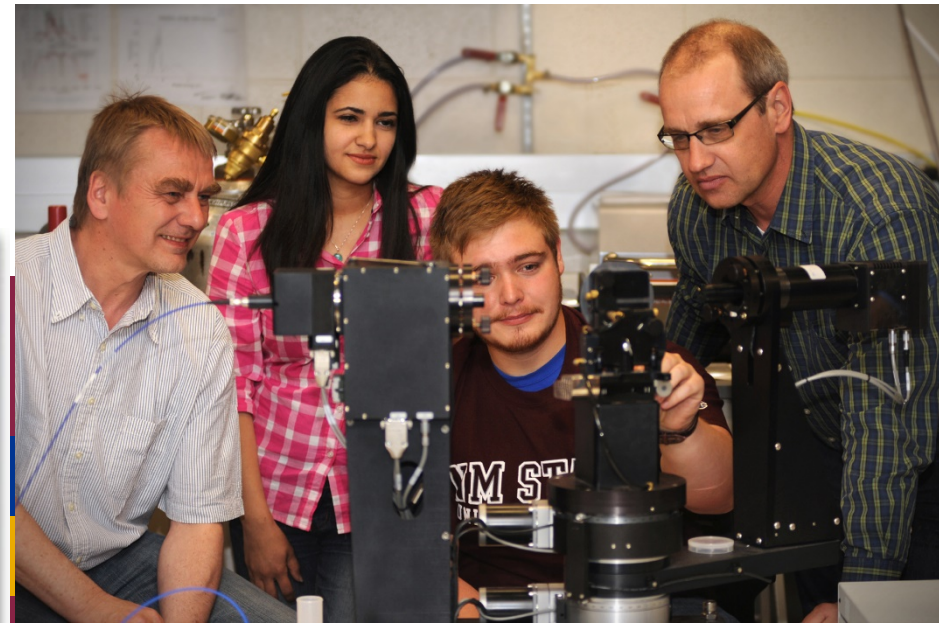
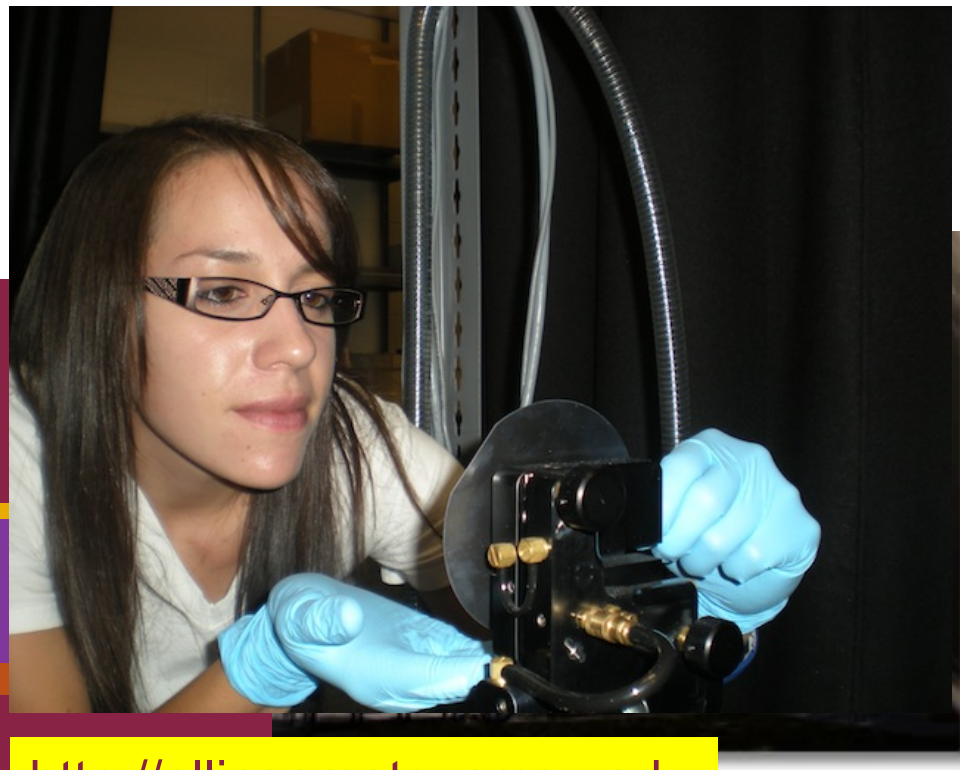


Optical Properties of Solids

Lecture 1

Stefan Zollner

New Mexico State University, Las Cruces, NM, USA
and Institute of Physics, CAS, Prague, CZR (Room 335)
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<http://ellipsometry.nmsu.edu>

NSF: DMR-1505172



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EUROPEAN UNION
European Structural and Investment Funds
Operational Programme Research,
Development and Education



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 GeO₂

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



6

Las Cruces, NM
Since 2010

Motorola (Mesa, Tempe)
Arizona, 1997-2005



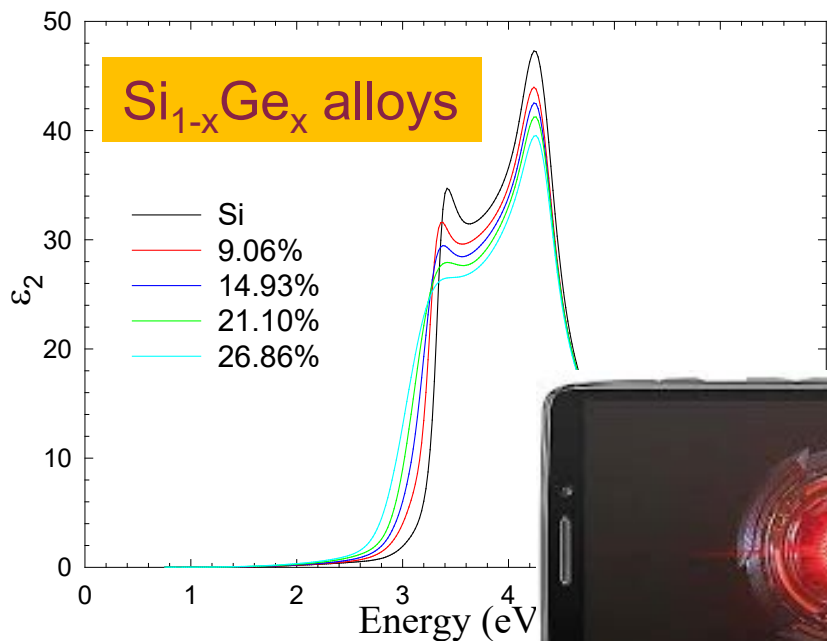
Freescale, IBM
New York, 91-92, 07-10

Motorola, Freescale
Texas, 2005-2007

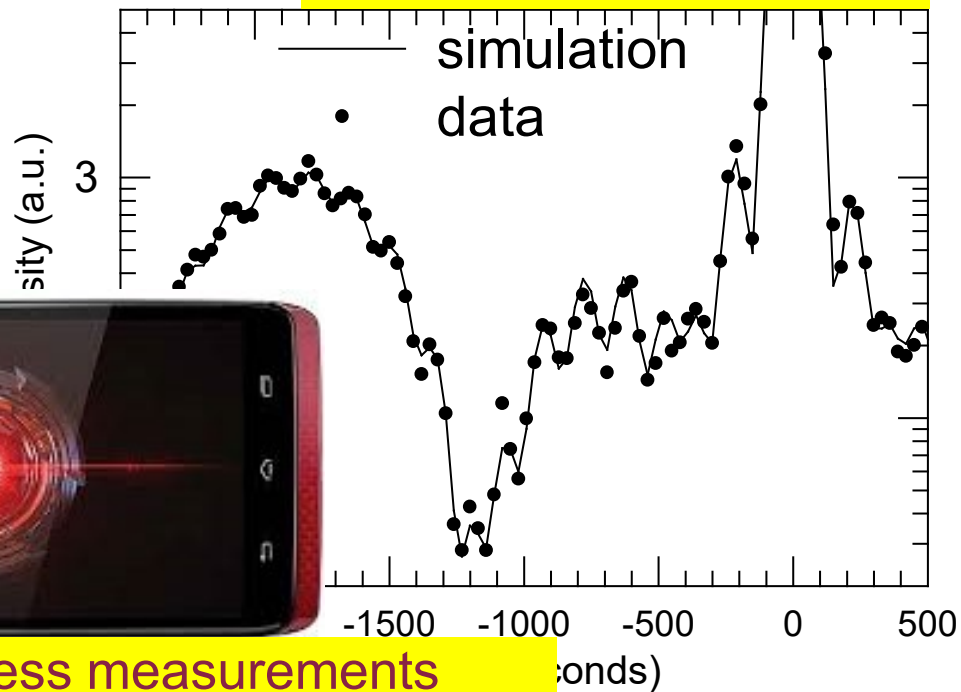


6

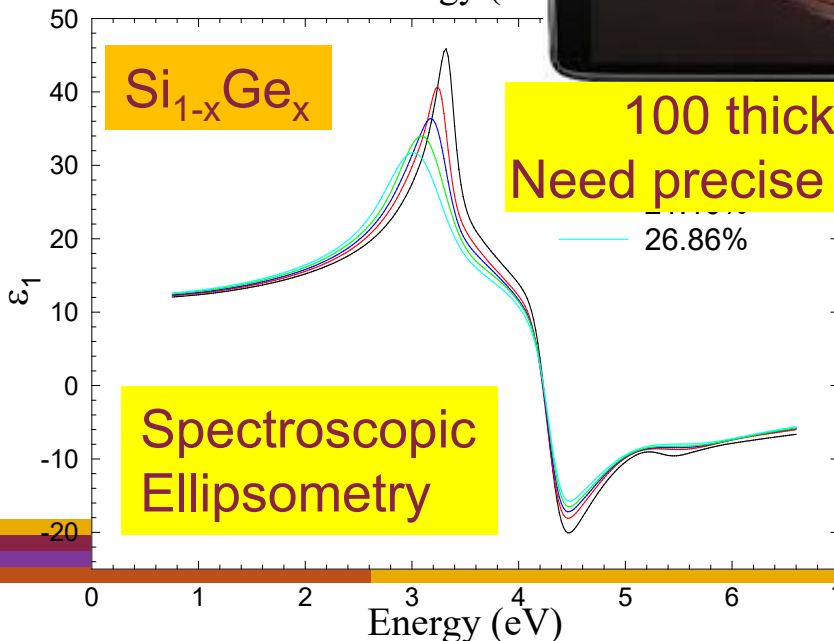
SiGe:C Metrology: How thick is my film?



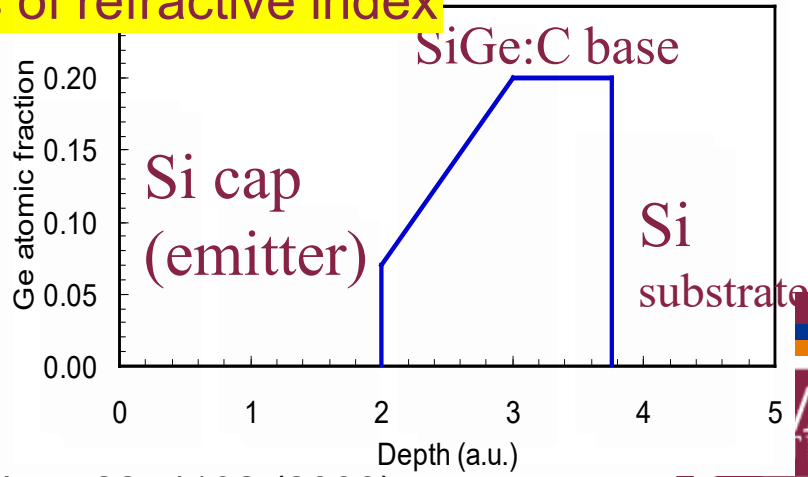
High-resolution XRD



100 thickness measurements
Need precise values of refractive index



Spectroscopic Ellipsometry



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

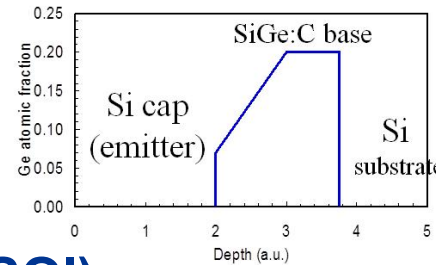
Laser annealing (>100 citations)

Nickel silicide Ohmic contacts

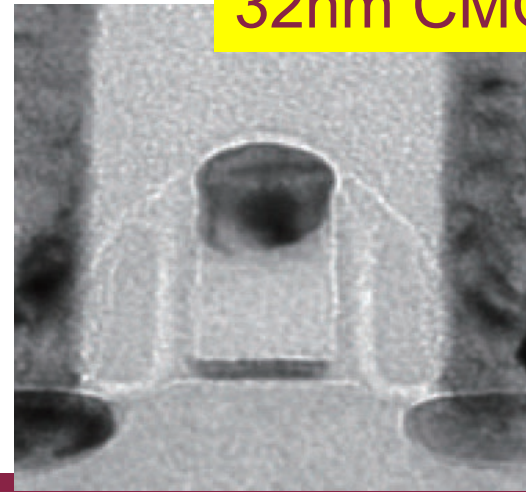
Copper interconnects

Low-k interlayer dielectrics

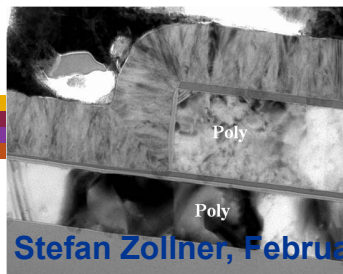
4. Power, analog, passives



32nm CMOS on SOI



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 mm², 190 nm to 40 μm, 10-800 K
low surface roughness, layers on single-side polished substrate

zollner@nmsu.edu

<http://ellipsometry.nmsu.edu>



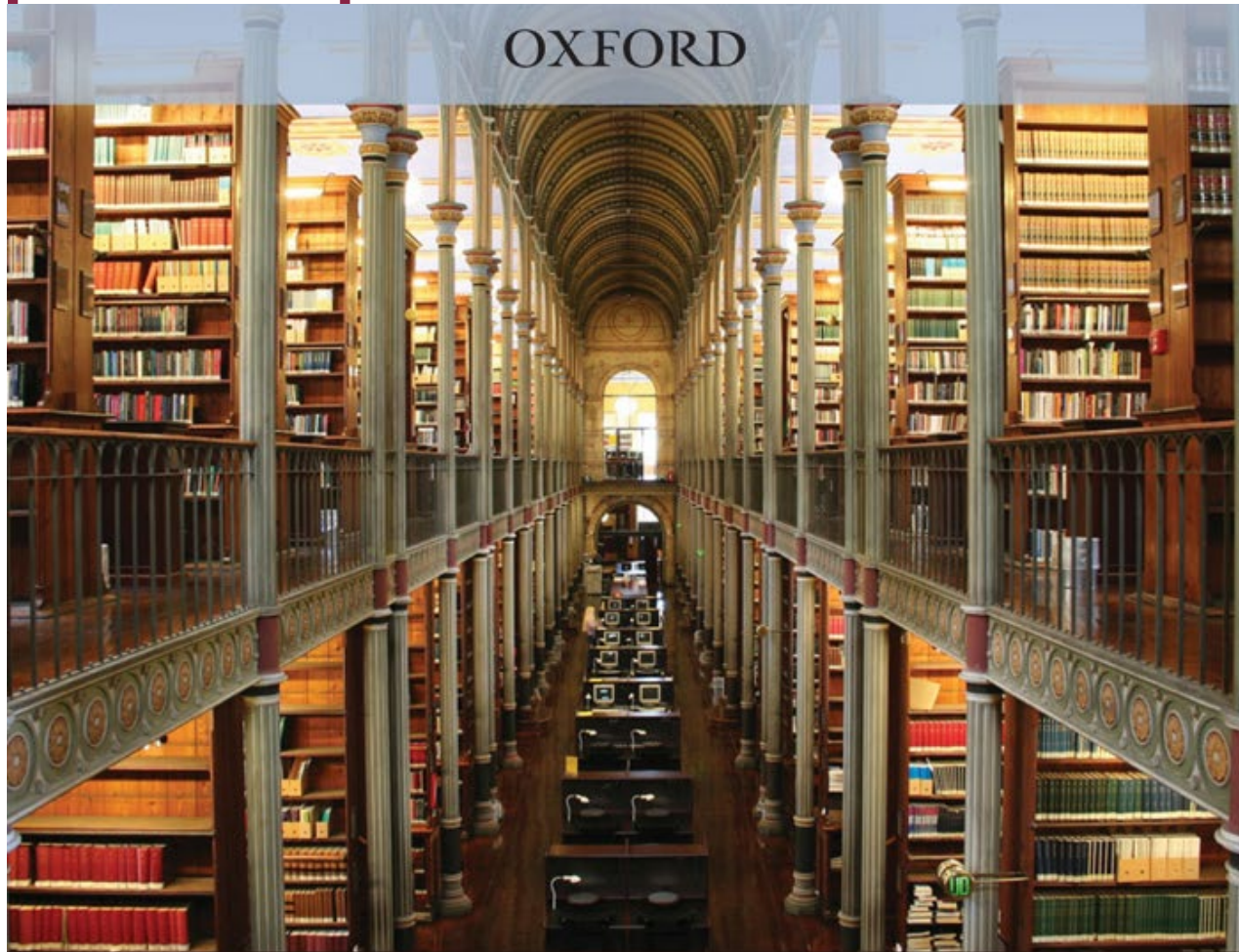
Introductions: Why are we here?



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

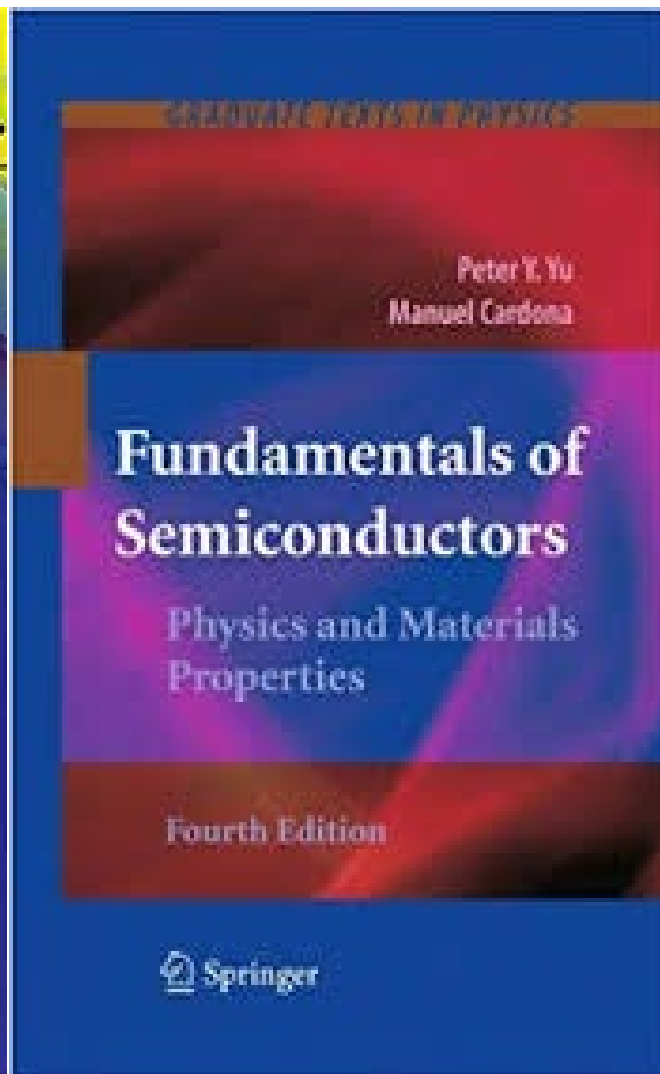
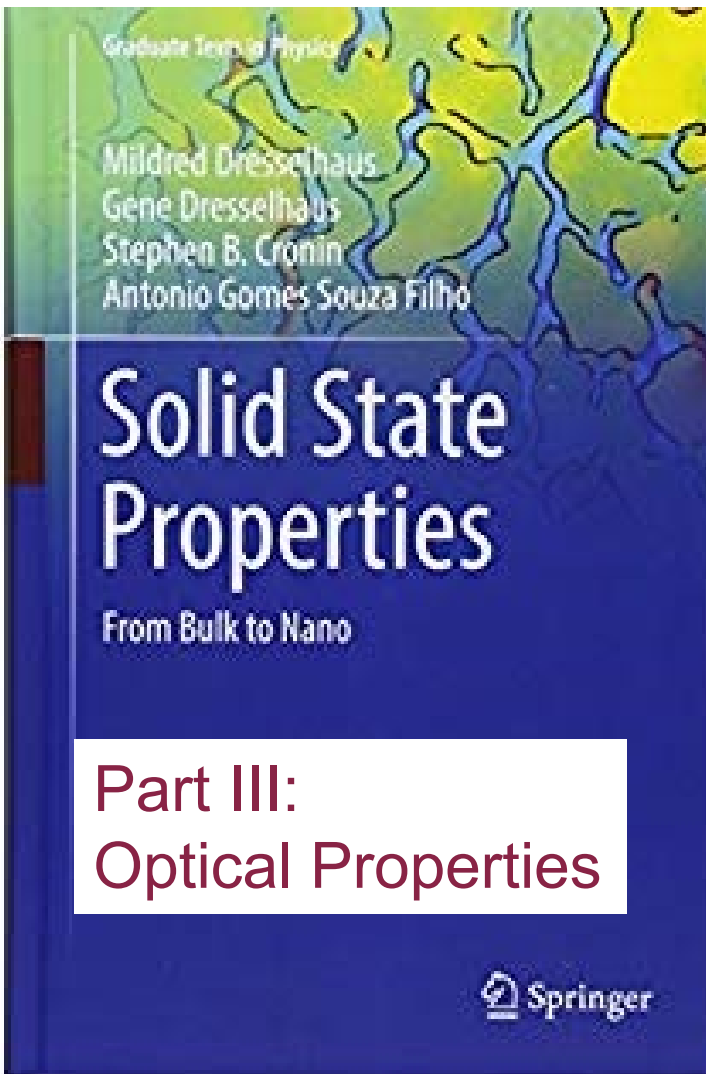


Mark Fox

Optical Properties of Solids



Optical Properties of Solids: Other Text Books



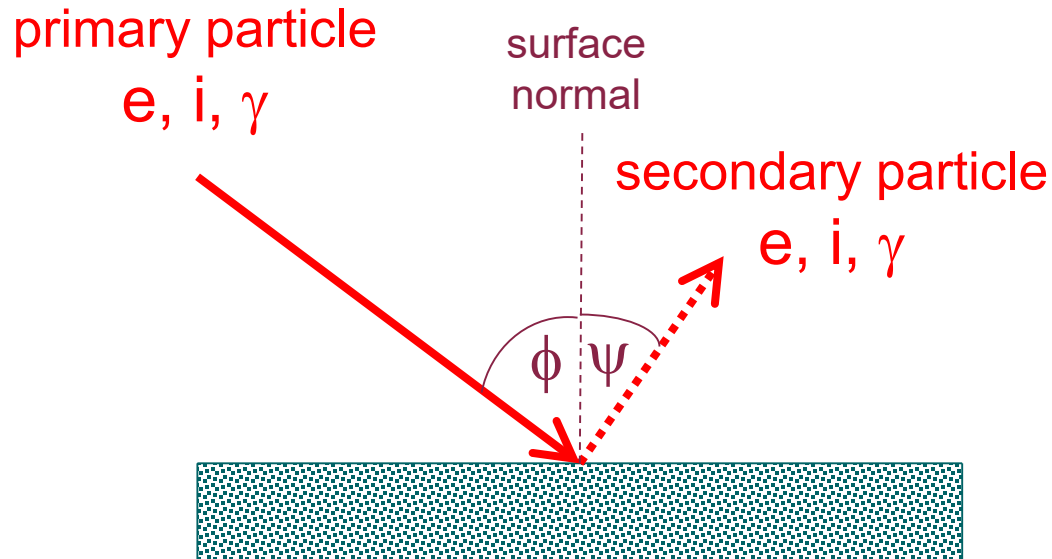
M.L. Cohen &
J. Chelikowsky:
Electronic Structure &
Optical Properties

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



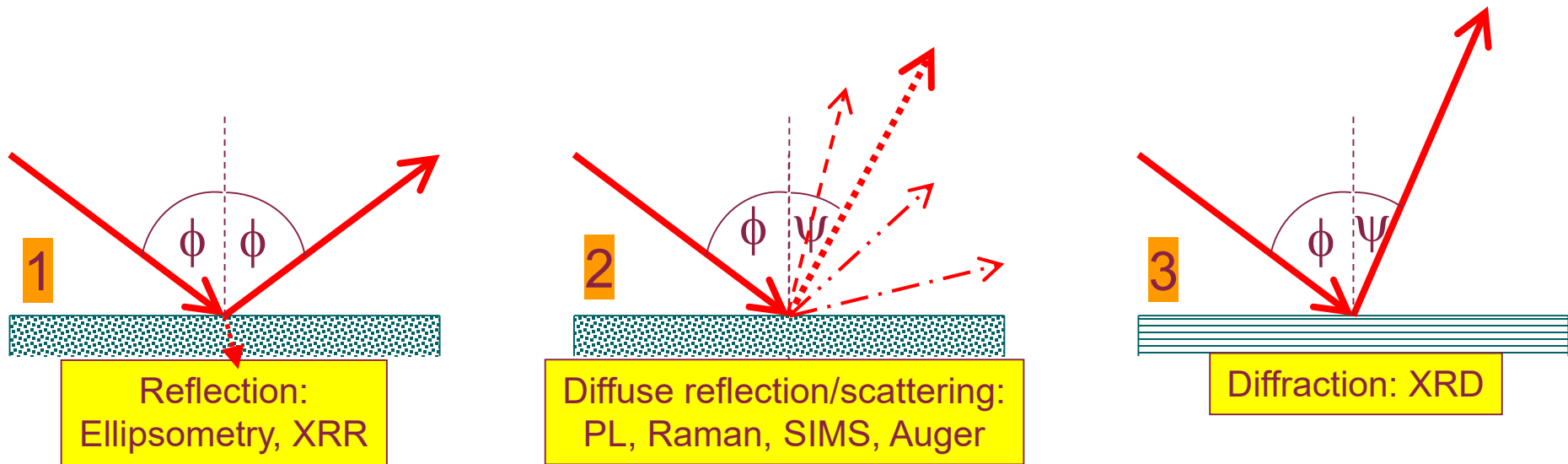
Particles: Electron (e), ion (i), or photon (γ)

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.

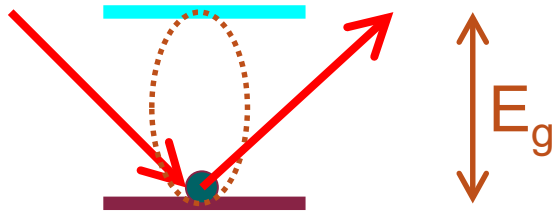
The **interaction depth** for thin films depends on the **penetration depth** of the primary particle and the **escape depth** of the secondary particle.
(This can be nanometers to micrometers, depends on each technique.)

Classification Schemes for Surface Spectroscopy II

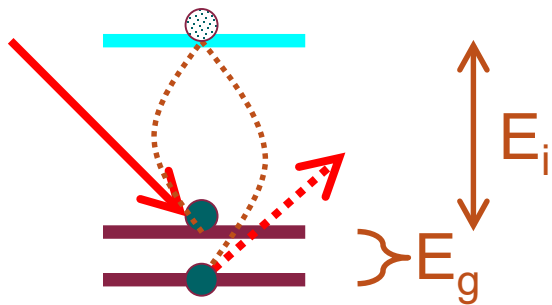


- 1. Specular reflection:** The angle of reflection is equal to the angle of incidence. For some spectroscopies, the angles are measured relative to the surface (XRR), for others relative to the surface normal (SE).
- 2. Diffuse reflection or scattering:** There is no well-defined direction, in which 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).



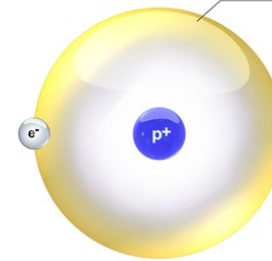
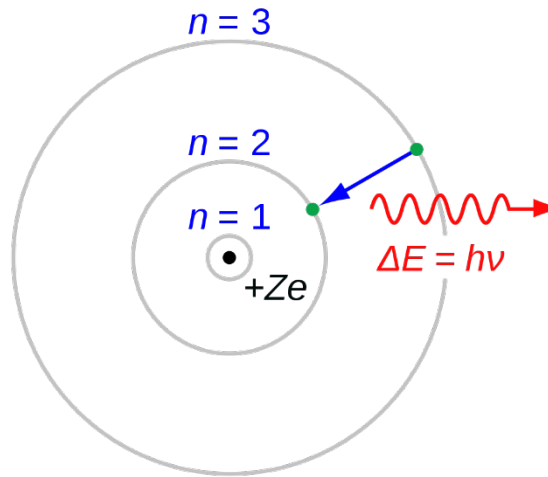
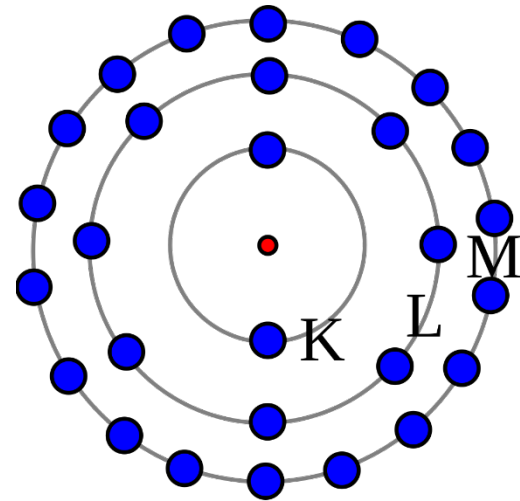
Inelastic: The energy difference (gain or loss) provides information about vibrational (Raman) or electronic (Auger) energy states. The strength of the scattering process depends on the interaction with an intermediate state.

- **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

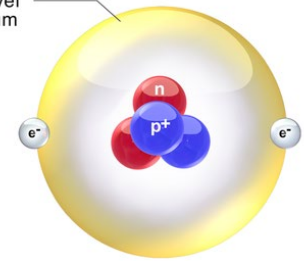
- Spectroscopic Ellipsometry: Elastic, specular, $\gamma \rightarrow \gamma$
Thickness, Energy (band gap), refractive index, composition
- X-ray reflectivity: Elastic, specular, $\gamma \rightarrow \gamma$
Thickness, density, surface/interface roughness
- X-ray diffraction: Elastic, diffracted, $\gamma \rightarrow \gamma$
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

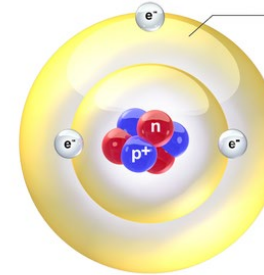


Hydrogen, H
Atomic number: 1
Mass number: 1
1 electron

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

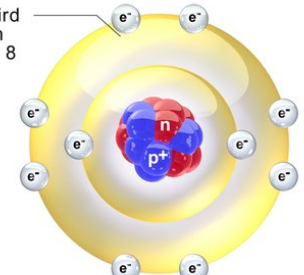


Helium, He
Atomic number: 2
Mass number: 4
(2 protons + 2 neutrons)
2 electrons



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

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



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

Quantum Numbers:

n	$1, 2, 3, \dots$
l	$0, \dots, n-1$
m	$-l, \dots, l$
s	$\pm 1/2$

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

$$R = 13.6 \text{ eV}$$

Relativistic corrections:

s electrons ($l=0$) close to the core

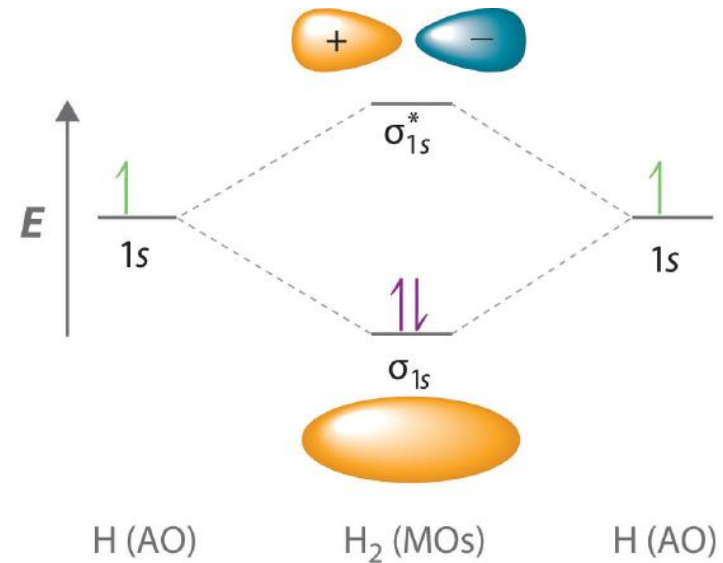
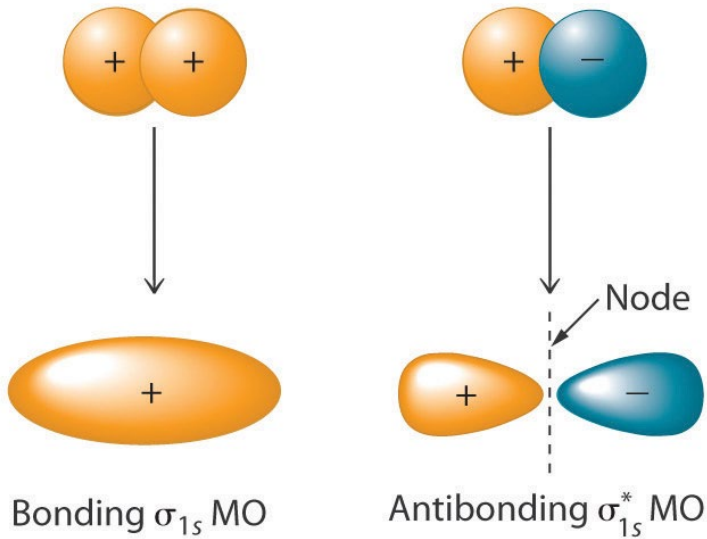
$\mathbf{J} = \mathbf{L} + \mathbf{S}$ total angular momentum

Spin-orbit coupling $\mathbf{L} \cdot \mathbf{S}$

$L=1, S=1/2$

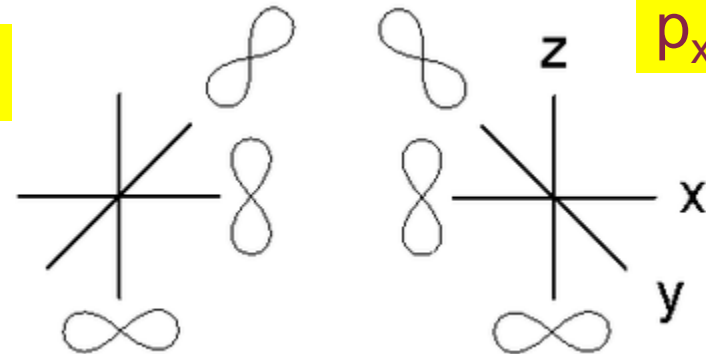
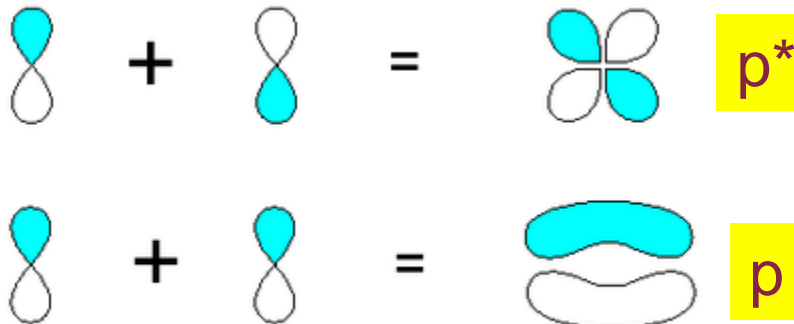
$J=1/2$ or $3/2$

Bonding and Anti-Bonding Orbitals



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

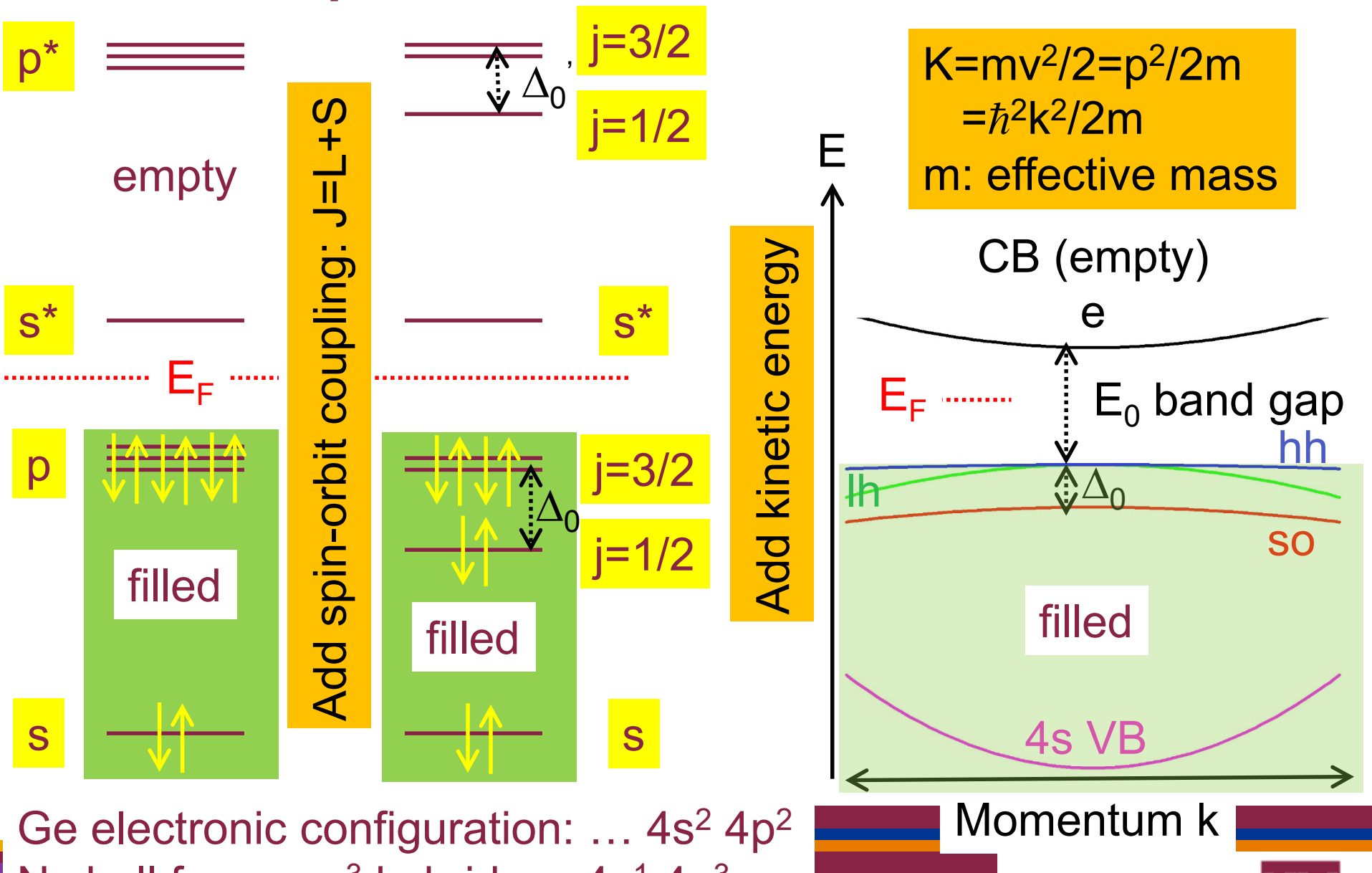
$$s^*: \Psi = \psi_1 - \psi_2$$



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

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

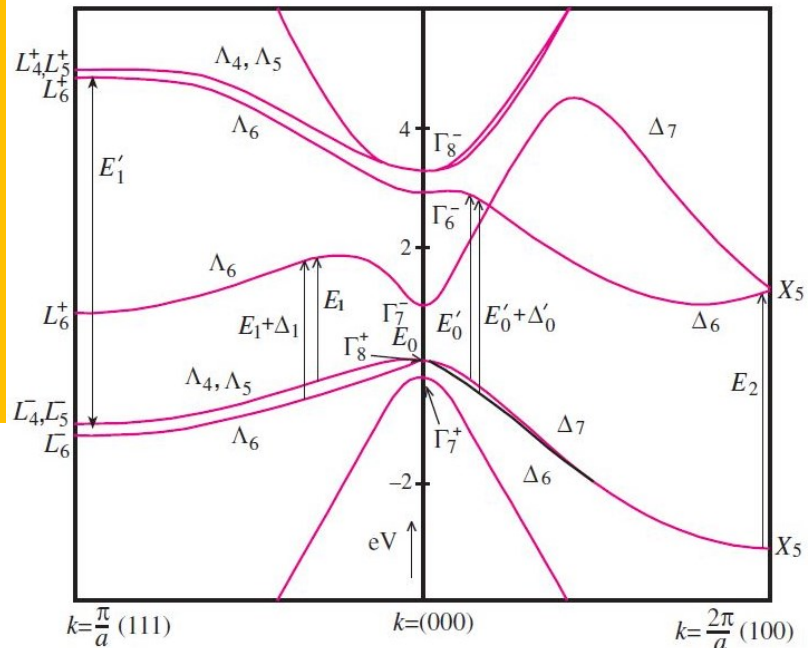
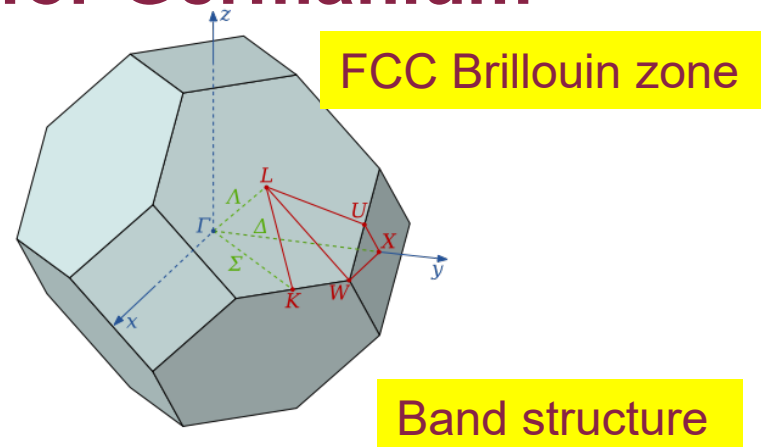
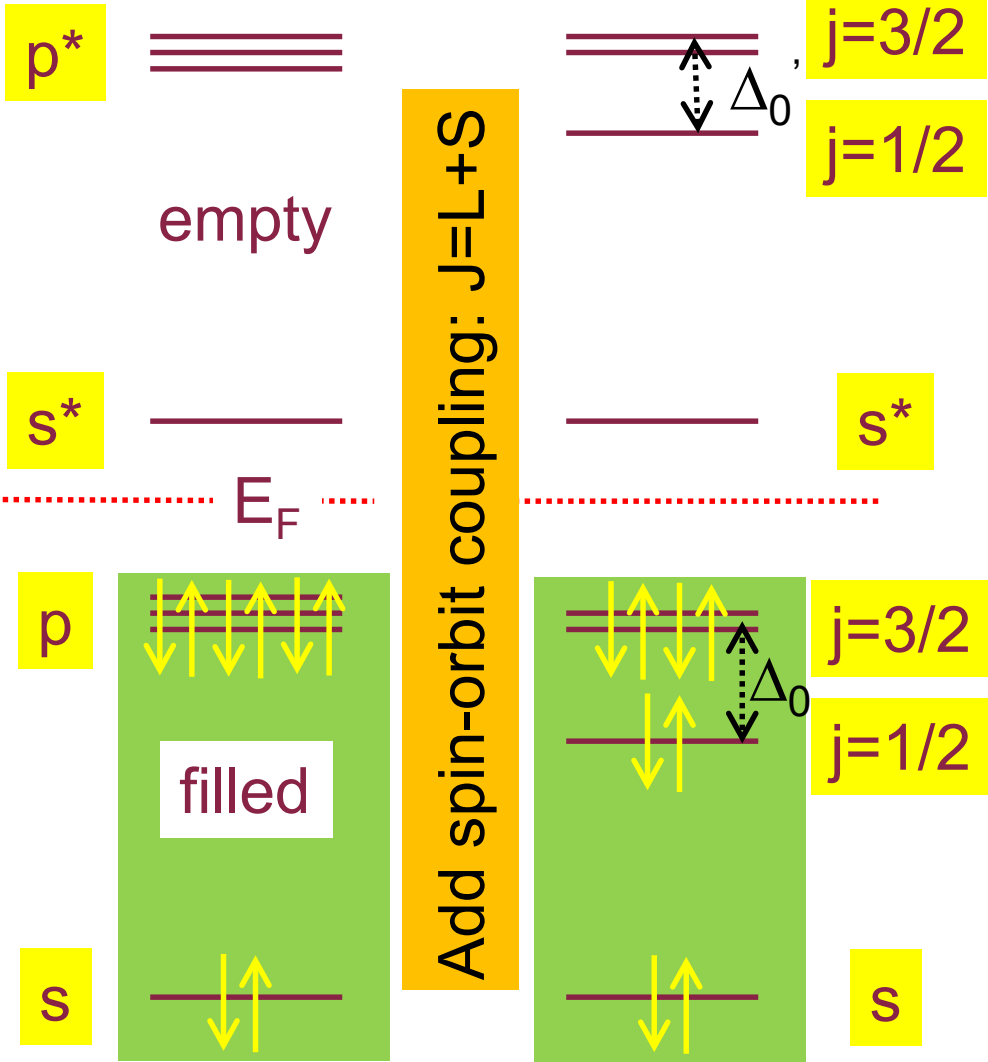
A simple band structure for Germanium



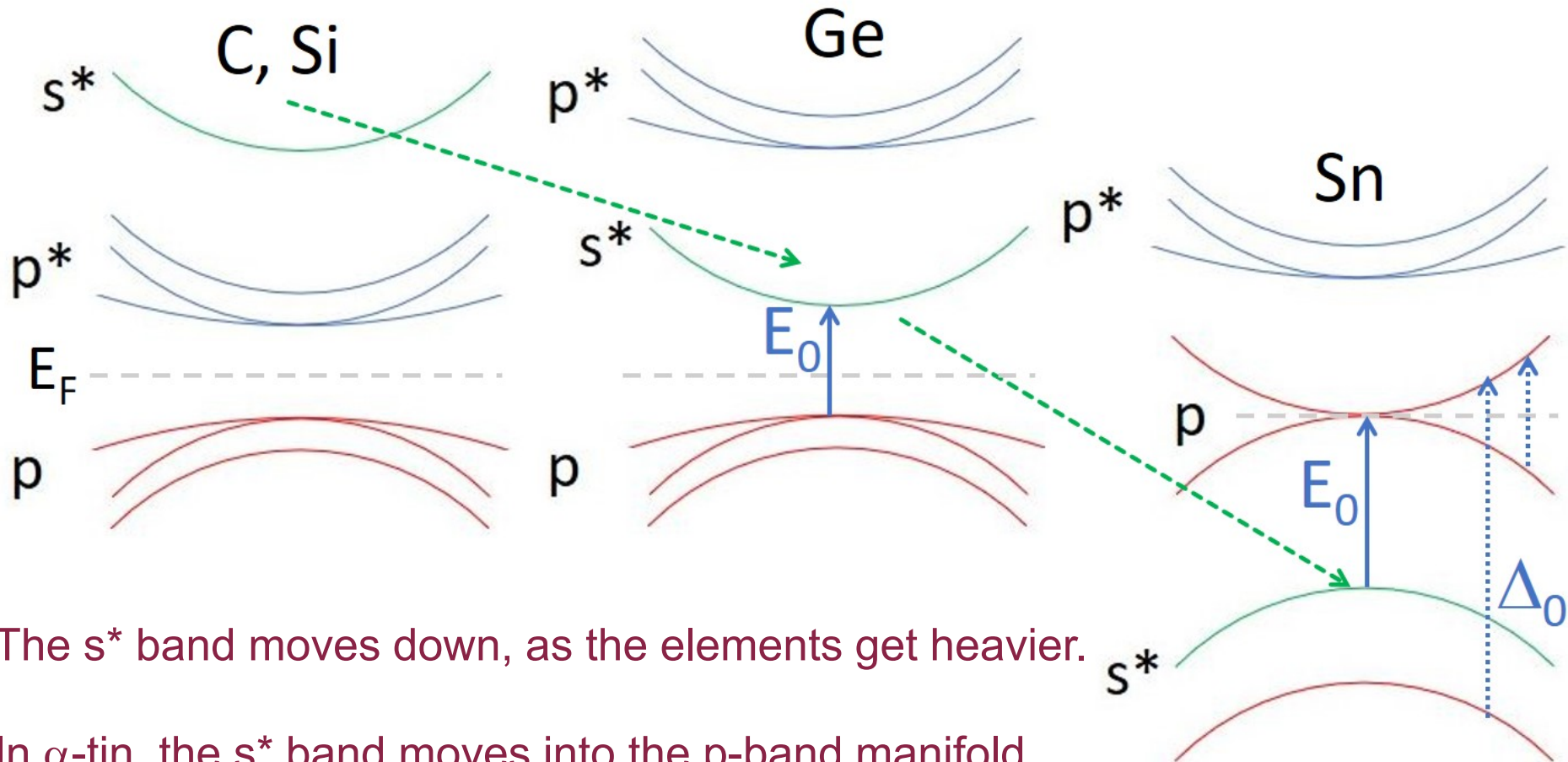
Ge electronic configuration: ... $4s^2 4p^2$
 N shell forms sp^3 hybrid: ... $4s^1 4p^3$



A simple band structure for Germanium



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.

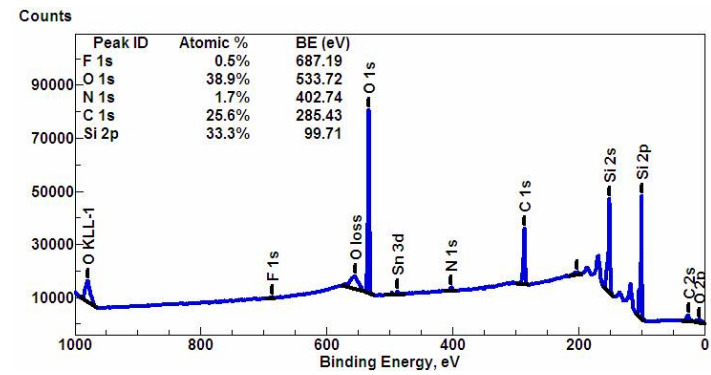
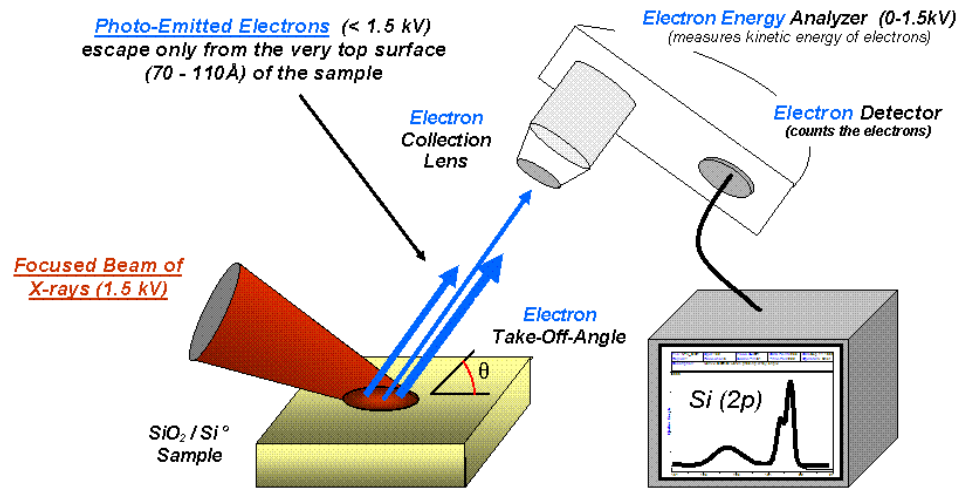
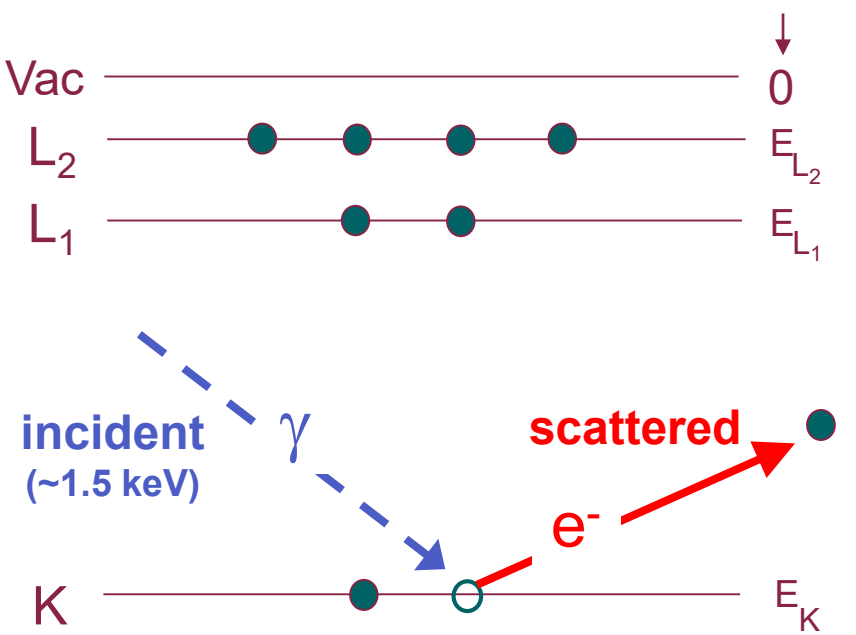
Classification Schemes for Surface Spectroscopy IV

- 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, $i \rightarrow i$
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

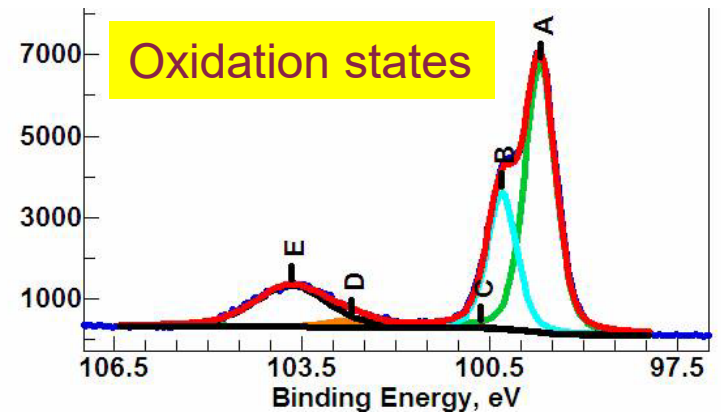
Example: X-ray Photoelectron Spectroscopy: $\gamma \rightarrow e^-$

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

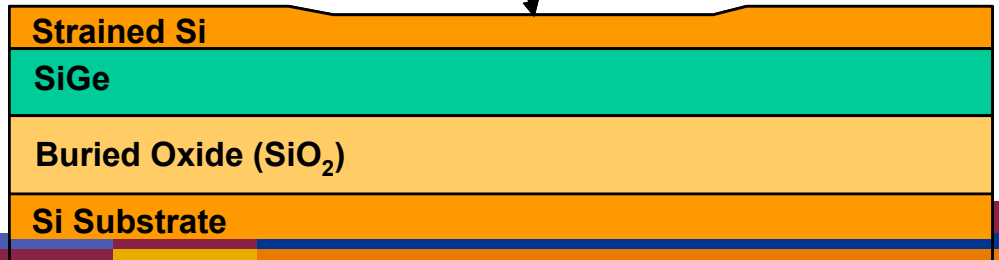
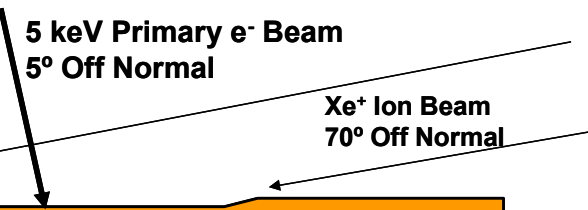
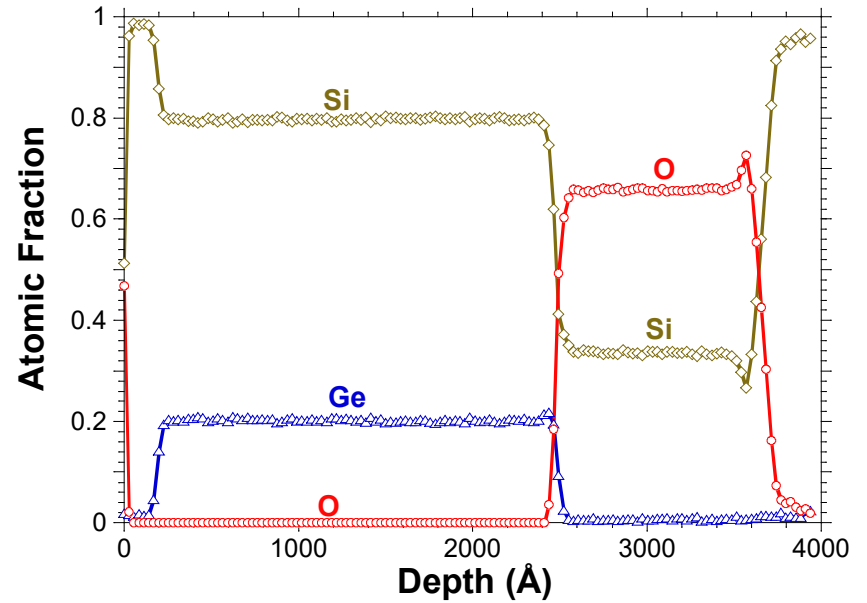
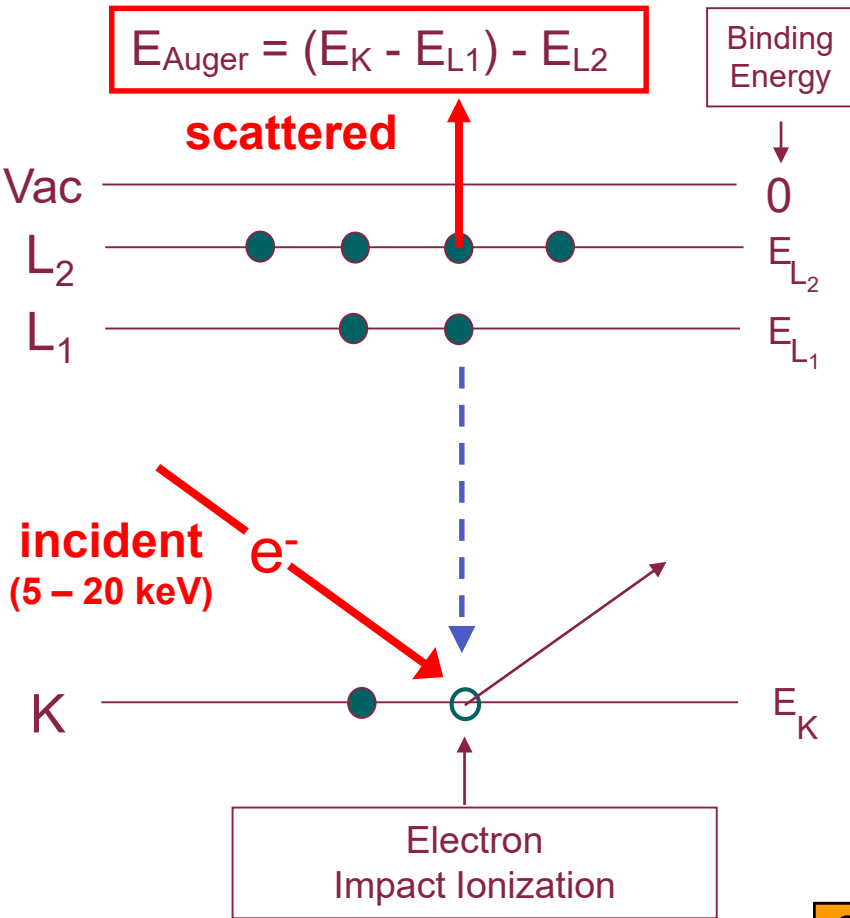
Binding Energy



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



Example: Auger Electron Spectroscopy: $e \rightarrow e$

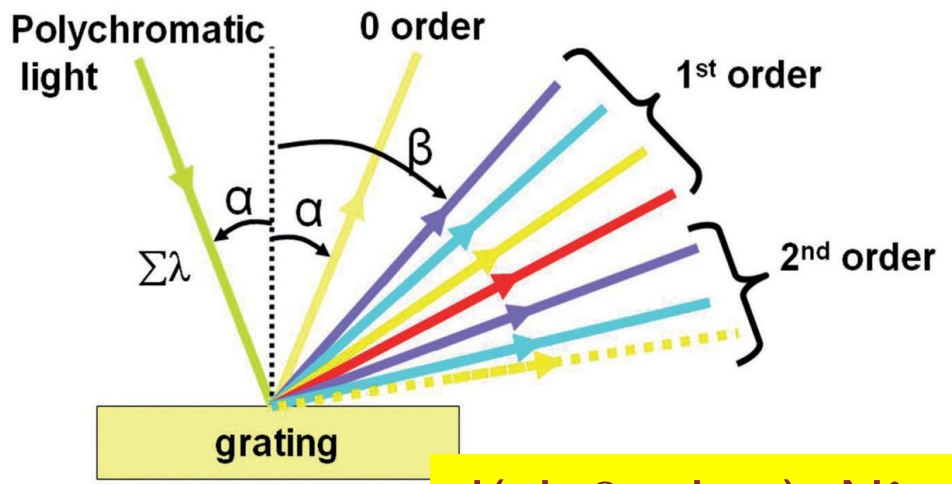


Quantification using RBS standards
 High depth resolution
 (small escape depth of L electrons)

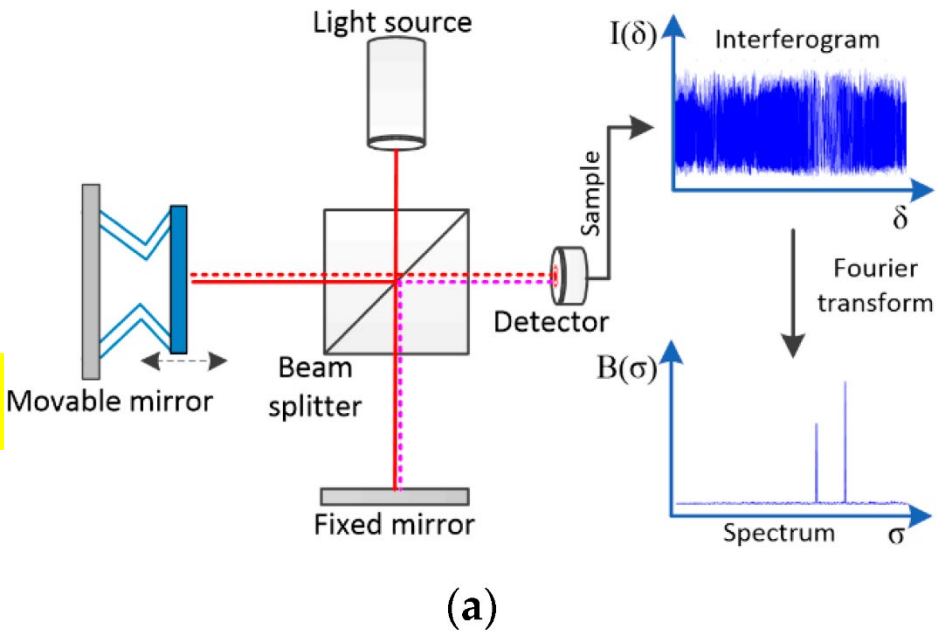


Grating Monochromator

Fourier-Transform Spectrometer

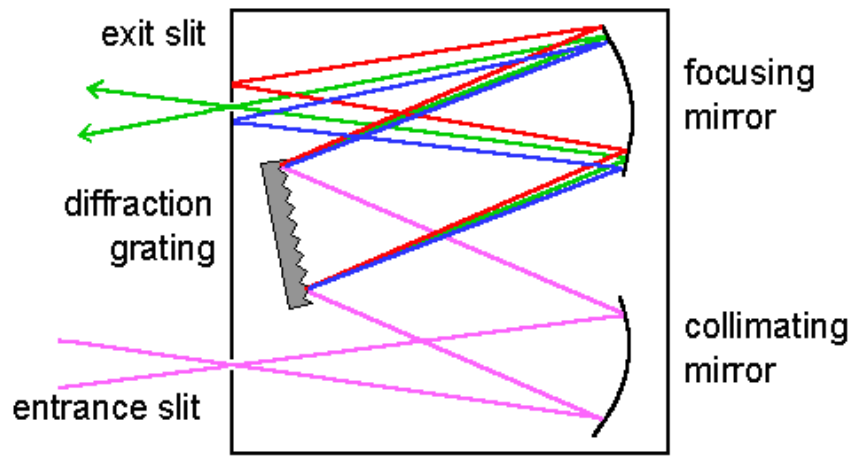


$$d(\sin\beta - \sin\alpha) = N\lambda$$



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

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



Diffracted intensity depends on angle and polarization.



Macroscopic Optical Constants

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

Why not $n-ik$?

Wave goes like $\exp[i(kx-\omega t)]$

R : reflectance at normal incidence (I_{refl}/I_0)

T : transmittance (I_{trans}/I_0)

$$R+T+A+S=1$$

α : absorption coefficient

$$\alpha=4\pi k/\lambda$$

ϵ : complex dielectric function

$$\epsilon=\epsilon_1+i\epsilon_2=(n+ik)^2$$

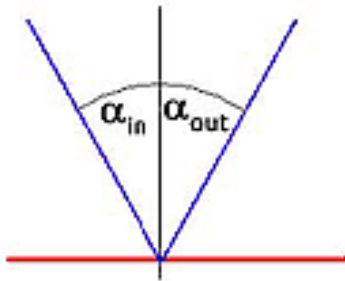
All are connected through
Maxwell's equations (Lectures 3/4).

Reflection and Transmission

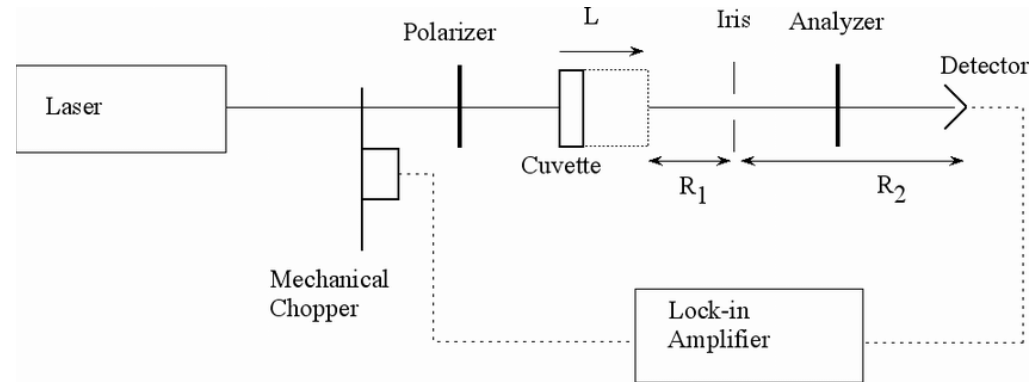
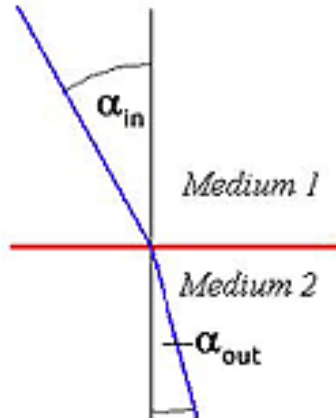
Also have diffuse scattering.

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

Reflection



Transmission



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

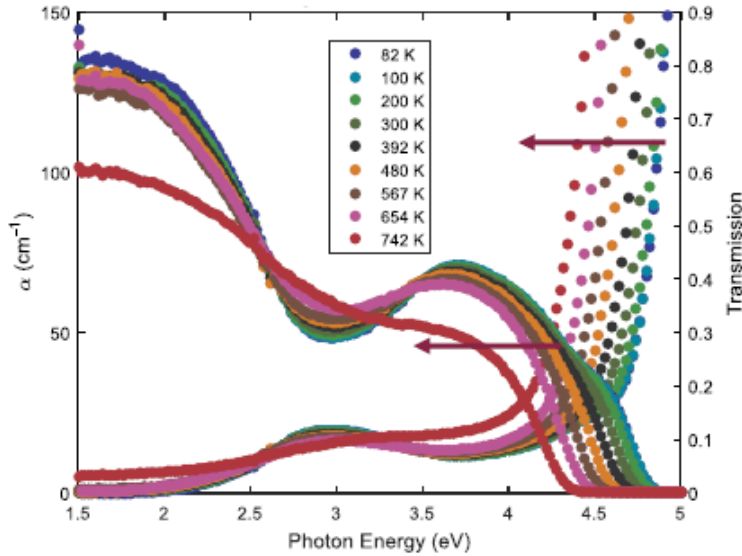
Absorption coefficient α (cm^{-1})
Consider reflection losses

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

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

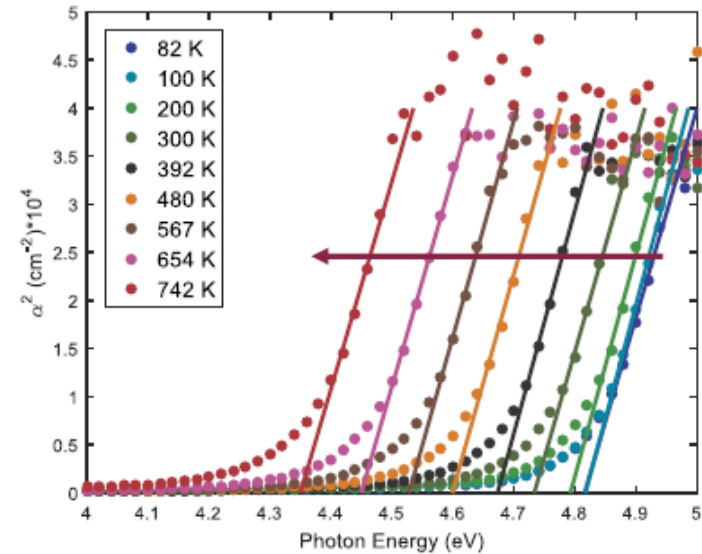
Transmission: LSAT or $(\text{LaAlO}_3)_{0.3}(\text{SrAlTaO}_6)_{0.35}$

Absorption Coefficient and Transmission Data

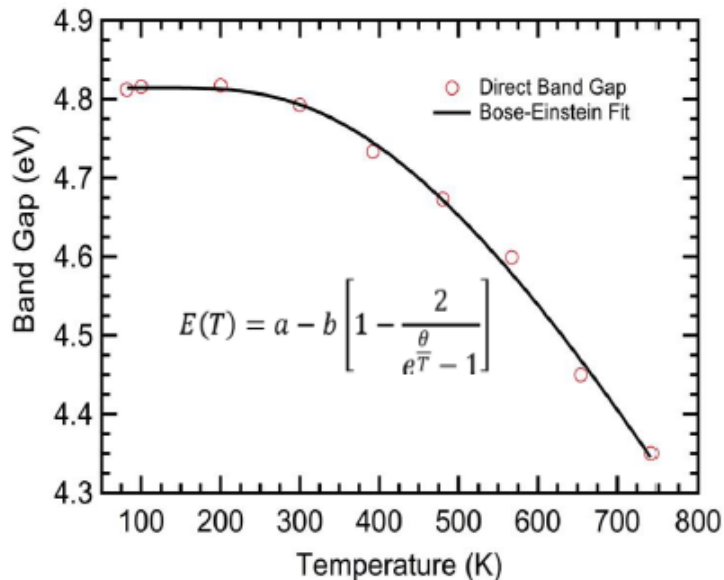


$$T = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}$$

Absorption Coefficient Squared



Direct Band Gap

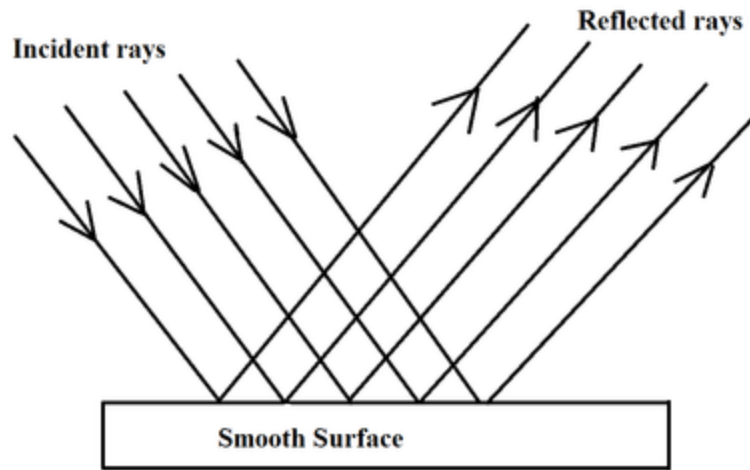


Bose-Einstein Model

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

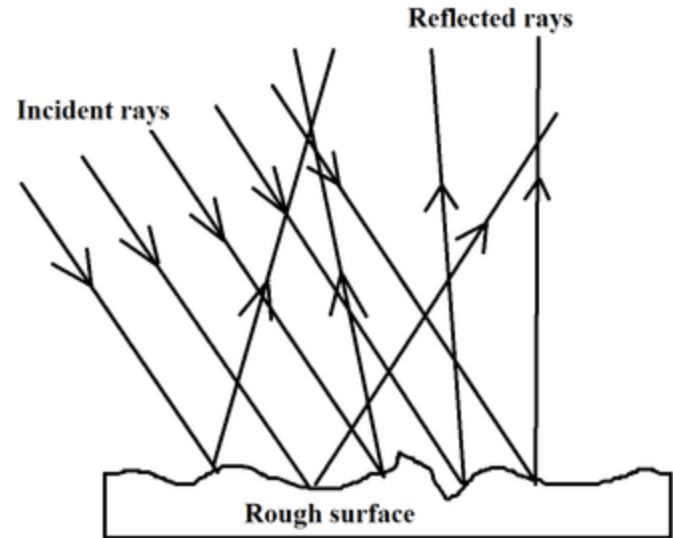
a (eV)	6.32 ± 0.29
b (eV)	1.50 ± 0.29
θ (K)	1486 ± 121

Reflection from a rough surface



I. Regular Reflection

Specular



II. Irregular Reflection

Specular+Diffuse

Debye-Waller correction:

Assumes sinusoidal roughness

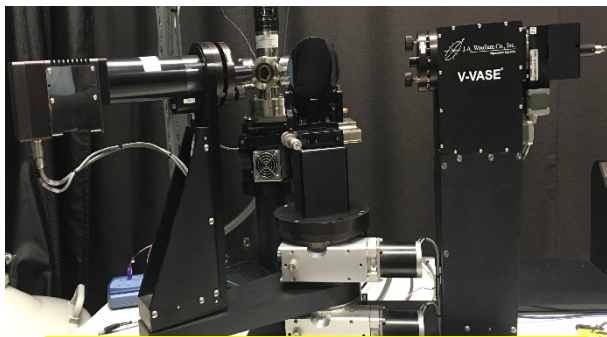
$$R_{\text{rough}} = R_0 \exp[-(4\pi\sigma n \cos\theta / \lambda)^2]$$

σ : rms surface roughness parameter

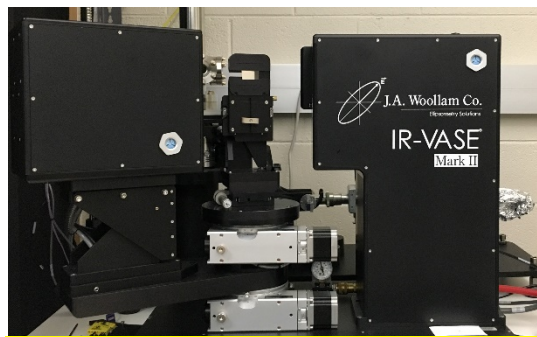
Also: I. Ohlidal, F. Lukes,
and K. Navratil, Surf. Sci.
45, 91 (1974). 98 citations.

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

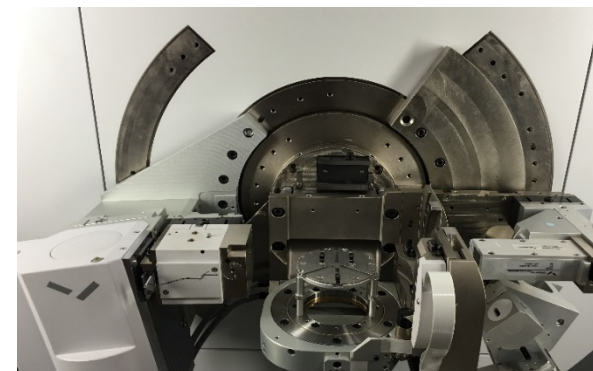
Reflectance Spectroscopy Instrumentation



Spectroscopic Ellipsometer (VUV/UV/VIS-VASE)



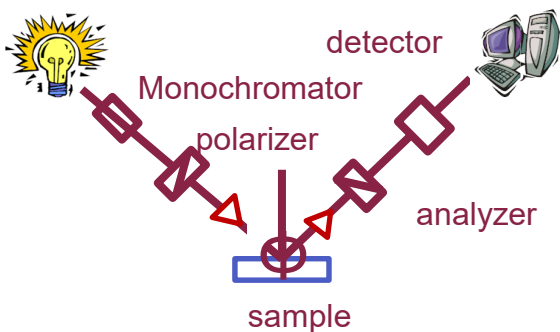
Spectroscopic Ellipsometer (IR-VASE)



X-ray diffraction & reflectance

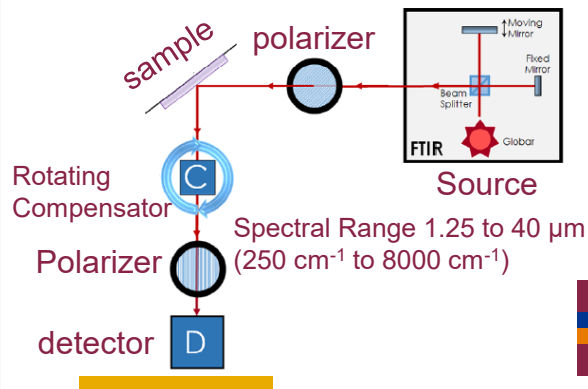
Spectroscopic Ellipsometry:

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



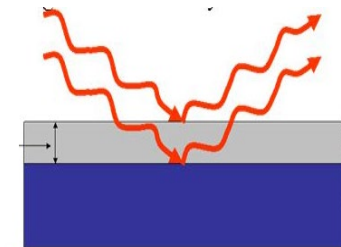
FTIR ellipsometry:

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

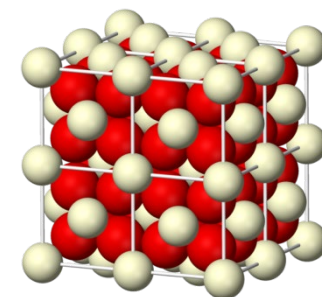
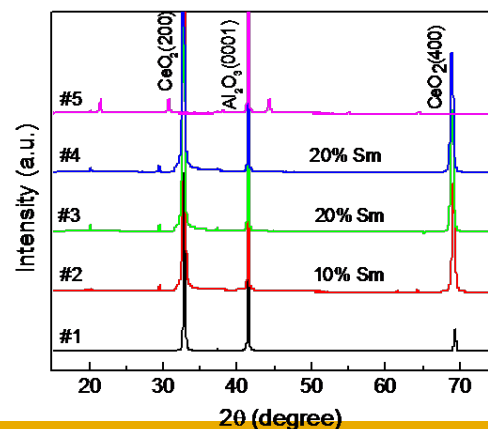
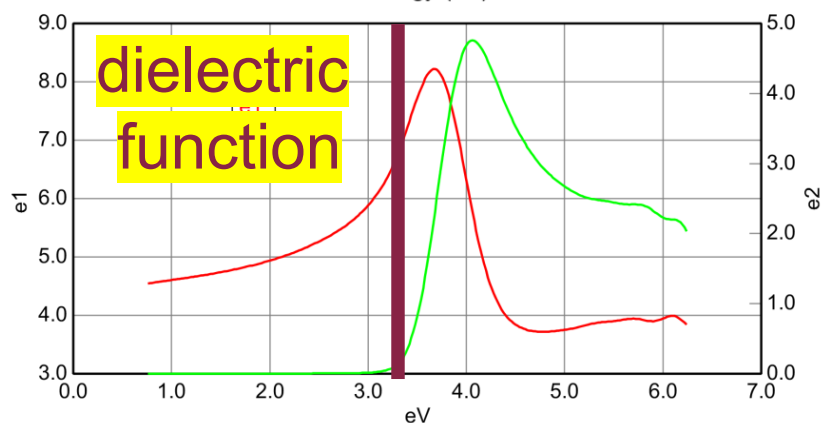
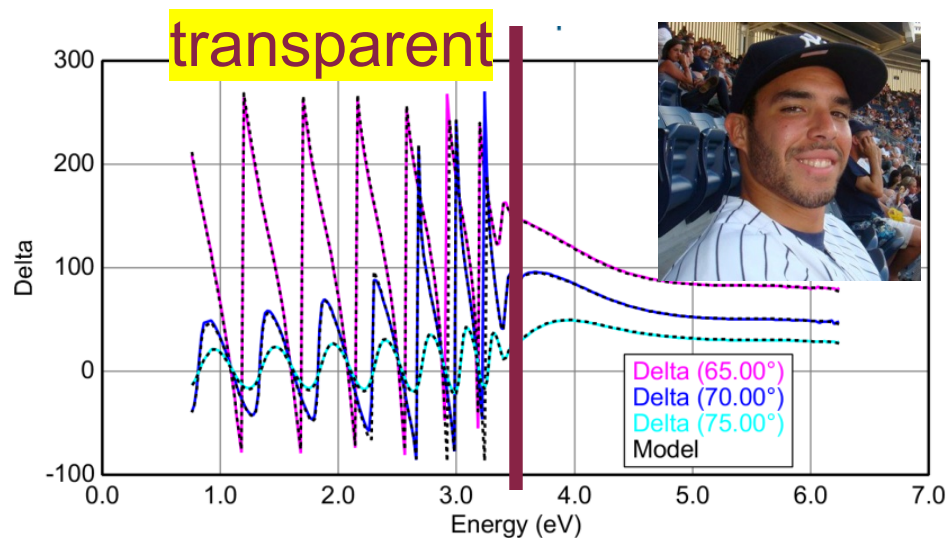
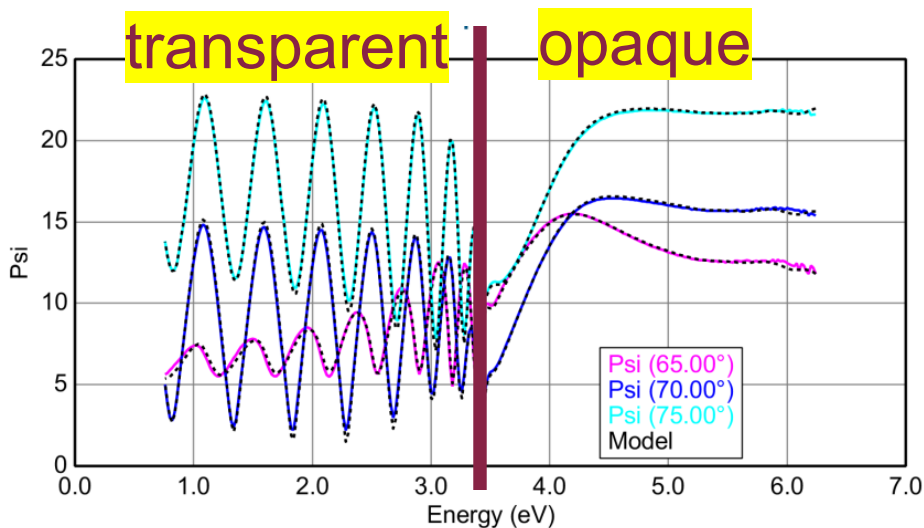


XRD/XRR:

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



Crystalline CeO₂ on sapphire (liquid deposition)



Fluorite (O_h⁵)

- Insulating CeO₂ 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?

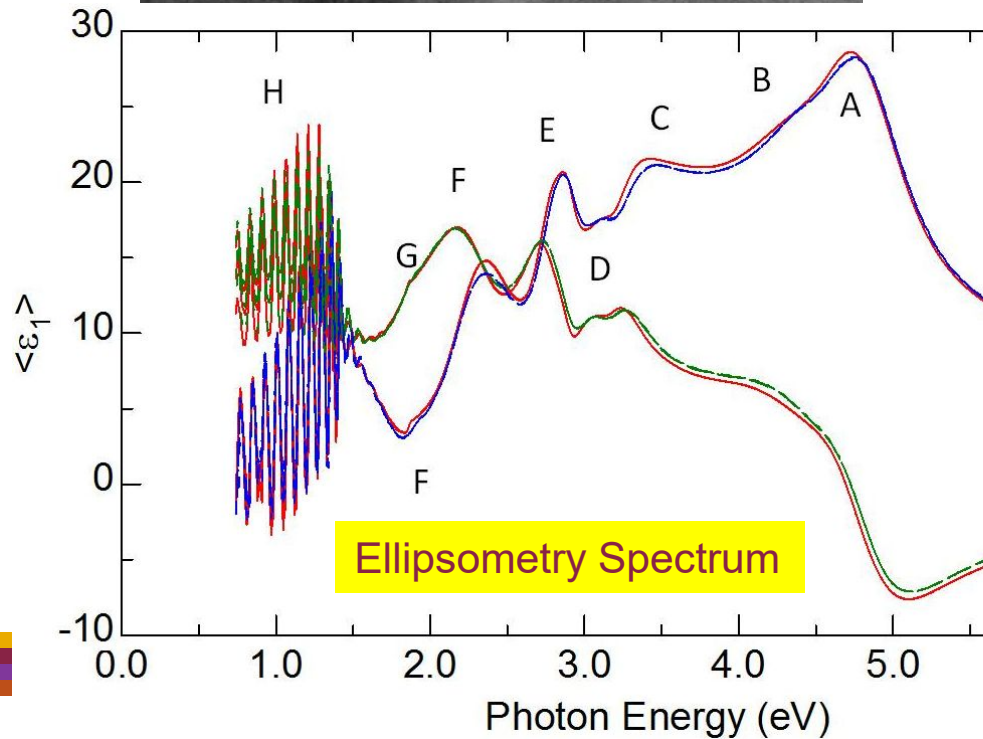
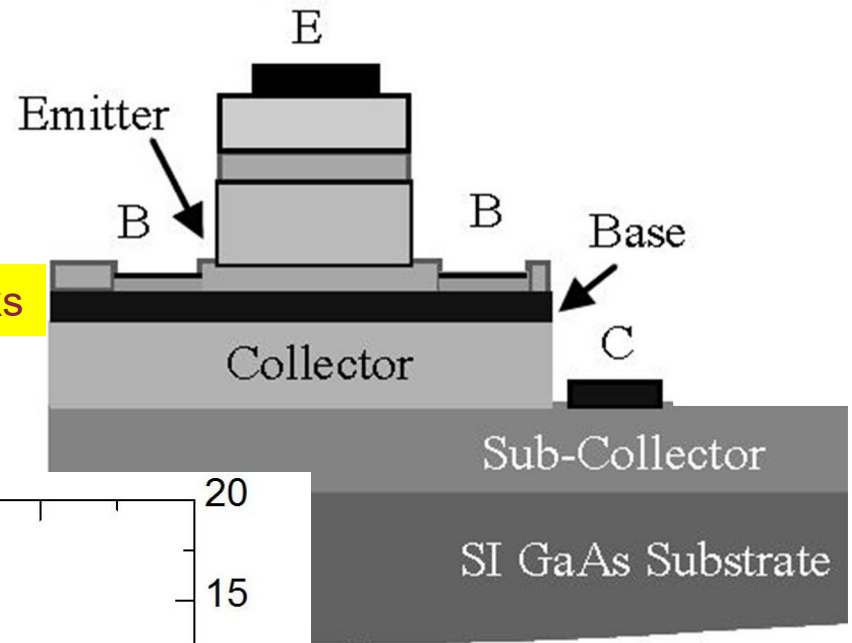
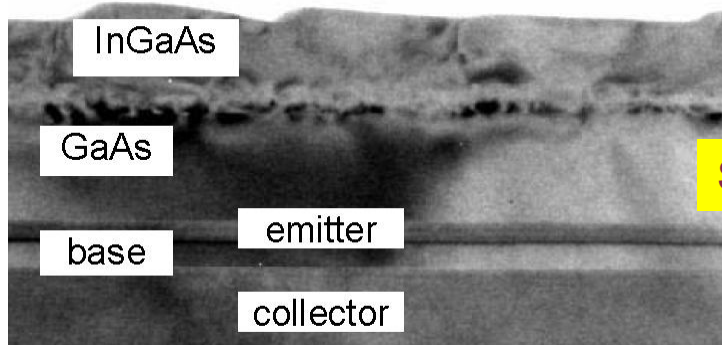
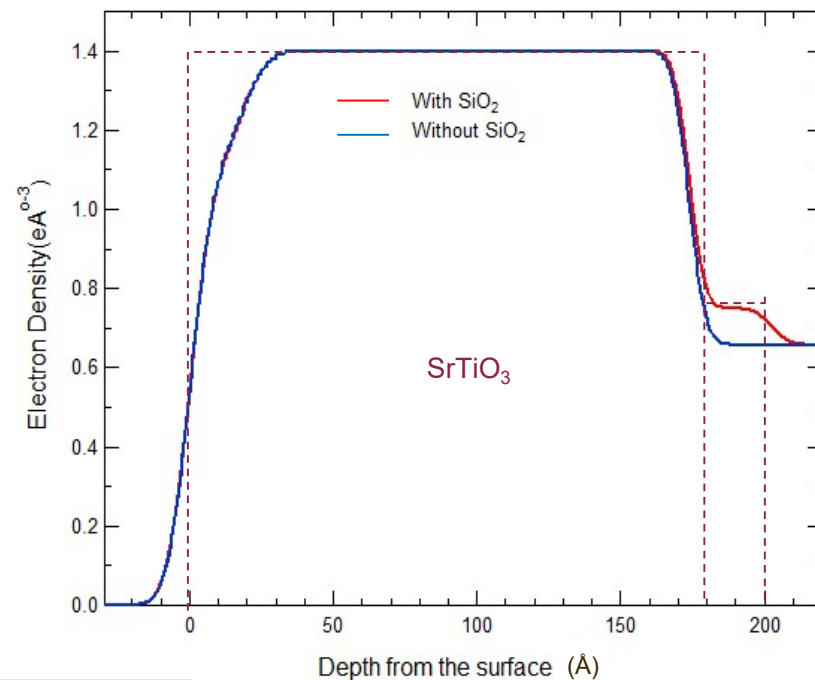
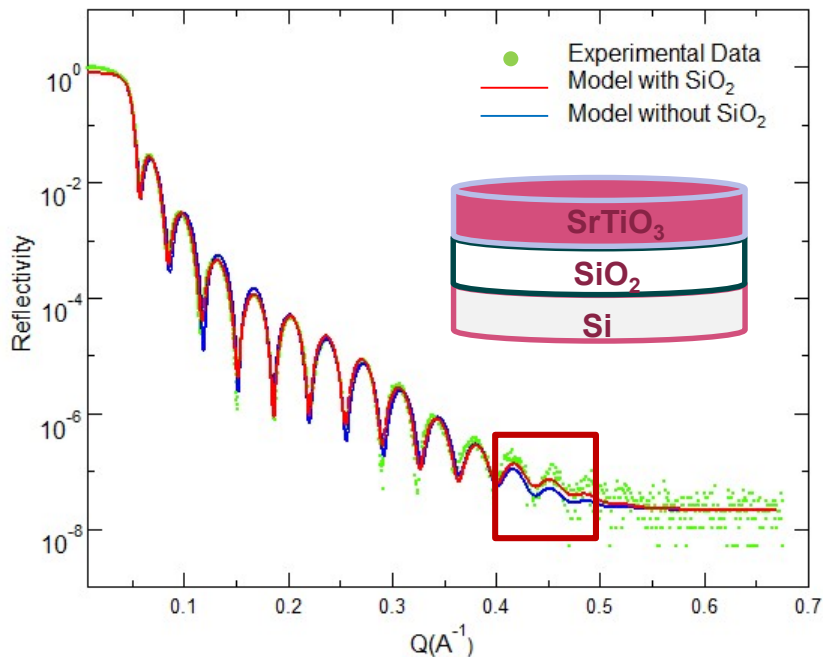


Table 2 Doping and layer content profile of a typical InGaP double heterojunction bipolar transistor (DHBT). Compare Ref. [28]. See also Ref. [42].

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

X-ray Reflectance: SrTiO₃ on Si



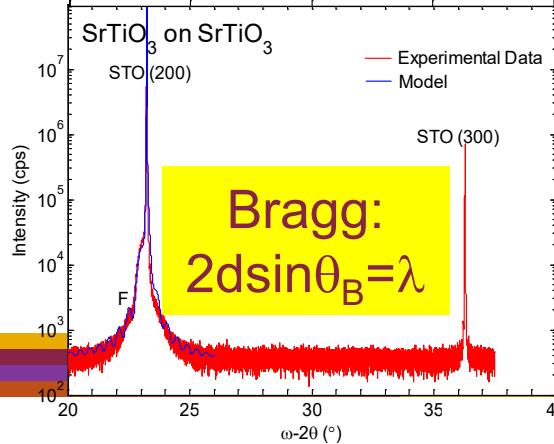
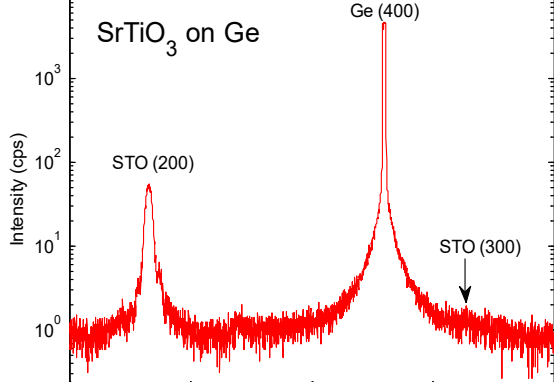
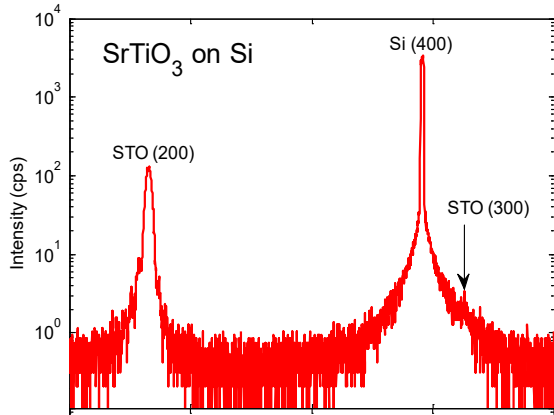
Layer	Electron Density (eÅ^{-3})	Bulk Electron density (eÅ^{-3})	Thickness (nm)	Roughness (nm)
SrTiO ₃	1.08	1.41	1.79	0.6152
SrTiO ₃	1.40	1.41	15.6	0.7396
SiO ₂	0.75	0.81	2.87	0.4202
Si	0.66	0.71	Substrate	0.4574

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

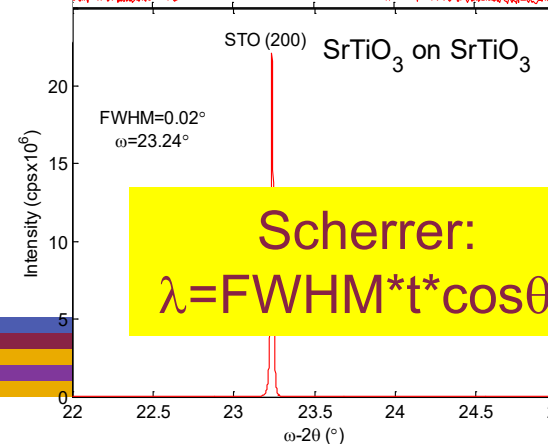
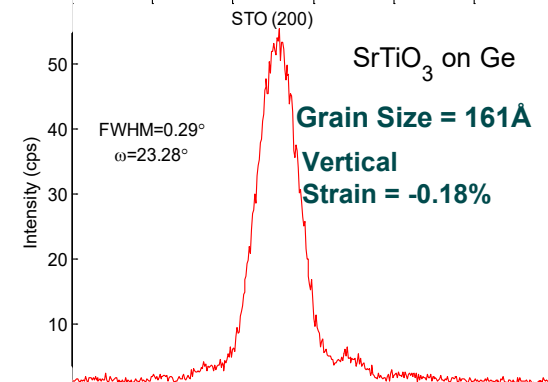
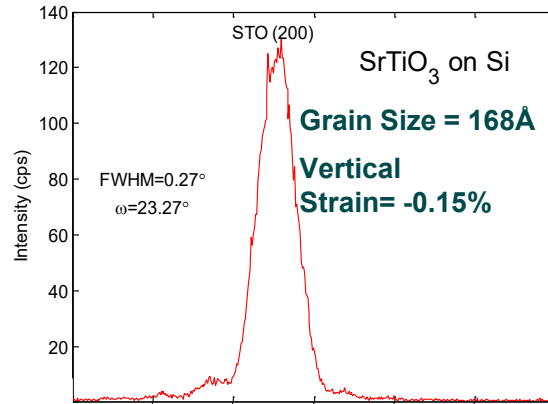
Small x-ray contrast between Si and SiO₂.



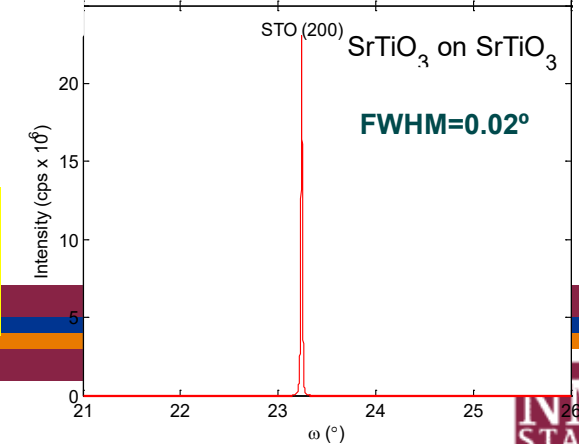
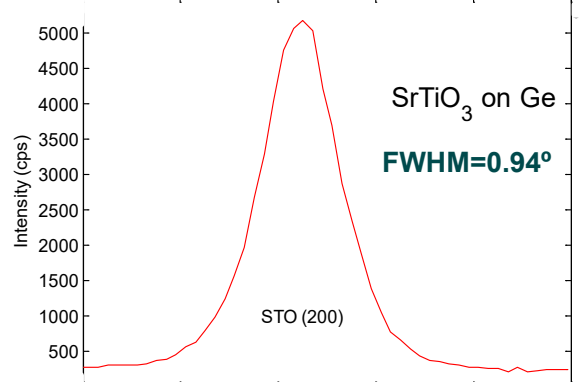
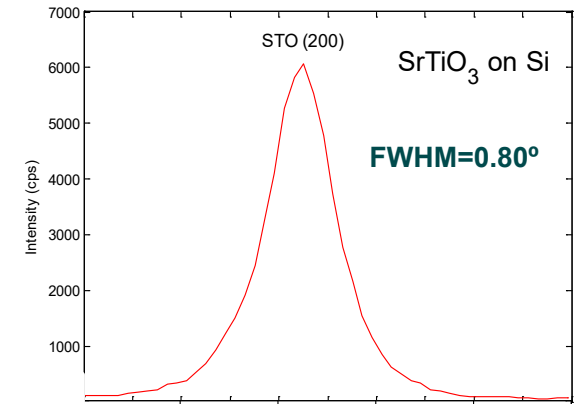
X-ray Diffraction: SrTiO₃ on Si, Ge, and SrTiO₃



ω -2 θ scan

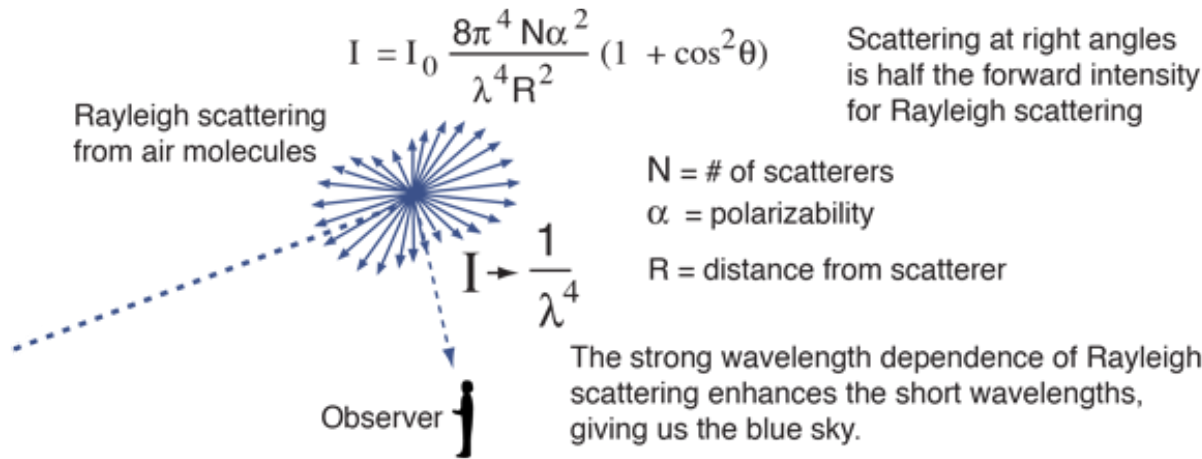
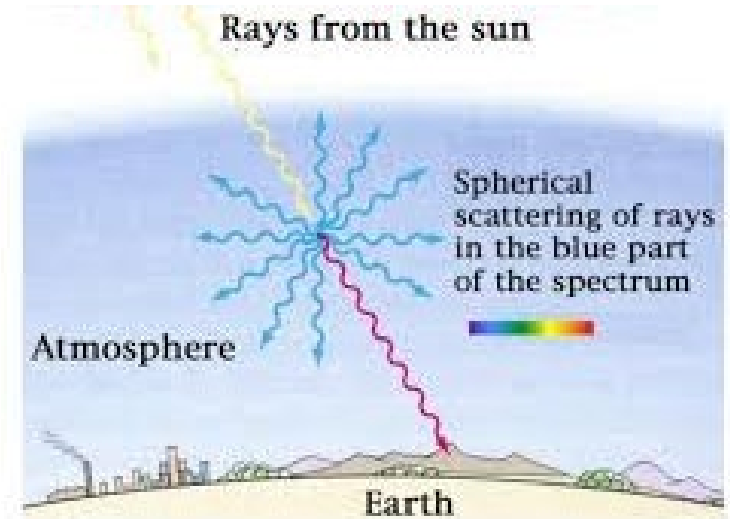
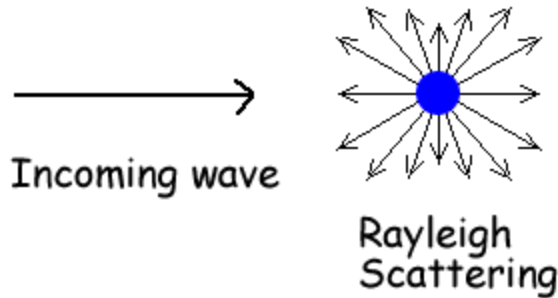


ω -2 θ scan (zoomed)

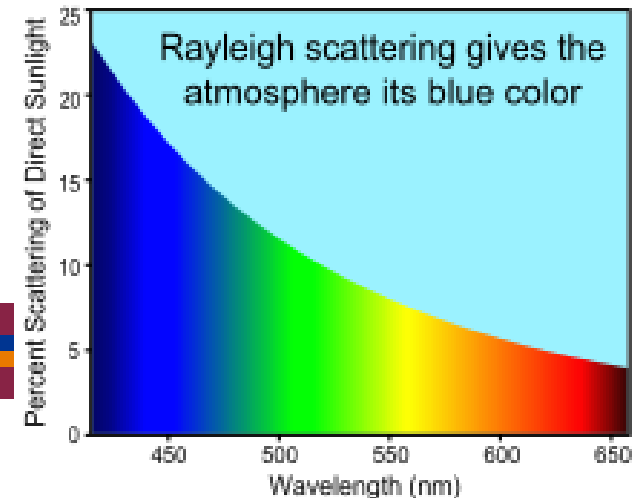


ω scan

Raleigh scattering (elastic)

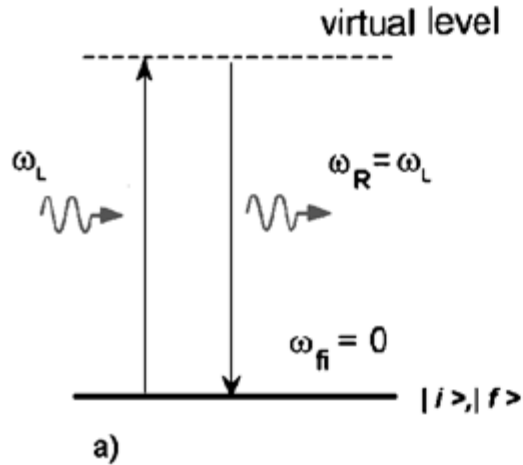


Why is the sky blue?

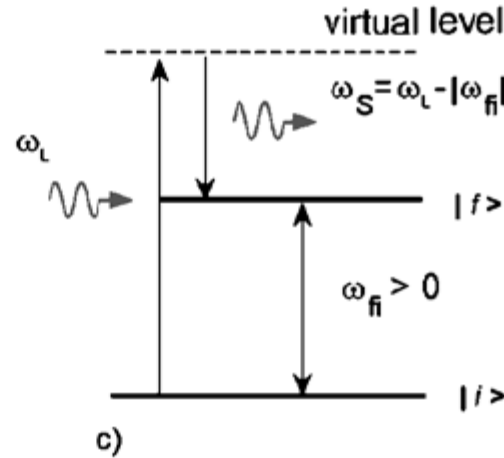


Elastic and Inelastic (Raman) Scattering

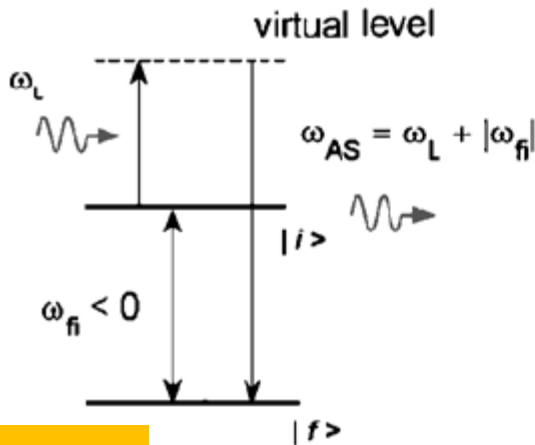
Raleigh
(elastic)



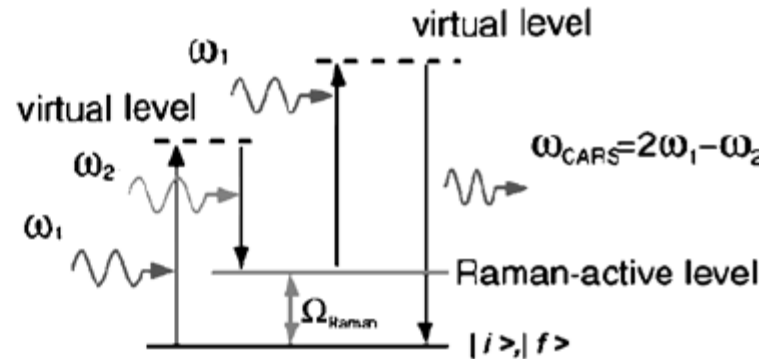
Raman
(Stokes)



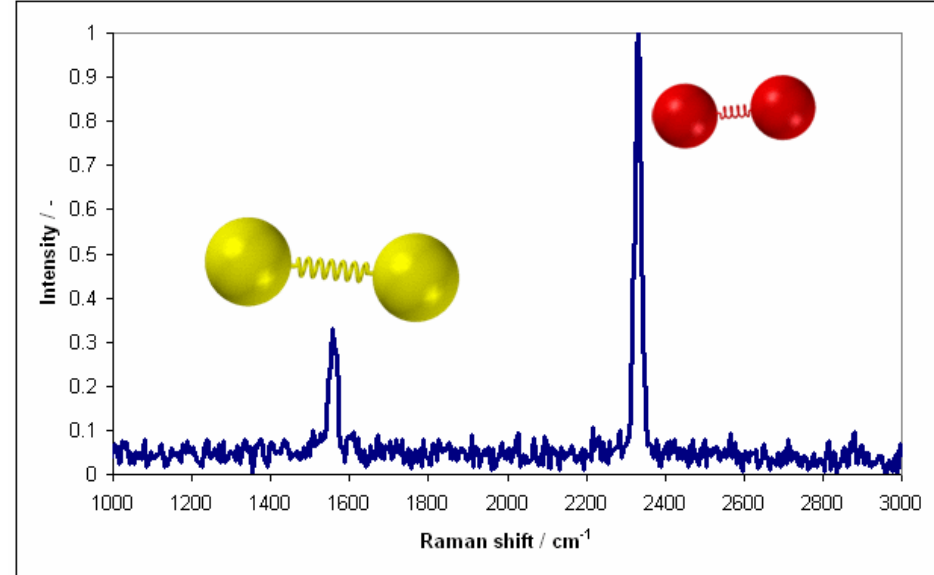
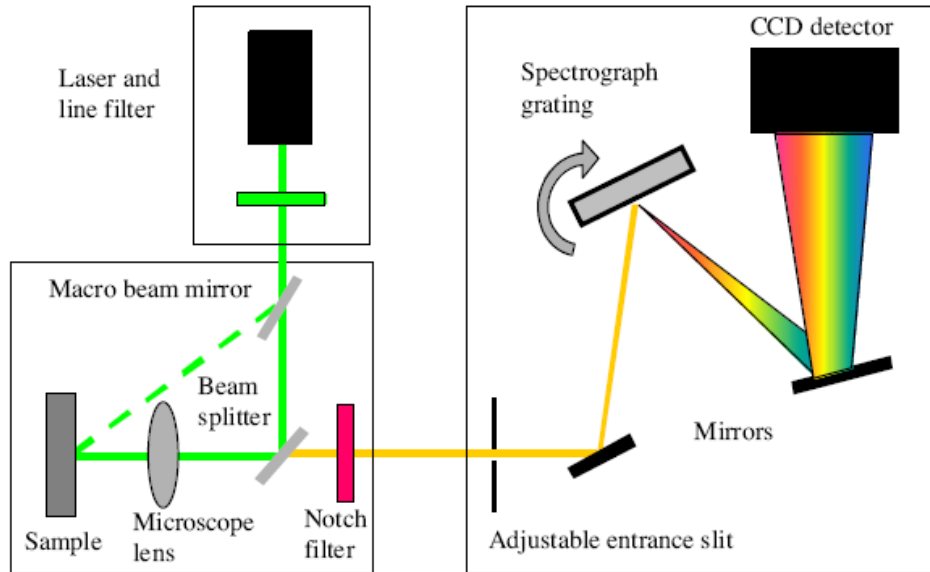
Raman
(Anti-Stokes)



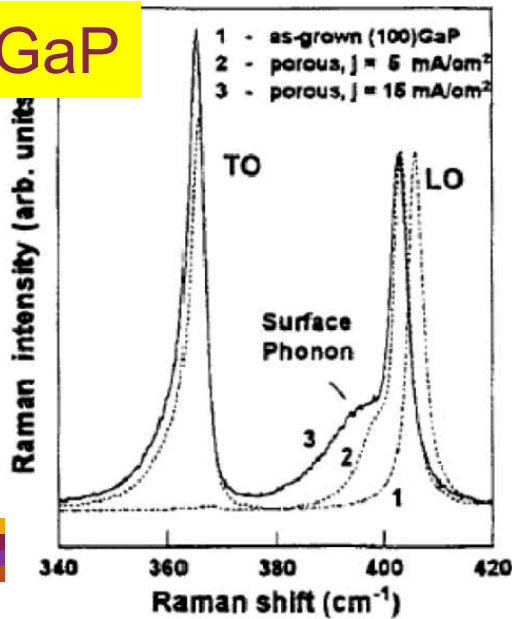
CARS



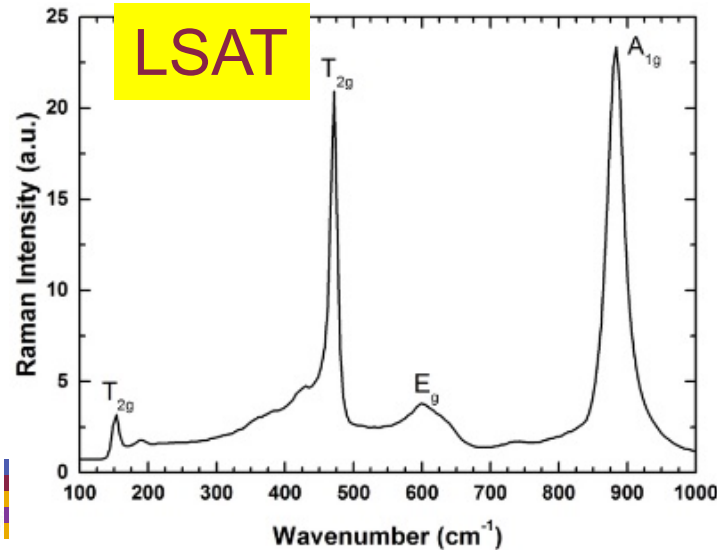
Raman Spectroscopy



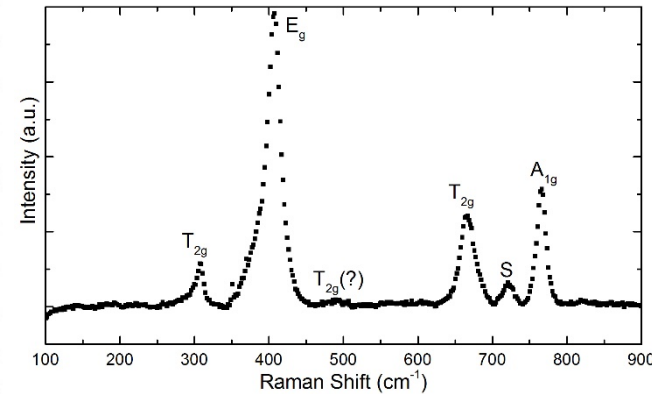
GaP



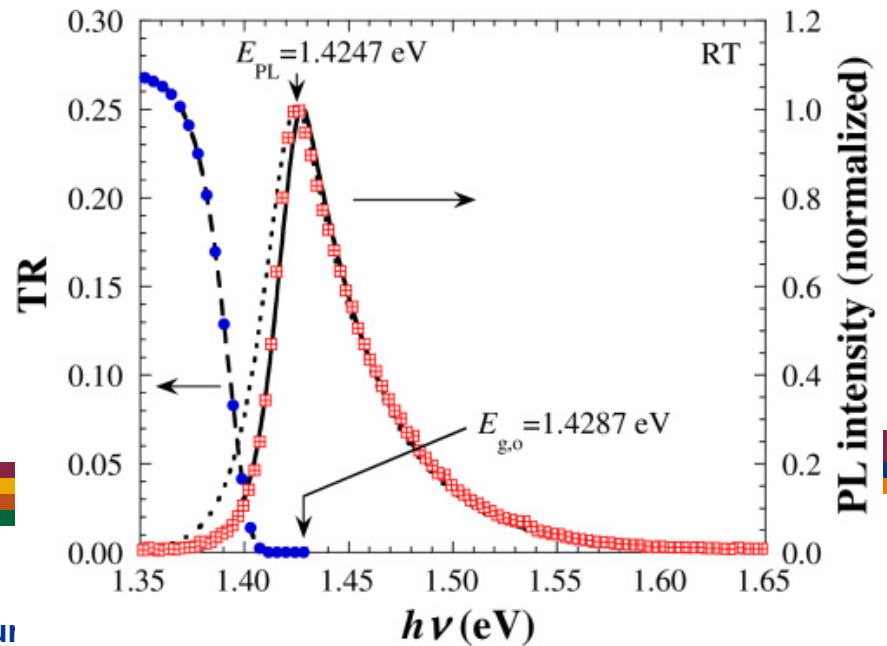
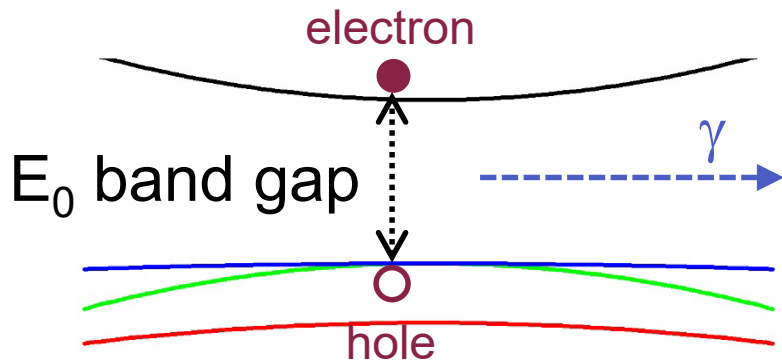
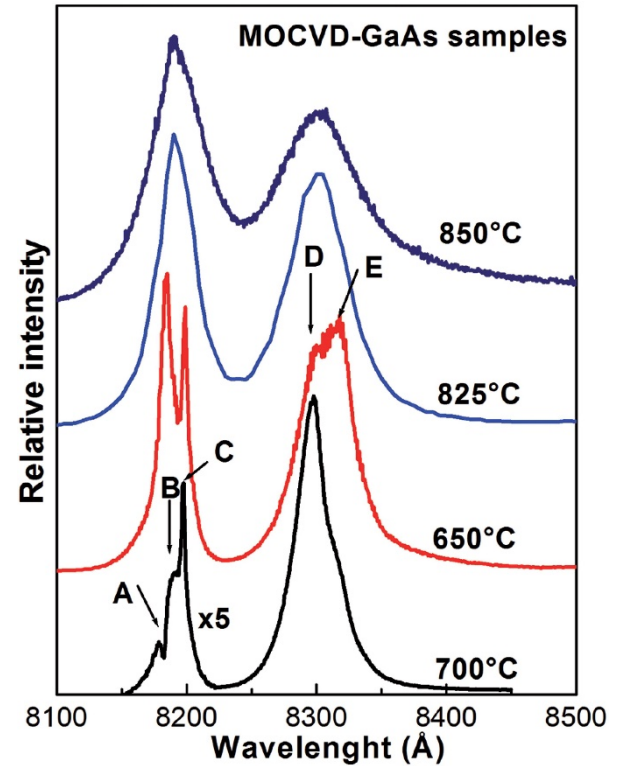
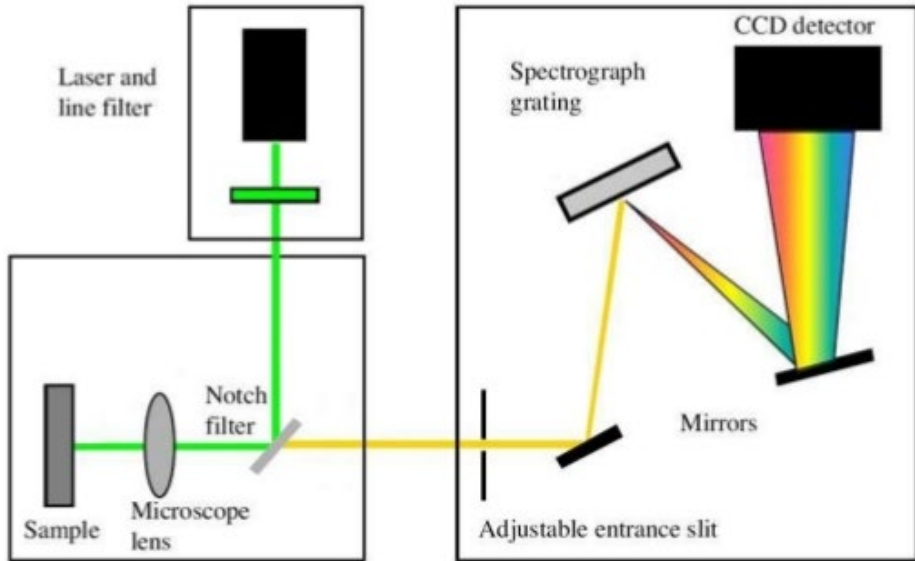
LSAT



Mg₂AlO₄ (spinel)

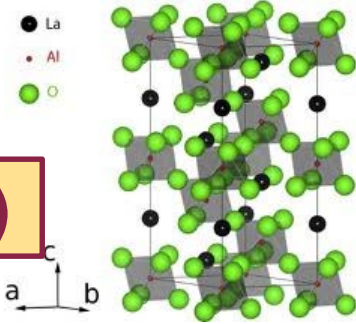


Photoluminescence



Solid State Physics (crystalline)

Crystal Structure (Point & Space Group)



Electrons

0.3-10 eV

Near-IR, VIS, UV

Phonons

10-80 meV

Far-IR to mid-IR

Defects

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:
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).