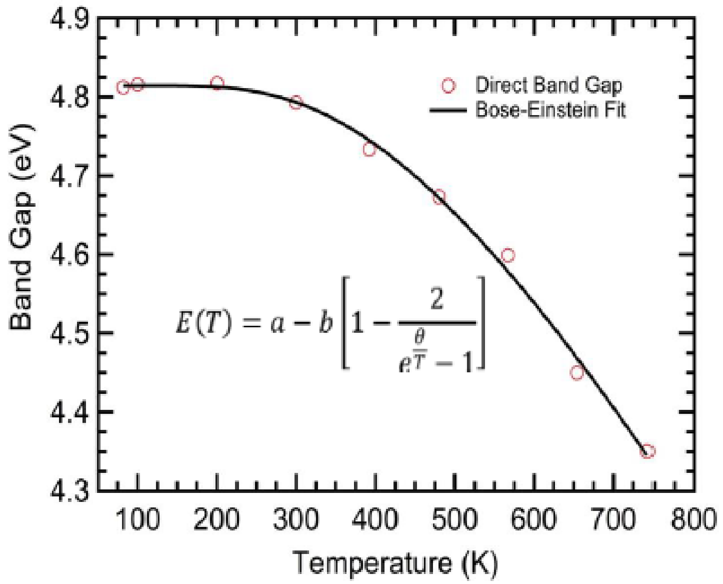


$$T = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}$$

## Absorption Coefficient Squared



## Direct Band Gap

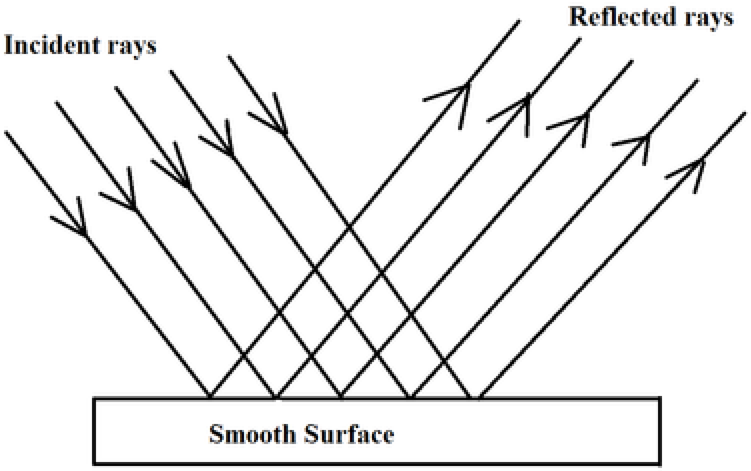


## *Bose-Einstein Model*

$$E(T) = a - b\left[1 - \frac{2}{e^{\frac{\theta}{T}} - 1}\right]$$

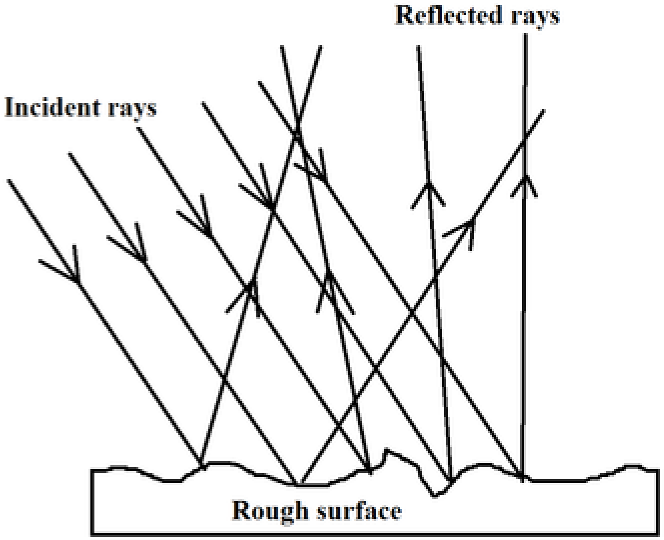
| | |
|---|---|
| **a (eV)** | 6.32±0.29 |
| **b (eV)** | 1.50±0.29 |
| **θ (K)** | 1486±121 |

# Reflection from a rough surface



**I. Regular Reflection**

Specular



**II. Irregular Reflection**

Specular+Diffuse

**Debye-Waller correction:**

Assumes sinusoidal roughness

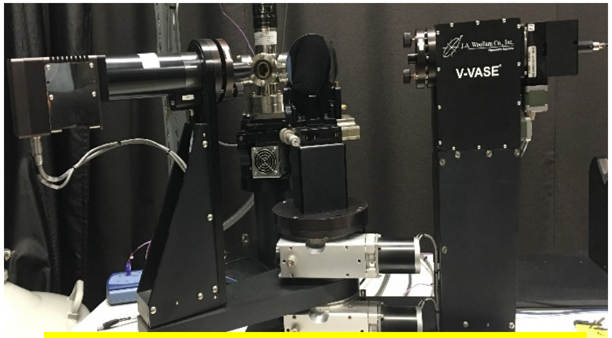
$R_{rough}=R_0\exp[-(4\pi\sigma n\cos\theta/\lambda)^2]$

$\sigma$: rms surface roughness parameter

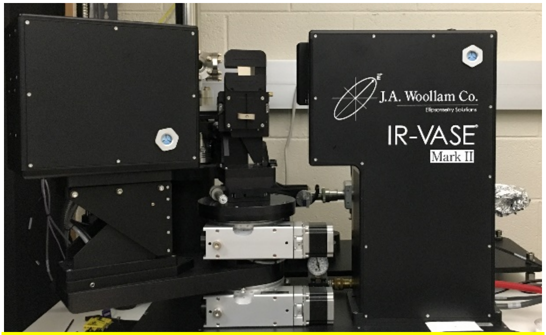
Also: I. Ohlidal, F. Lukes, and K. Navratil, Surf. Sci. **45**, 91 (1974). 98 citations.

D.K.G. de Boer, Phys. Rev. B **49**, 5817 (1994).

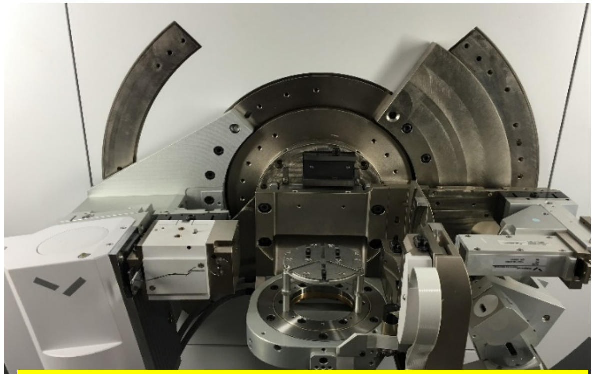
# Reflectance Spectroscopy Instrumentation



**Spectroscopic Ellipsometer (VUV/UV/VIS-VASE)**



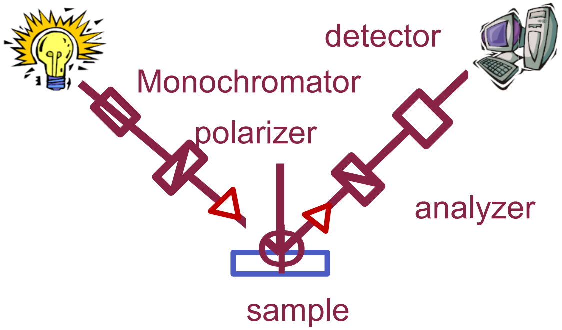
**Spectroscopic Ellipsometer (IR-VASE)**



**X-ray diffraction & reflectance**

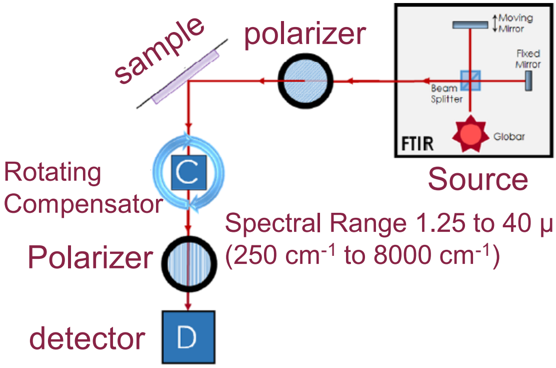
## Spectroscopic Ellipsometry:

- **Thickness (100 to 10000 Å)**
- **Absorption, band gap**
- **Refractive index**



## FTIR ellipsometry:

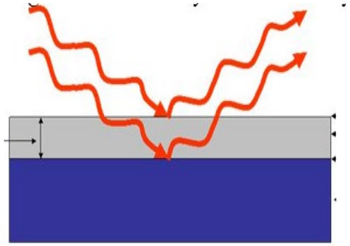
- **Very thick films (> 5000 Å)**
- **Phonon absorption**
- **Optical Constants**



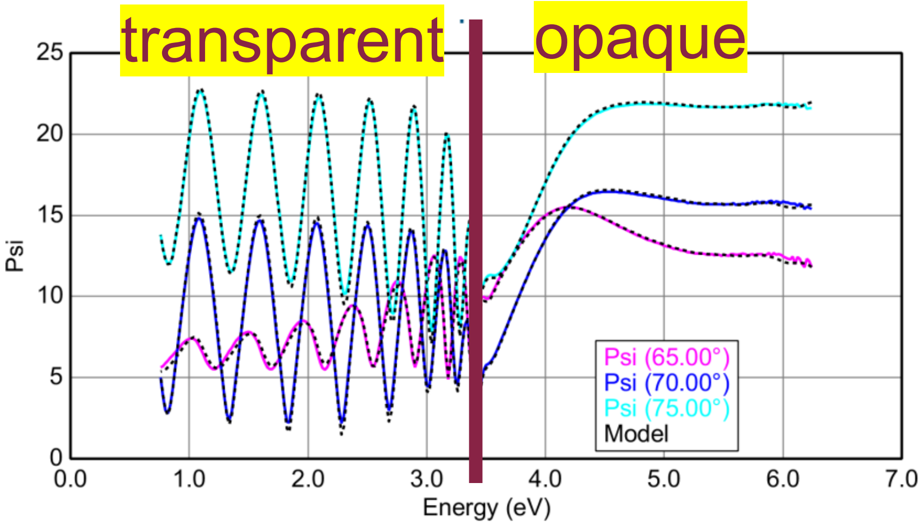
Spectral Range 1.25 to 40 µm ($250\ \mathrm{cm}^{-1}$ to $8000\ \mathrm{cm}^{-1}$)

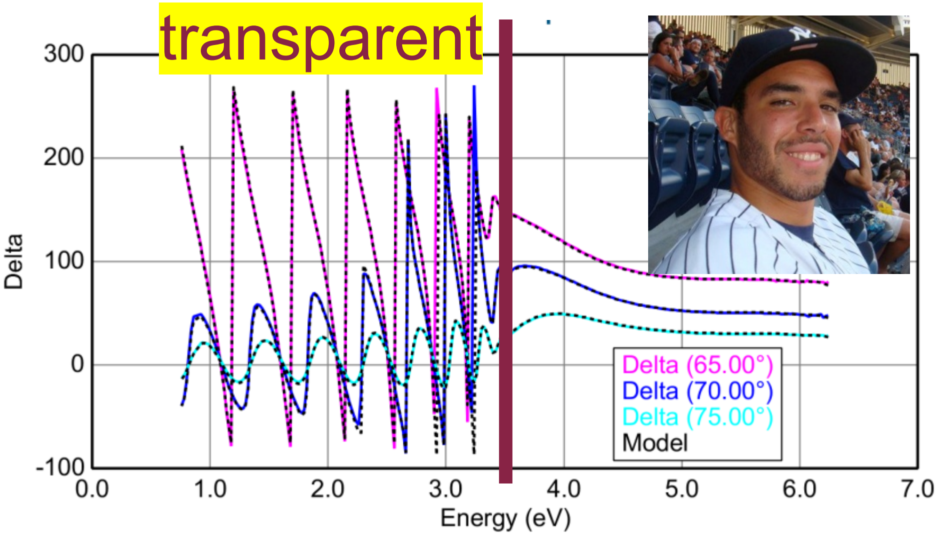
## XRD/XRR:

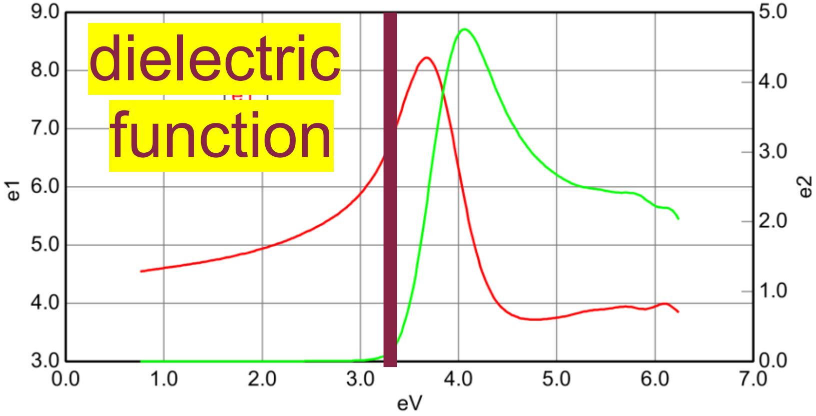
- **Crystal structure**
- **Lattice spacings** (strain)
- **Thickness** (5 Å to 1000 Å)
- **Surface, roughness** layer thickness
- **Density**

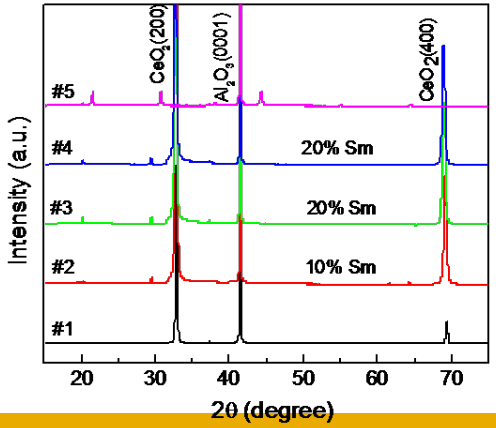


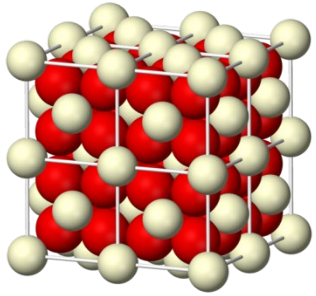
# Crystalline $CeO_2$ on sapphire (liquid deposition)











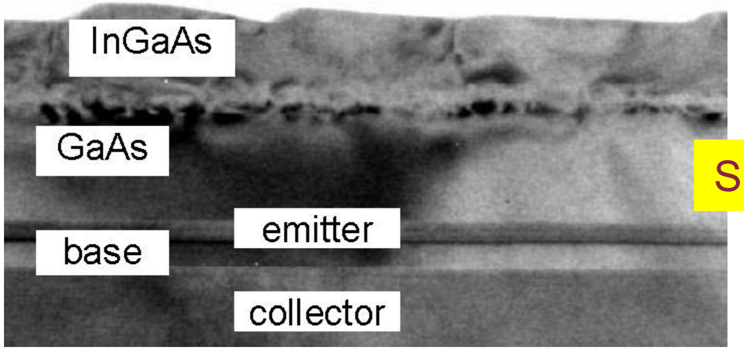
Fluorite ($O_h^5$)

- Insulating $CeO_2$ film on sapphire, with **band gap near 3.7 eV.**
- Determine **film thickness** from interference fringes in transparent region.
- Fit **optical constants** with basis spline polynomials.

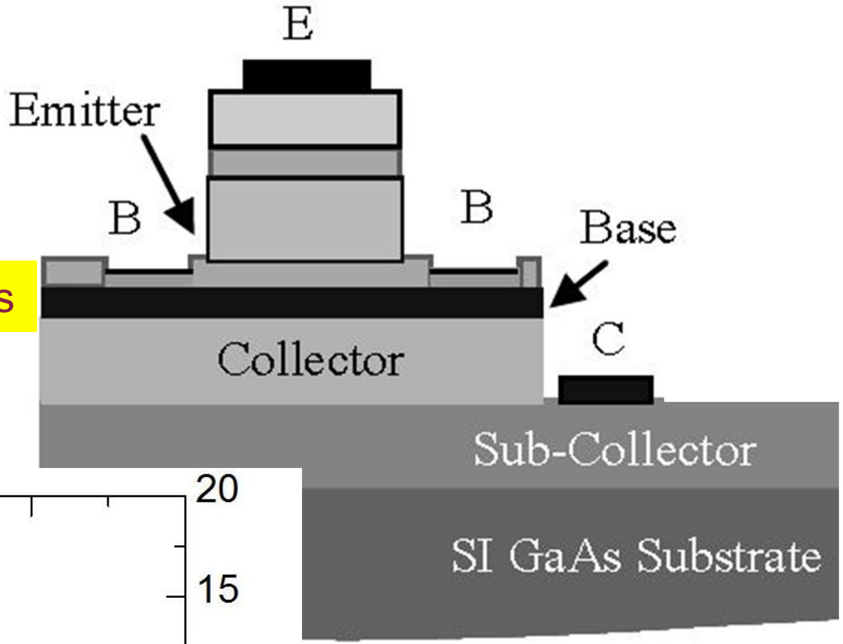
K. Mitchell, C.O. Rodriguez, Y. Li, 2013; X. Guo, Boston Applied Technologies, Inc.

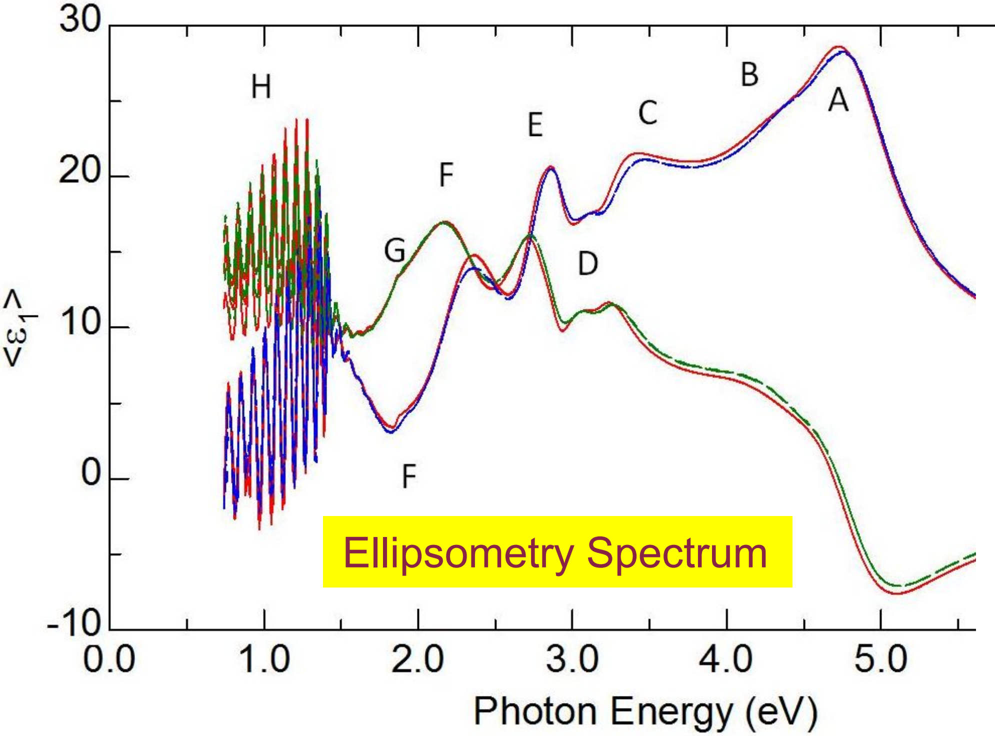
# Thickness Measurements: InGaP HBT

- How thick is my film?



Skyworks





Ellipsometry Spectrum

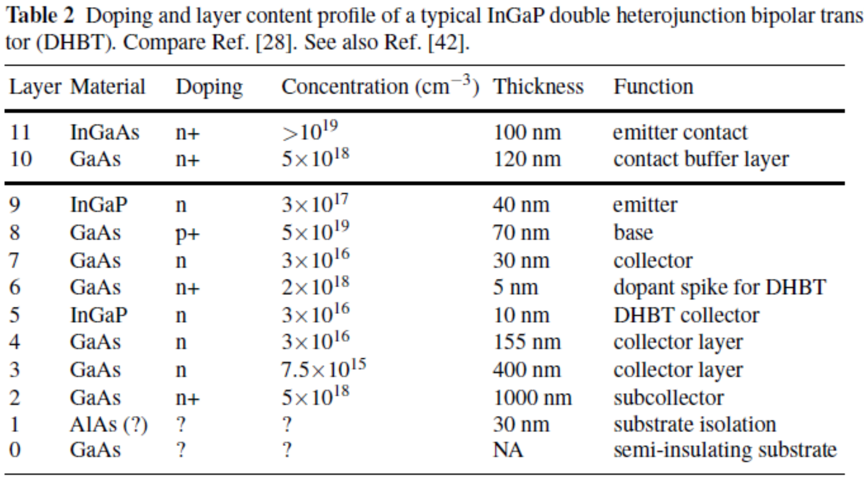
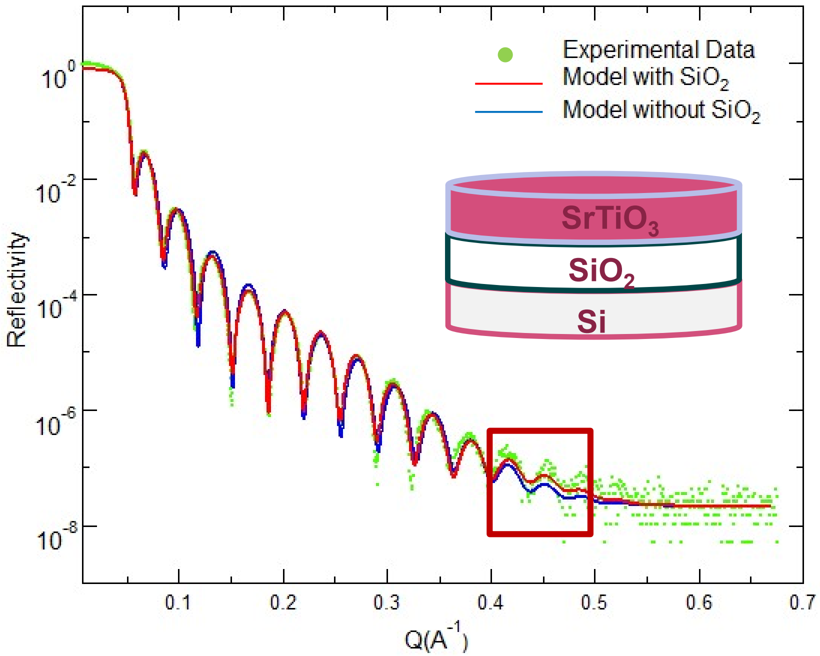
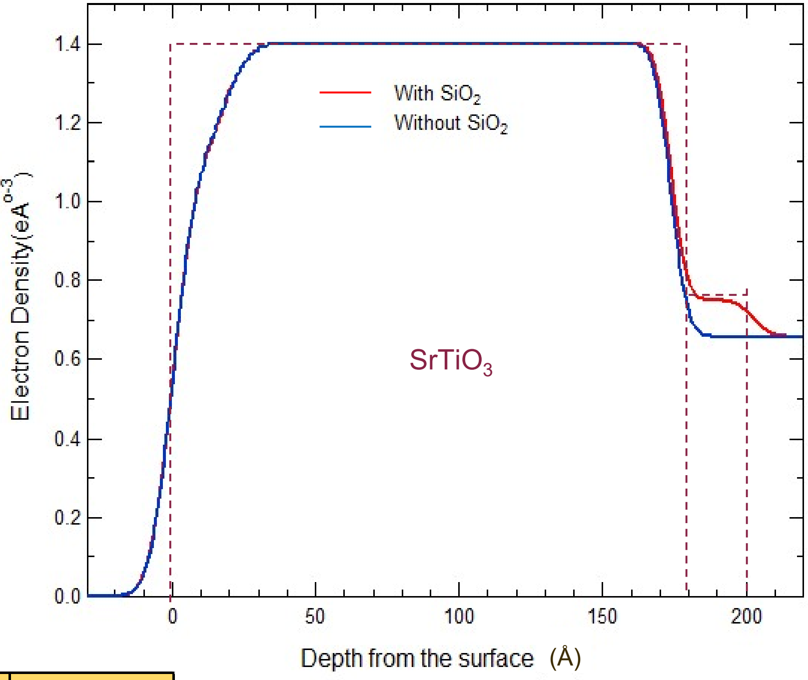


**Table 2** Doping and layer content profile of a typical InGaP double heterojunction bipolar transistor (DHBT). Compare Ref. [28]. See also Ref. [42].

| Layer | Material | Doping | Concentration ($\mathrm{cm}^{-3}$) | Thickness | Function |
|---|---|---|---|---|---|
| 11 | InGaAs | n+ | $>10^{19}$ | 100 nm | emitter contact |
| 10 | GaAs | n+ | $5\times10^{18}$ | 120 nm | contact buffer layer |
| 9 | InGaP | n | $3\times10^{17}$ | 40 nm | emitter |
| 8 | GaAs | p+ | $5\times10^{19}$ | 70 nm | base |
| 7 | GaAs | n | $3\times10^{16}$ | 30 nm | collector |
| 6 | GaAs | n+ | $2\times10^{18}$ | 5 nm | dopant spike for DHBT |
| 5 | InGaP | n | $3\times10^{16}$ | 10 nm | DHBT collector |
| 4 | GaAs | n | $3\times10^{16}$ | 155 nm | collector layer |
| 3 | GaAs | n | $7.5\times10^{15}$ | 400 nm | collector layer |
| 2 | GaAs | n+ | $5\times10^{18}$ | 1000 nm | subcollector |
| 1 | AlAs (?) | ? | ? | 30 nm | substrate isolation |
| 0 | GaAs | ? | ? | NA | semi-insulating substrate |

# X-ray Reflectance: $SrTiO_3$ on Si



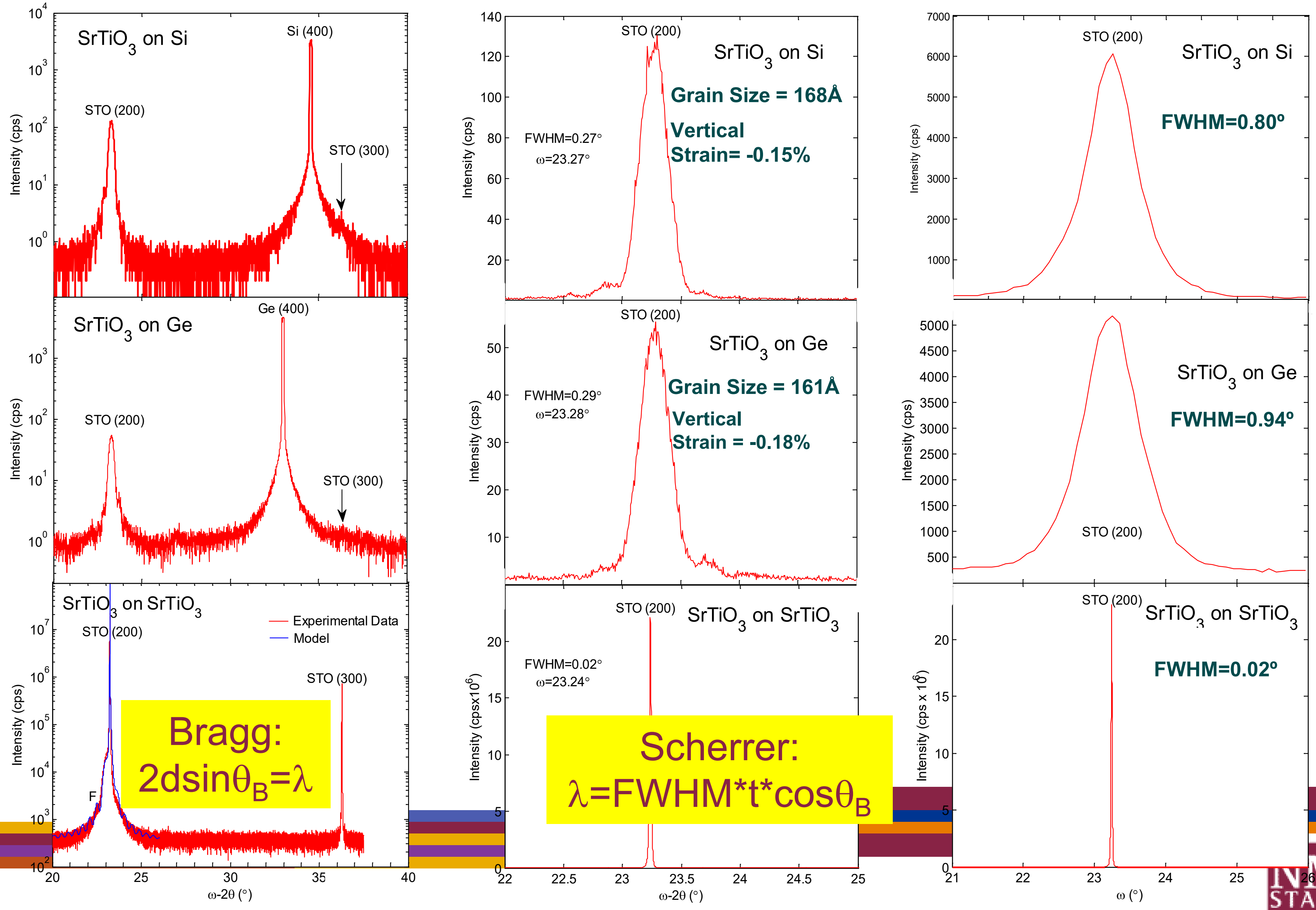


$$Q=\frac{4\pi \sin \vartheta}{\lambda}$$

| Layer | Electron Density ($eÅ^{-3}$) | Bulk Electron density ($eÅ^{-3}$) | Thickness (nm) | Roughness (nm) |
|---|---|---|---|---|
| $SrTiO_3$ | 1.08 | 1.41 | 1.79 | 0.6152 |
| $SrTiO_3$ | 1.40 | 1.41 | 15.6 | 0.7396 |
| $SiO_2$ | 0.75 | 0.81 | 2.87 | 0.4202 |
| Si | 0.66 | 0.71 | Substrate | 0.4574 |

Small x-ray contrast between Si and $SiO_2$.

# X-ray Diffraction: $SrTiO_3$ on Si, Ge, and $SrTiO_3$

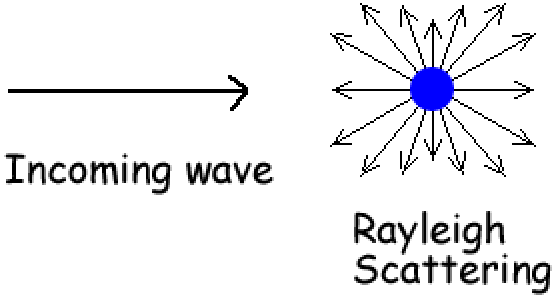


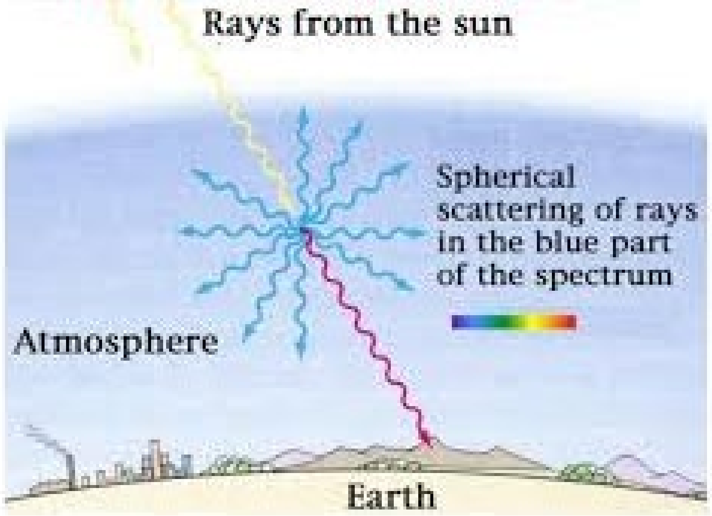
Bragg:
$2d\sin\theta_B=\lambda$

Scherrer:
$\lambda=\mathrm{FWHM}*t*\cos\theta_B$

**ω-2θ scan** **ω-2θ scan (zoomed)** **ω scan**

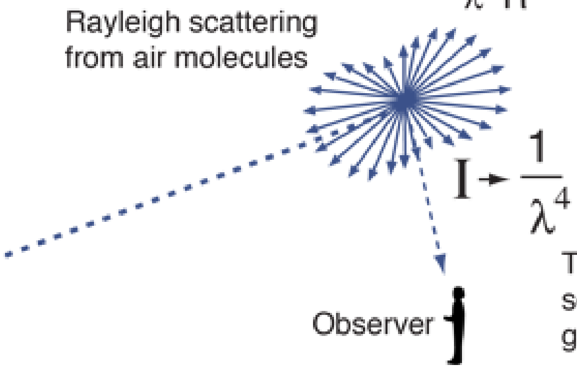
# Raleigh scattering (elastic)





$$I = I_0 \frac{8\pi^4 N\alpha^2}{\lambda^4 R^2}(1 + \cos^2\theta)$$

Scattering at right angles is half the forward intensity for Rayleigh scattering



$$I \rightarrow \frac{1}{\lambda^4}$$

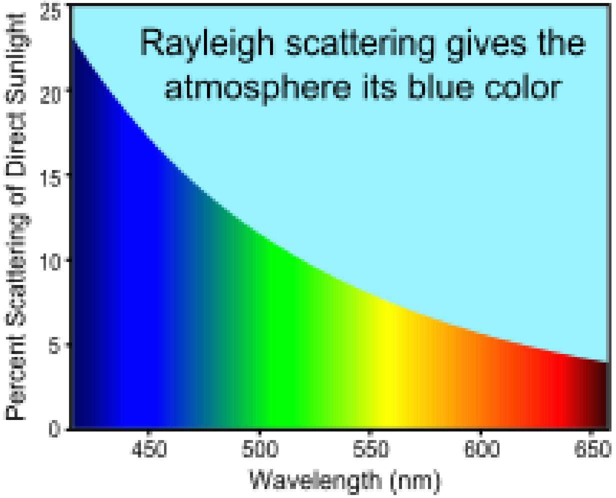
N = # of scatterers

$\alpha$ = polarizability

R = distance from scatterer

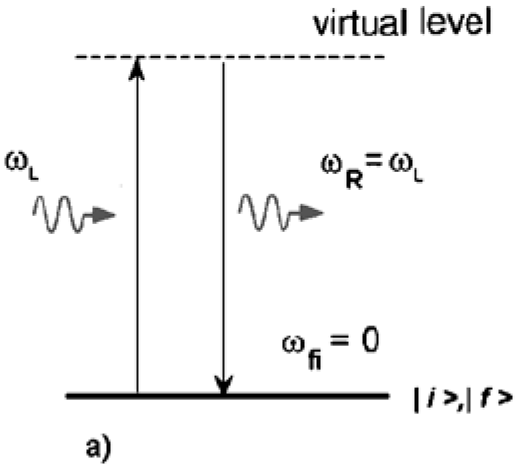
The strong wavelength dependence of Rayleigh scattering enhances the short wavelengths, giving us the blue sky.

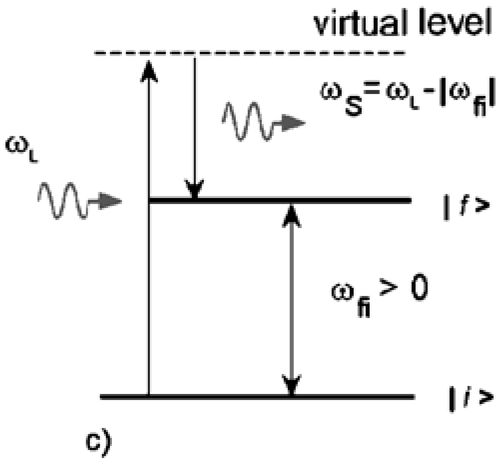
**Why is the sky blue?**



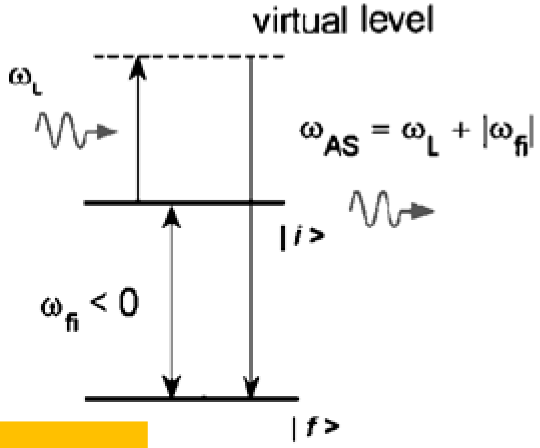
# Elastic and Inelastic (Raman) Scattering

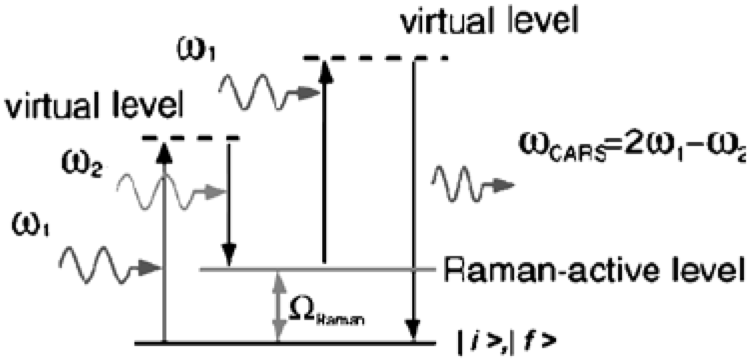
Raleigh (elastic)





Raman (Stokes)

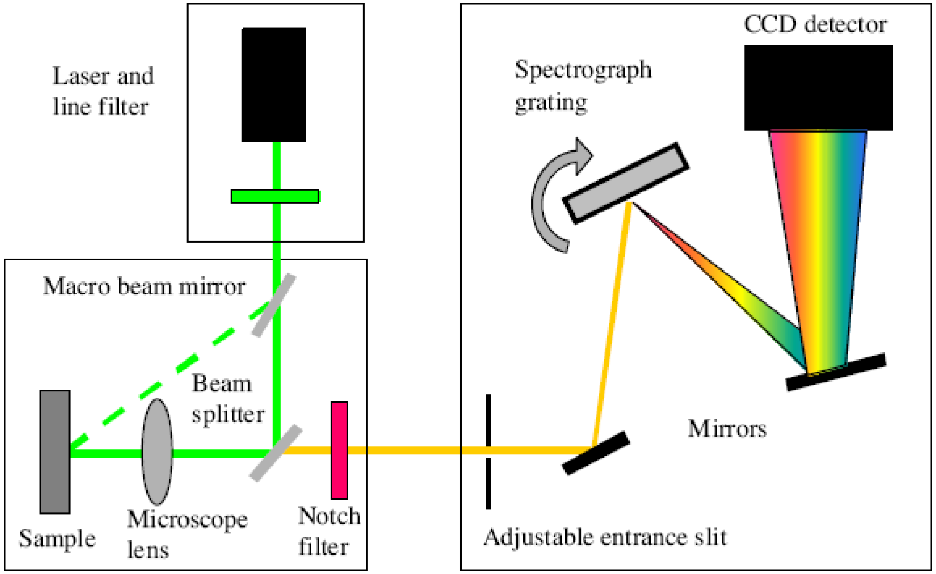


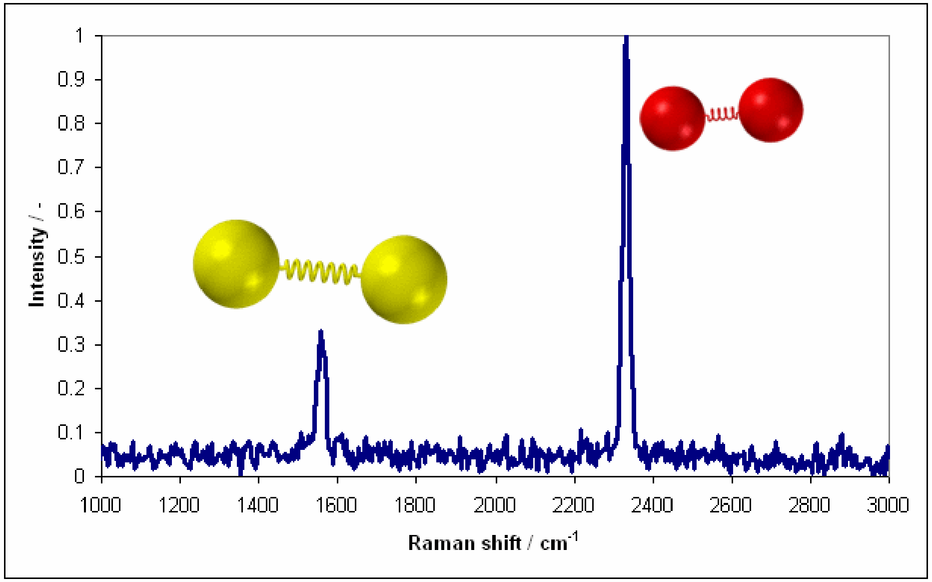


Raman (Anti-Stokes)

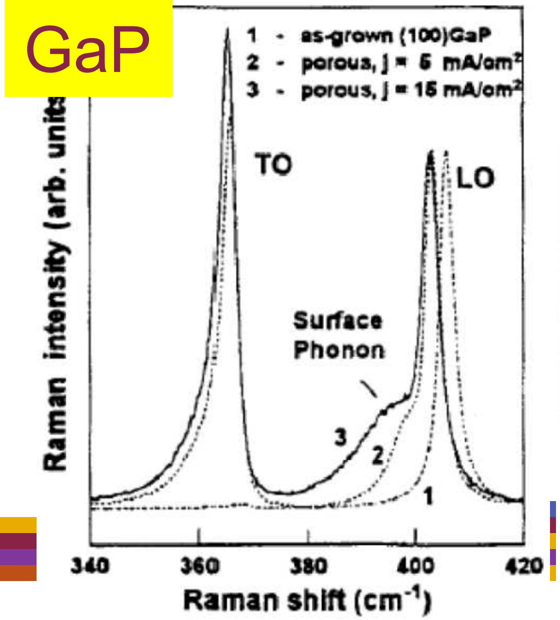
CARS

# Raman Spectroscopy

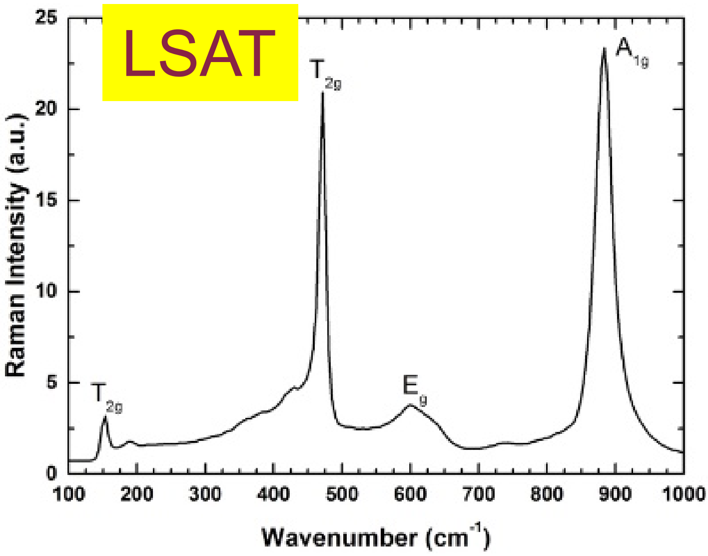




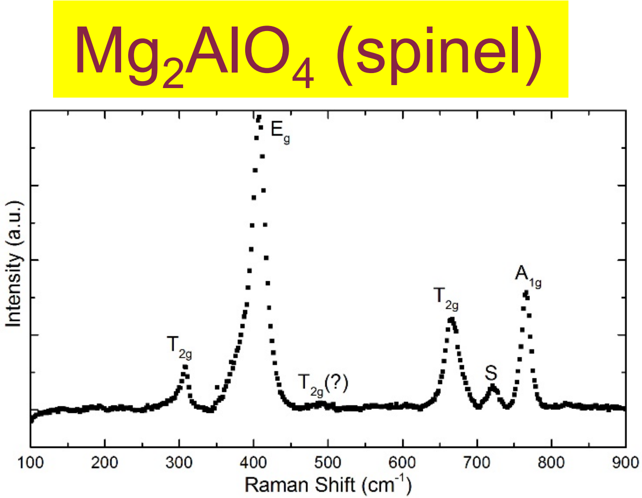
GaP



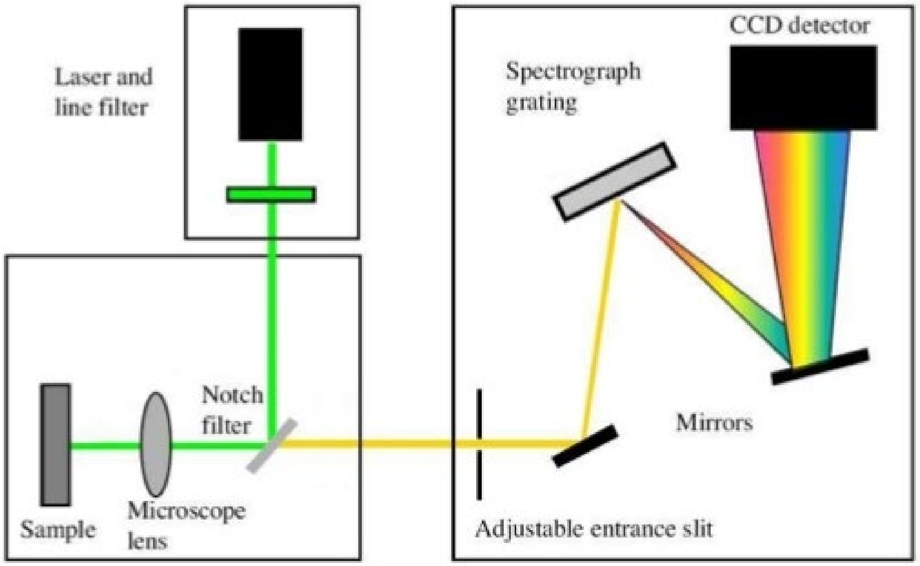
LSAT

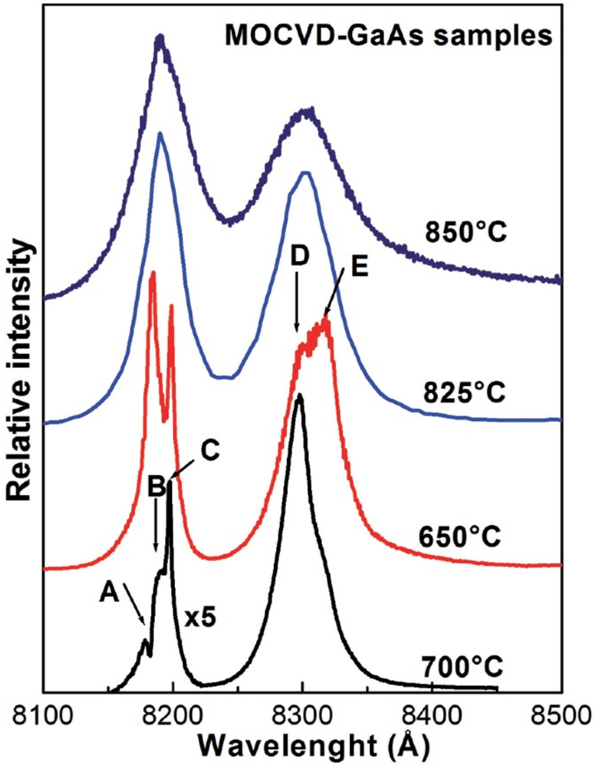


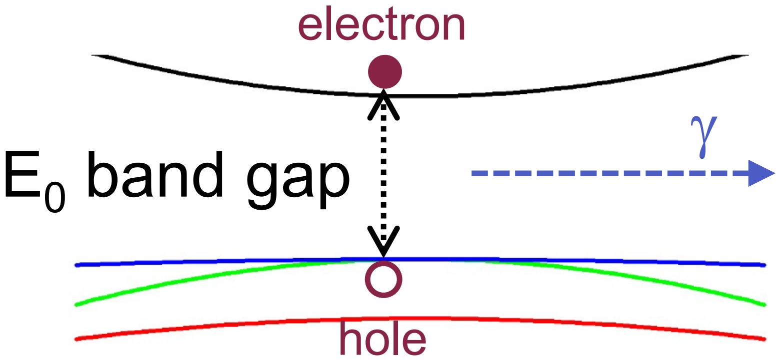
$Mg_2AlO_4$ (spinel)

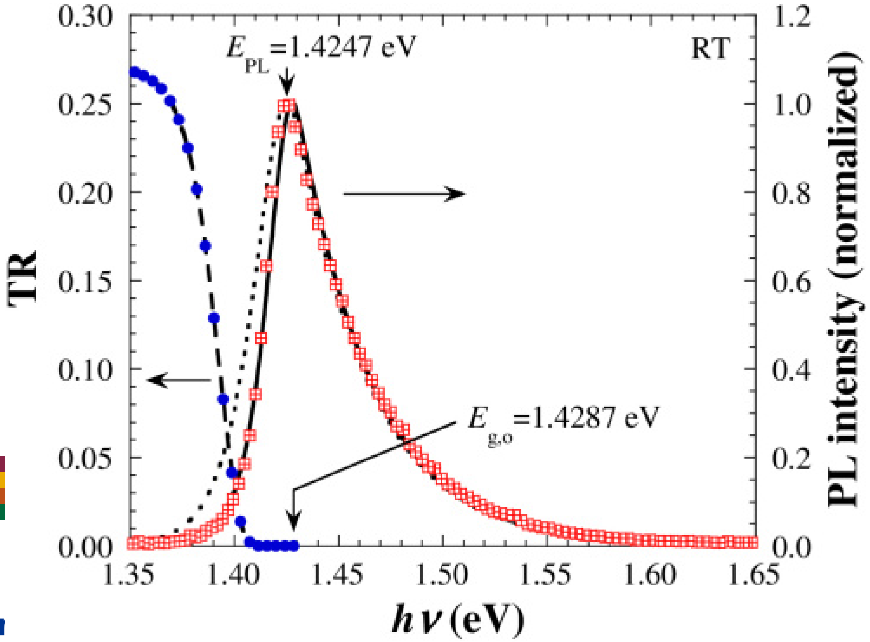


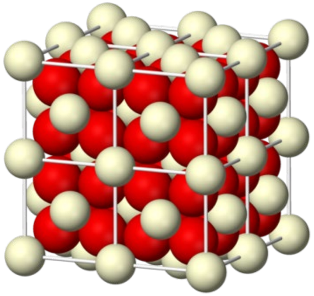
# Photoluminescence



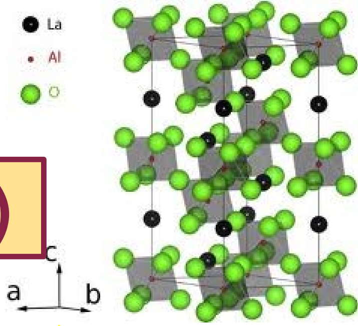








# Solid State Physics (crystalline)



## Crystal Structure (Point & Space Group)

**Electrons** ↔ **Phonons**

~~Defects~~

| Electrons | Phonons |
|---|---|
| 0.3-10 eV | 10-80 meV |
| Near-IR, VIS, UV | Far-IR to mid-IR |

Magnetism

Superconductivity

Excitons

Phase Transitions

Surfaces

Topological Insulators

Transport

Polaritons

CMOS

RF

Power

Analog

Magnetic Storage

Catalysis

Photovoltaics

Energy Conversion

Lasers

Sensors

# Materials properties accessible by optical spectroscopy

- Mid-infrared spectral range
  - Insulator/semiconductor:<br>Lattice vibrations (phonons)
  - Metal: Free carrier properties (density, scattering rate)
- Visible to UV range:
  - Electronic excitations
  - Band gap, interband transitions
- Ellipsometry allows us to study semiconductors, insulators, and metals.
- Thin films and surfaces can be investigated with proper data analysis (curve fitting).