

# AP 5301/8301

## Instrumental Methods of Analysis and Laboratory

### Lecture 7

### Optical spectroscopies

**Prof YU Kin Man**

E-mail: [kinmanyu@cityu.edu.hk](mailto:kinmanyu@cityu.edu.hk)

Tel: 3442-7813

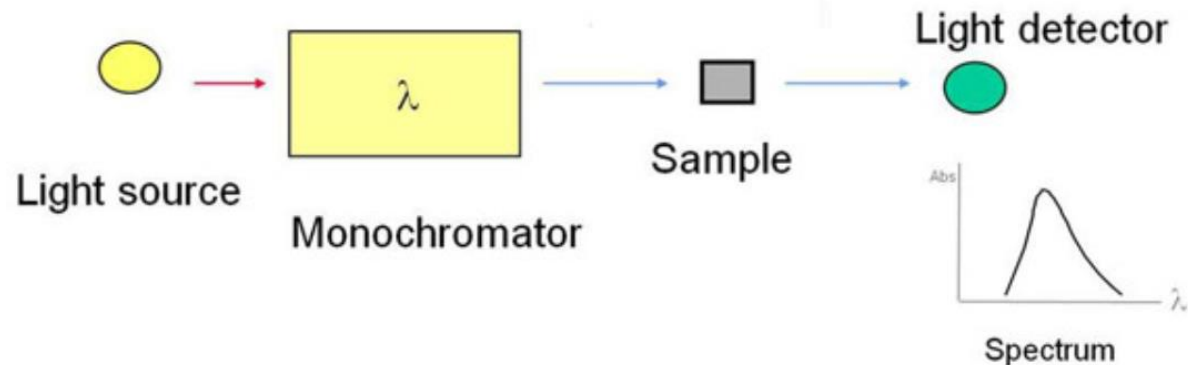
Office: P6422

# Lecture 7: outline

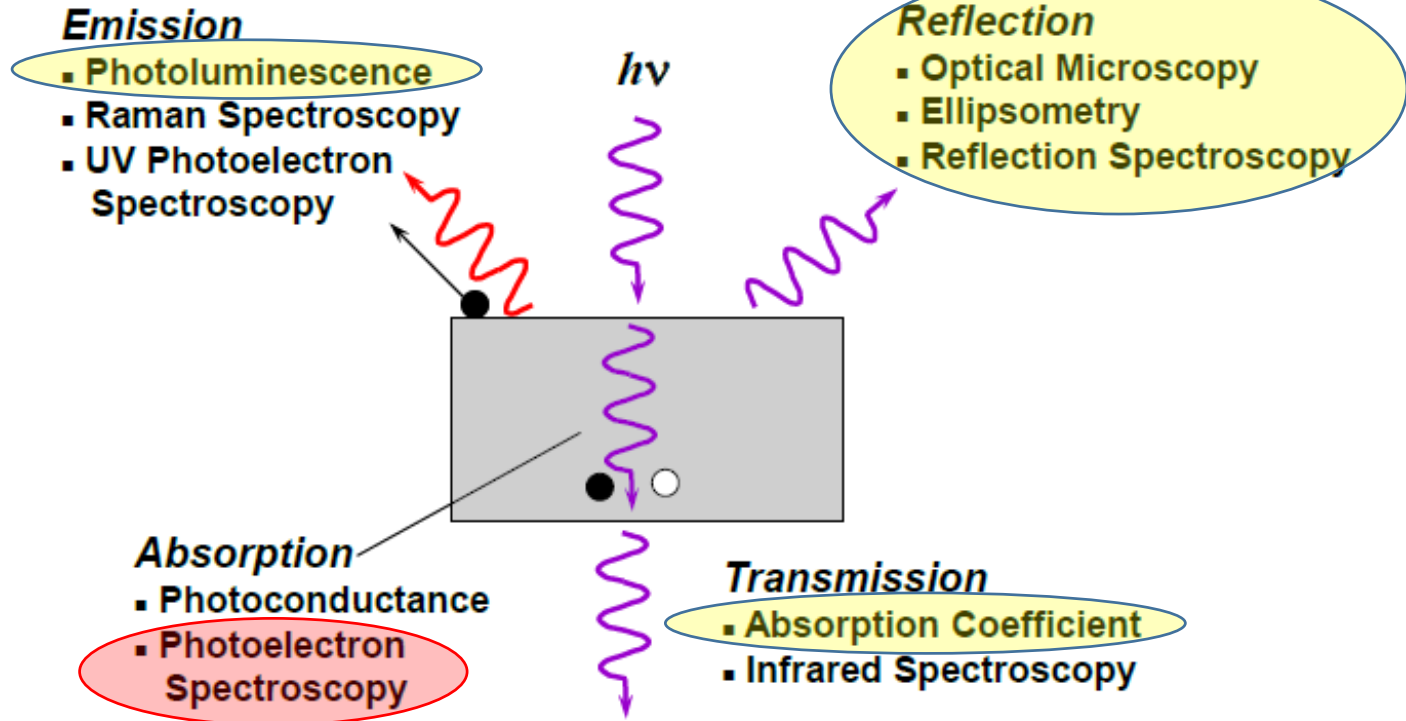
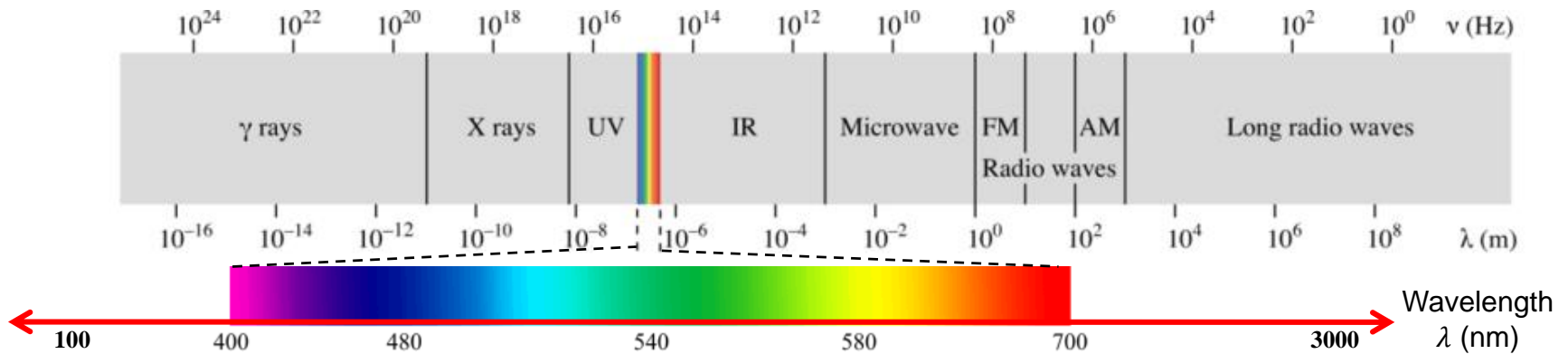
- Introduction
  - Optical spectroscopy
  - Dielectric function
  - Optical constants
  - Photon-solid interaction
- Spectrophotometry
  - Reflectance
  - Transmission/absorption
  - Optical absorption in semiconductors
- Spectroscopic ellipsometry
  - SE data analysis
  - SE examples
  - Advantages and limitations
- Photoluminescence spectroscopy
- Modulation spectroscopy

# Optical spectroscopy

- Spectroscopy is basically the measurement of **the interaction of light** with various materials. The optical **response intensity** as a function of the **wavelength** (or energy) of light is analyzed to determine various properties of the material.
- Basically, two things can happen when light hits a sample: **absorption or emission**.
  - In absorption, the sample absorbs some of the energy (photons).
  - Emission occurs when we hit a sample with some light and it emits light of a different wavelength: **fluorescence, luminescence** and **phosphorescence**
- A **spectrometer** is an instrument for making relative measurements in the optical spectral region, using light that is **spectrally dispersed** by means of a dispersing element.



# Optical excitation

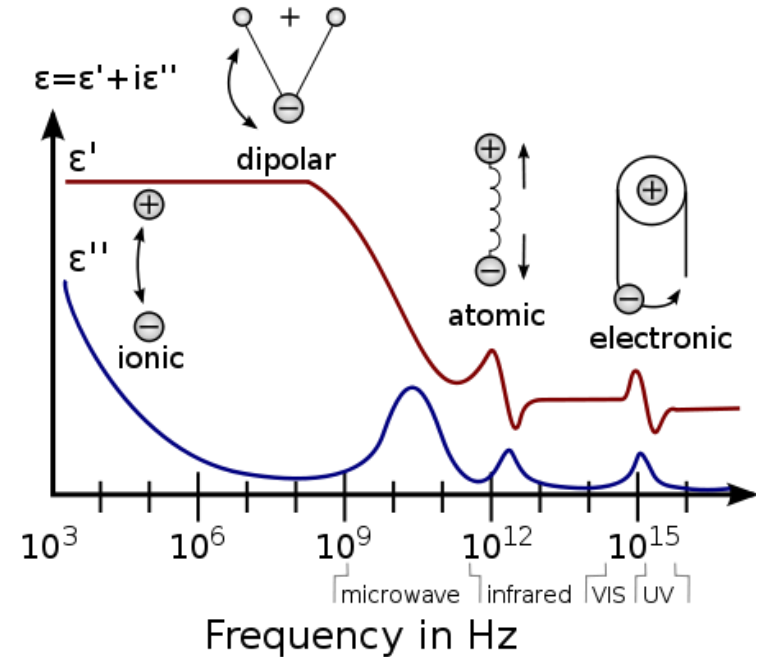


# The complex dielectric function

- As electromagnetic wave interact with a medium, **polarization** of the medium occurs and this is dependent on the permittivity  $\varepsilon$  of the medium.
- Permittivity**  $\varepsilon$  is the ability of a material to polarize and store a charge within it, and the relative permittivity  $\varepsilon_r = \varepsilon / \varepsilon_0$ ,  $\varepsilon_0$  is the permittivity in vacuum.
- Hence the permittivity of a material determines how the material react to an incident light (EM wave)
- The relative permittivity  $\varepsilon_r$  (or dielectric constant) is frequency dependent and is a complex function

$$\varepsilon_r(\omega) = \varepsilon'_r(\omega) + i\varepsilon''_r(\omega)$$

- $\varepsilon'_r$  is the in-phase component of the frequency response of the medium
- $\varepsilon''_r$  is the out-of-phase component of the frequency response



$$\varepsilon_r(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}$$

$$\varepsilon_r(\omega) = \varepsilon'_r(\omega) + i\varepsilon''_r(\omega)$$

Debye Equations:

$$\varepsilon'_r = \text{Re}\{\varepsilon_r\} = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau)^2}$$

$$\varepsilon''_r = \text{Im}\{\varepsilon_r\} = \frac{\omega\tau(\varepsilon_s - \varepsilon_\infty)}{1 + (\omega\tau)^2}$$

# Optical constants $n$ and $k$

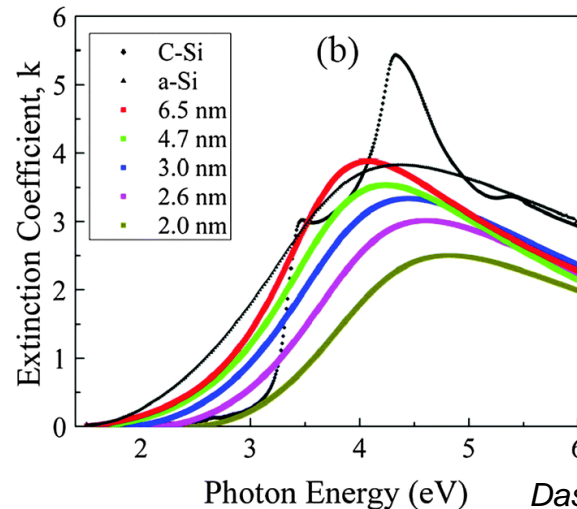
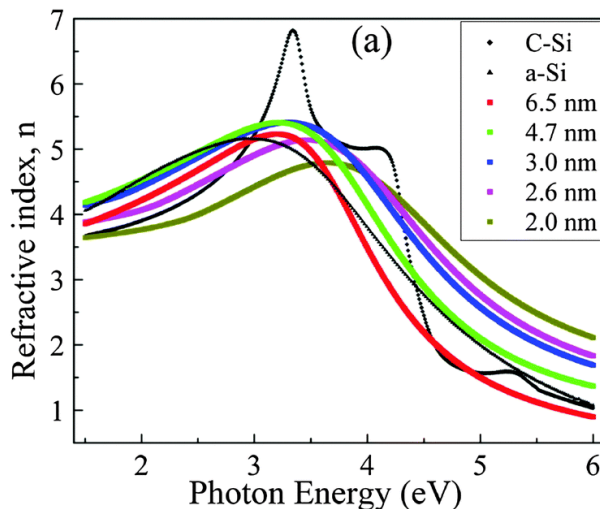
The complex refractive index  $\tilde{n}(\omega)$  of the material is related to  $\epsilon_r(\omega)$

**Maxwell relation:**  $\tilde{n}(\omega) = \sqrt{\epsilon_r(\omega)} = n(\omega) + ik(\omega)$

$\epsilon_r'(\omega) = n^2(\omega) - k^2(\omega)$  and  $\epsilon_r''(\omega) = 2n(\omega)k(\omega)$

- $n$  and  $k$  are **optical constants** of the material.
- $n$  is the **refractive index**, and  $k$  is the **extinction coefficient** related to the **absorption coefficient  $\alpha$**  and **reflectance  $R$**

$$\alpha = \frac{4\pi k}{\lambda}, \text{ and } R = \left| \frac{1 - \tilde{n}}{1 + \tilde{n}} \right|^2 = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}$$

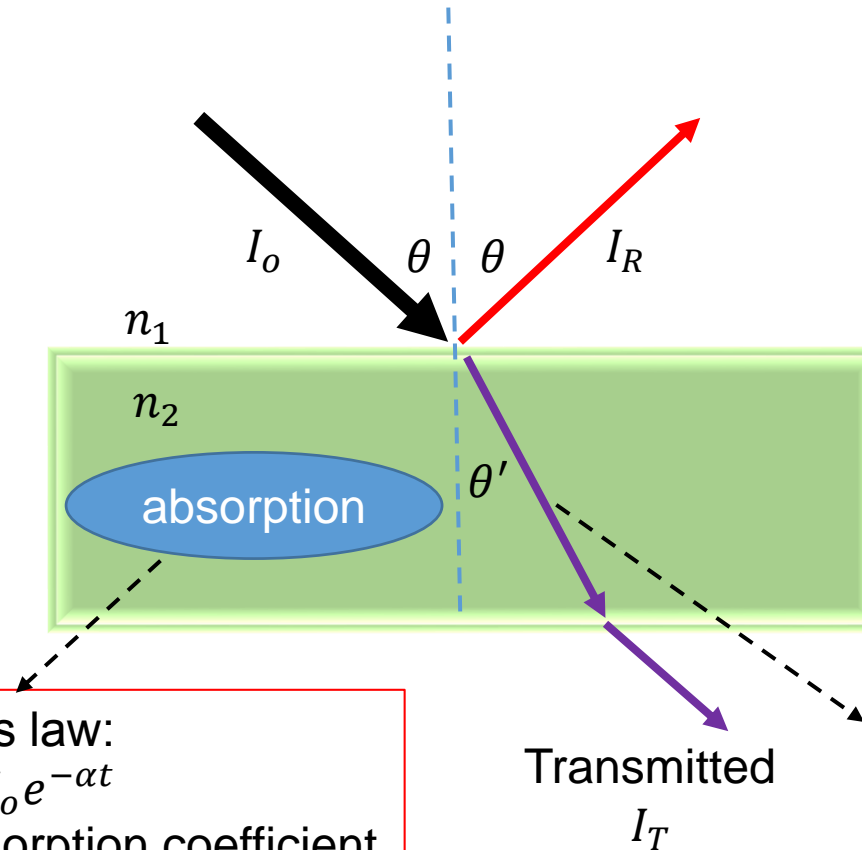


Refractive index ( $n$ ) and extinction coefficient ( $k$ ) spectra of the nc-Si QDs of varying average sizes.

Das and Samanta, *Phys.Chem.Chem.Phys.*, **17**, 5063--5071 (2015).

# Photon-solid interaction

When light incident on a solid, it is reflected, absorbed or transmitted



## Specular reflection

Fresnel's law:

$$I_R = \left| \frac{1 - \tilde{n}}{1 + \tilde{n}} \right|^2 = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}$$

Beer's law:

$$I_T = I_o e^{-\alpha t}$$

where  $\alpha$  is the absorption coefficient  
 $t$  is the thickness of the absorber

Transmitted  
 $I_T$

Snell's law:

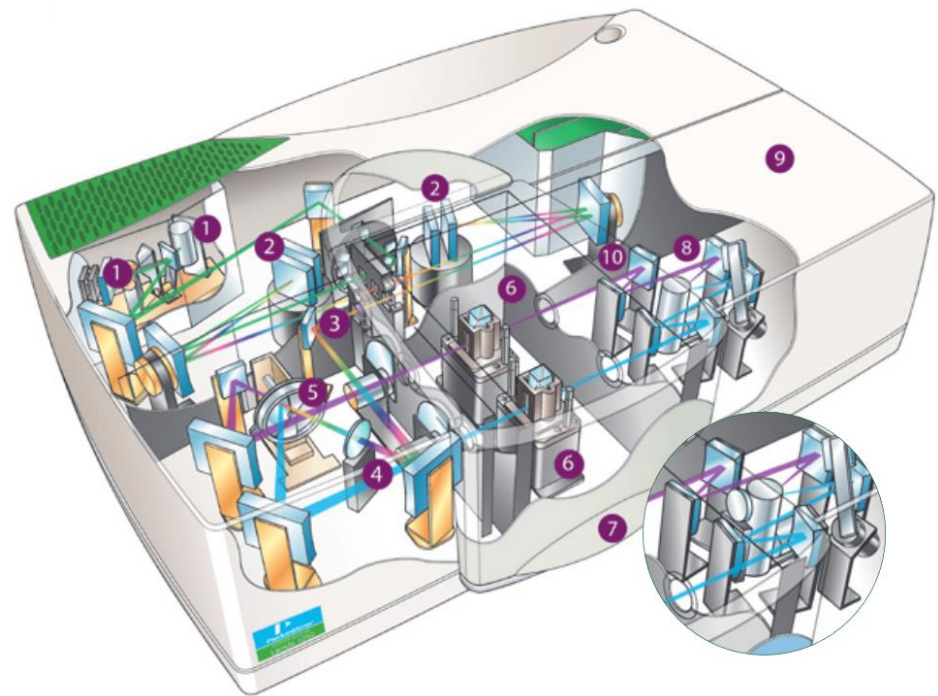
$$n_1 \sin \theta = n_2 \sin \theta'$$

By passing light through a solid, we can learn about its refractive index, absorption coefficient and thickness, as well as its electronic band structure



# Spectrophotometry

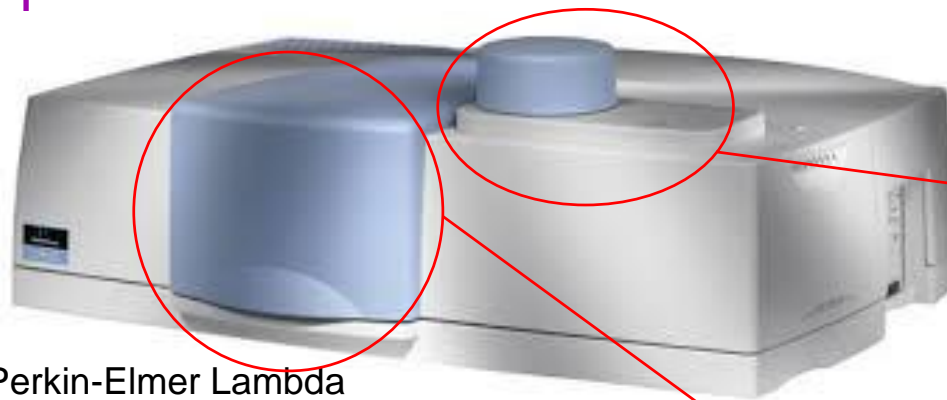
- Spectrophotometry is the quantitative measurement of the **reflection or transmission** properties of a material as a function of wavelength in the spectral range of visible light (Vis), near-ultraviolet (UV), and near-infrared (NIR). It is more commonly called **UV-Vis-NIR spectroscopy**.
- Typically a dual beam configuration is used, one beam pass through a **reference cell** (air, substrate) getting an accurate measure of the incident light intensity ( $I_o$ ), the other passing through the sample ( $I_T$ ).
- Both transmission and reflection can be measured.



Perkin-Elmer Lambda 950 Spectrophotometer



# Spectrophotometer

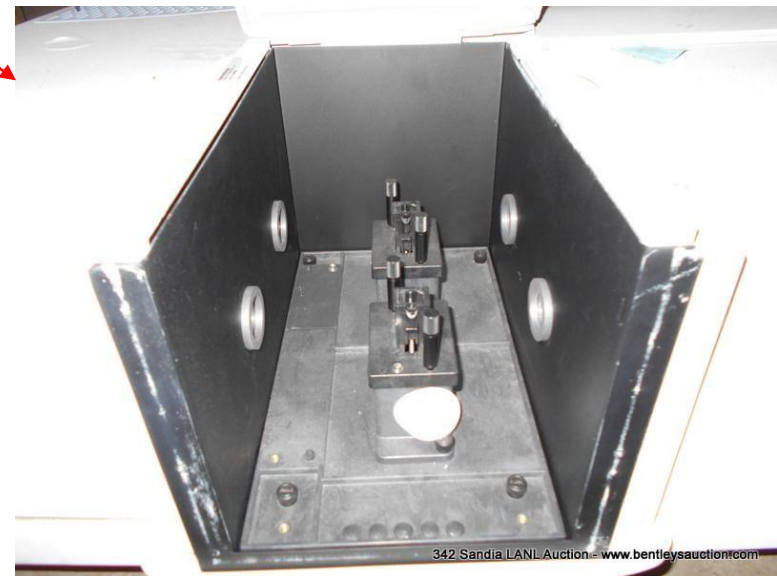
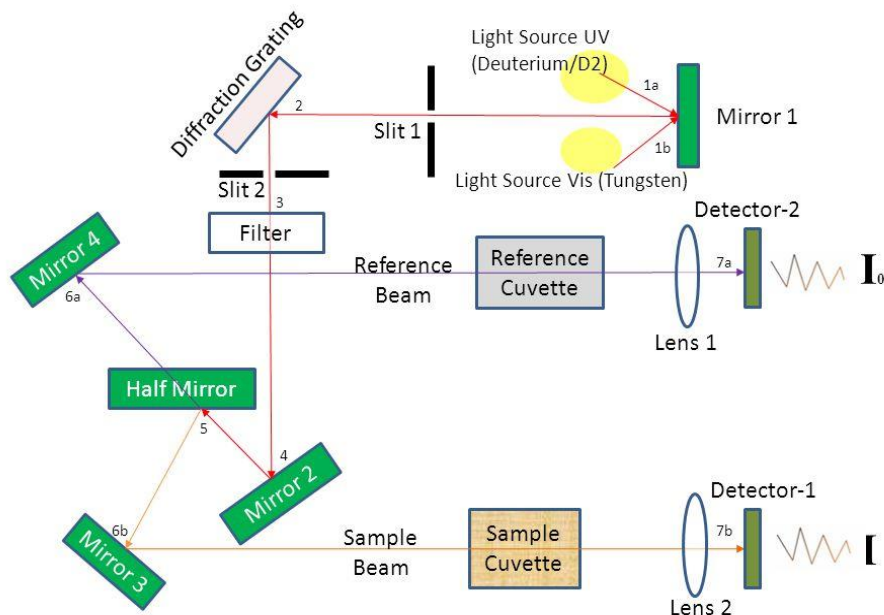


Perkin-Elmer Lambda Spectrophotometer



Reflectance

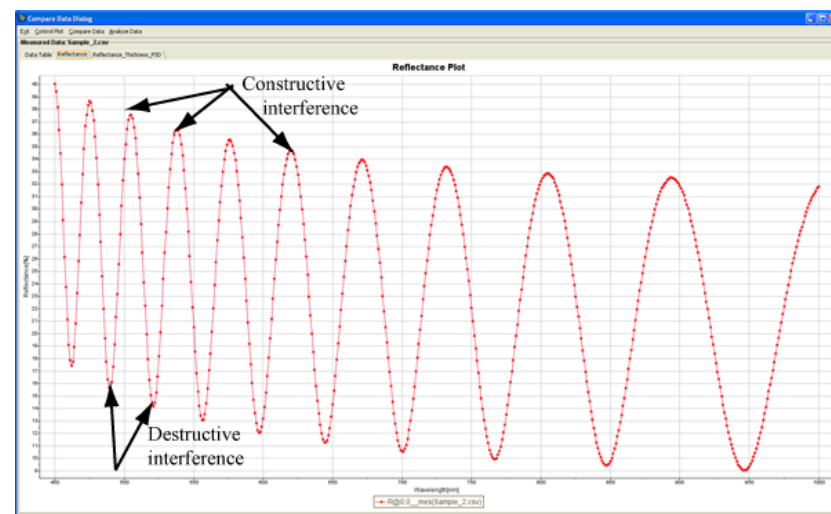
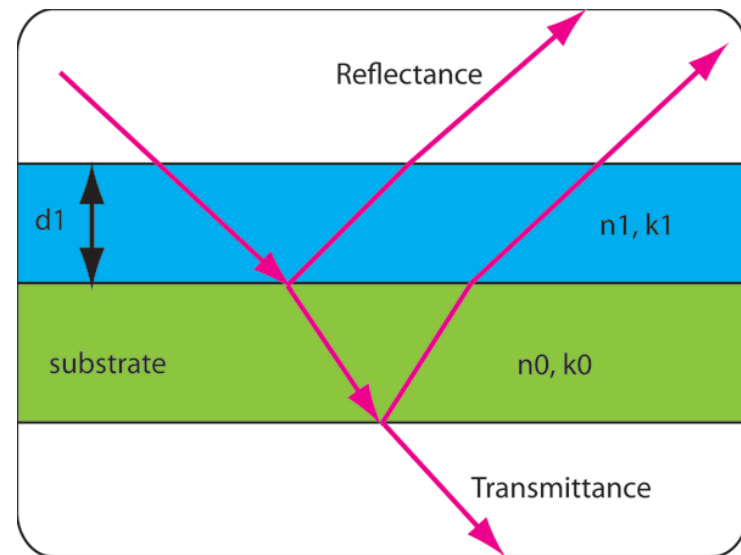
## Uv-Vis Spectrometer Double Beam



Transmittance

# Spectrophotometry: reflectance

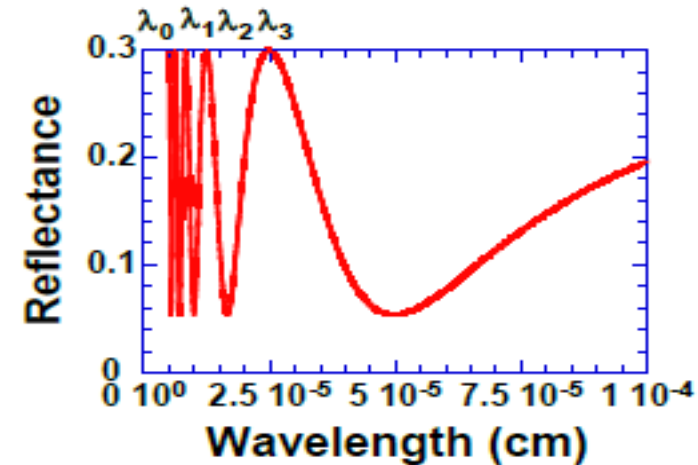
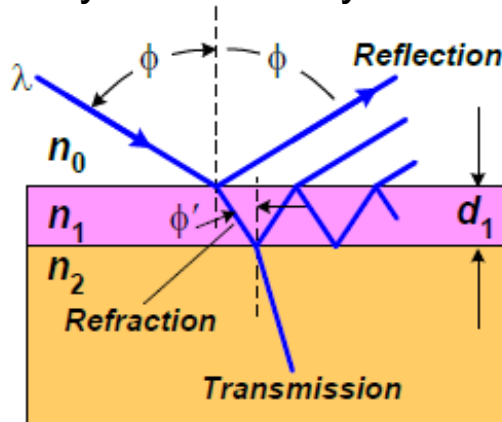
- The light intensity reflected from the layer structure is measured in a specific spectral range.
- From Fresnel law:  $R = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2}$
- The **optical constants**: refractive index ( $n$ ) and extinction coefficient ( $k$ ) are related to refraction and absorption (respectively).
- Light reflected from the different interfaces can be in or out of phase, resulting in **intensity oscillation**.
- Typically the reflectance data are analyzed by a **curve fitting** method, using calculated theoretical reflectance of the stack and parameters are adjusted to achieve best fit to the measured data.
- $n$  and  $k$  can be calculated using the **Forouhi-Bloomer dispersion** equations



<http://www.semiconsoft.com/>

# Spectrophotometry: reflectance

- For a simple structure with a thin film on a substrate, the **thickness** of the film can be easily obtained by the reflectance spectrum



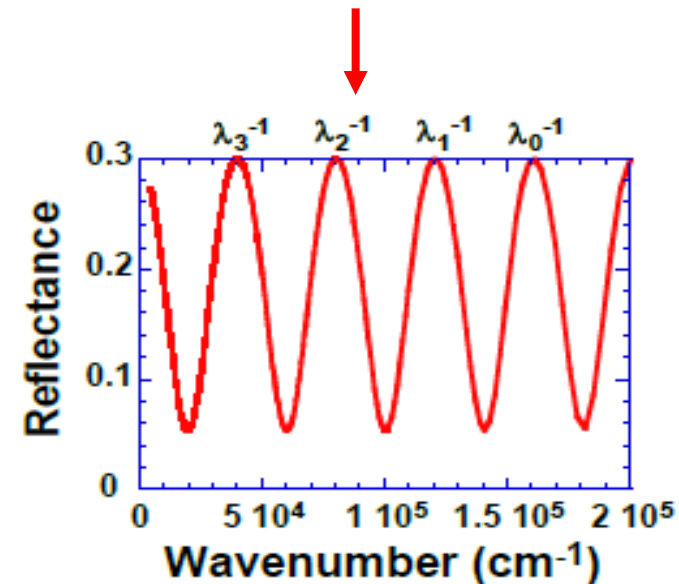
- R versus  $\lambda$  yields plots with unequal  $\lambda$  spacings
- R versus  $1/\lambda$  (wavenumber) gives equal spacings

$$\lambda_{max} = \frac{2n_1 d_1 \cos \phi'}{m}, m = 1, 2, 3 \dots$$

$$d_1 = \frac{i \lambda_o \lambda_i}{2n_1 (\lambda_i - \lambda_o) \cos \phi'}$$

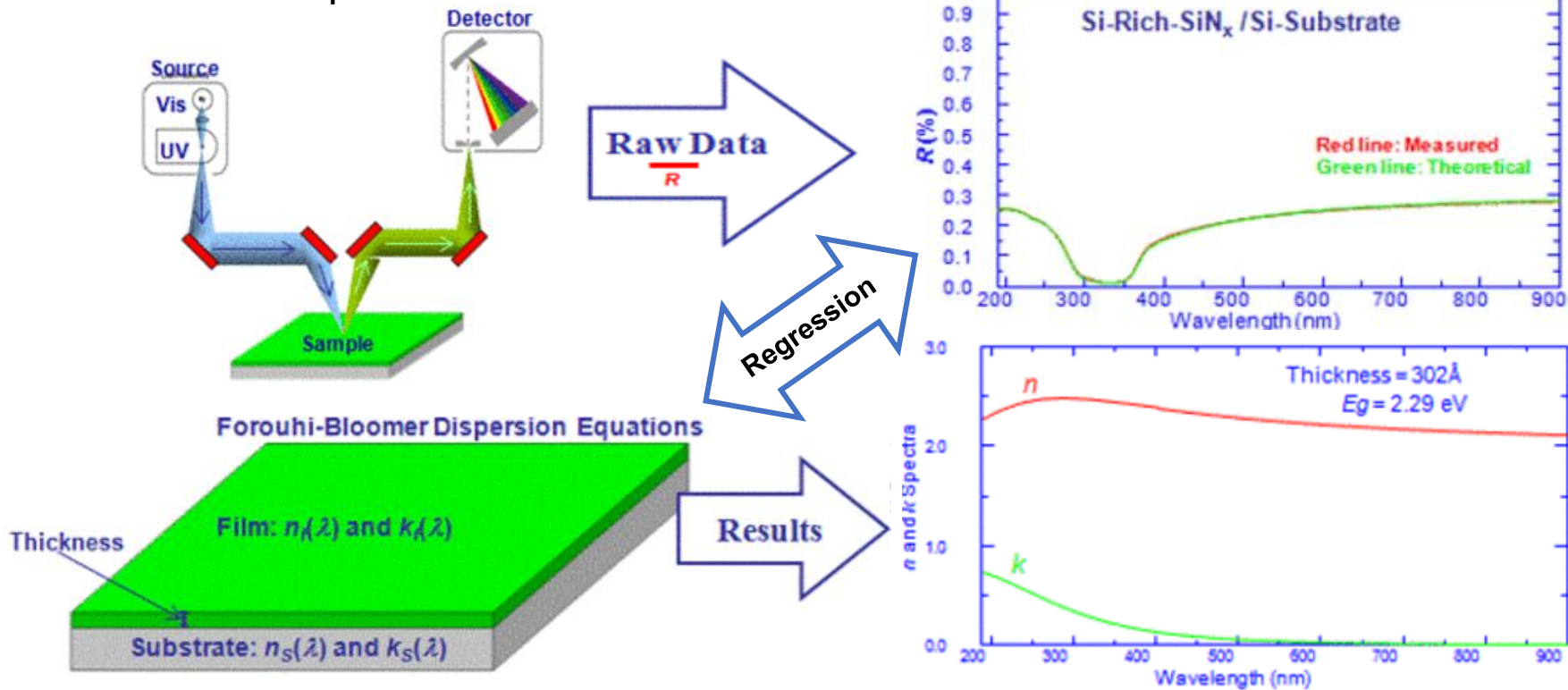
$i$  is the number of complete cycles from  $\lambda_o$  to  $\lambda_i$

$$d_1 = \frac{i}{2n_1 (1/\lambda_o - 1/\lambda_i) \cos \phi'}$$

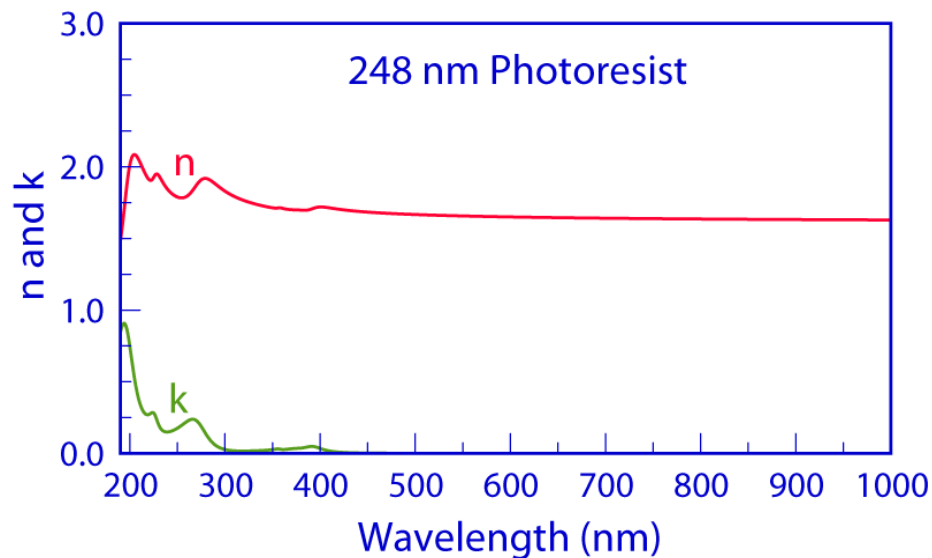
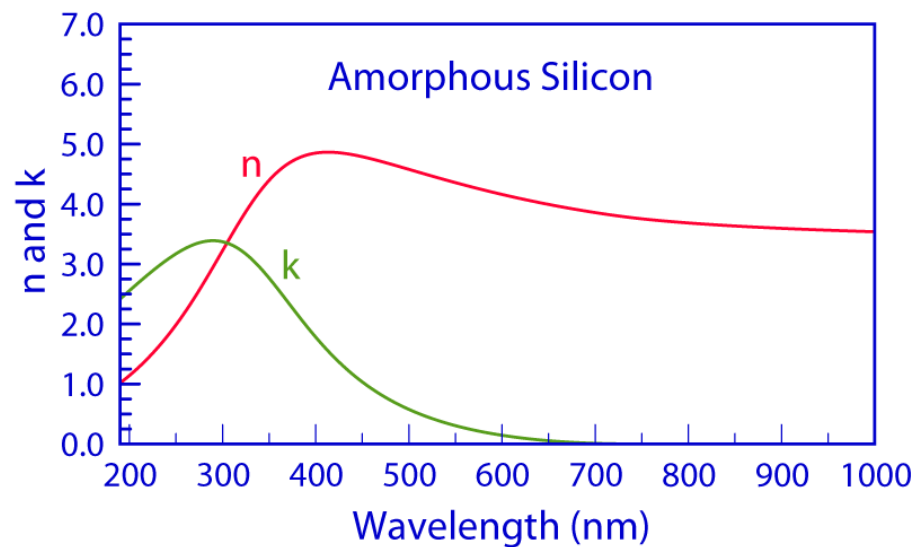
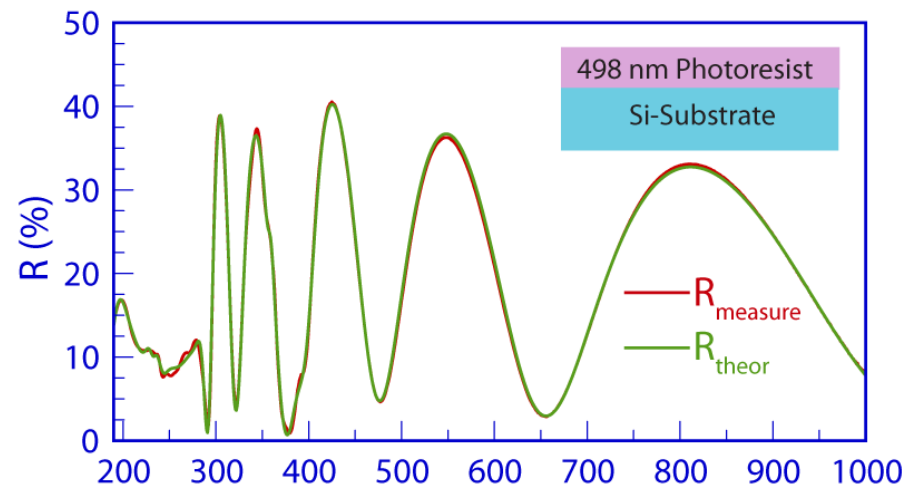
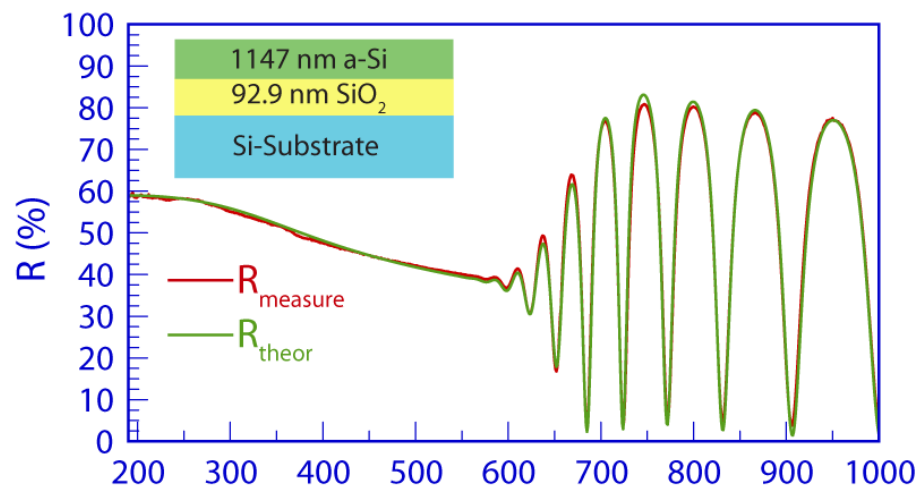


# Spectrophotometry: reflectance

- Thin films parameters: film thickness  $t$ ,  $n(\lambda)$  and  $k(\lambda)$  can be extracted from the measurement of  $R(\lambda)$  and/or  $T(\lambda)$  by combining the **Forouhi-Bloomer** dispersion equations for  $n(\lambda)$  and  $k(\lambda)$  with the **Fresnel equations** for the reflection and transmission of light at an interface to obtain theoretical, physically valid, expressions for reflectance and transmittance.
- Nonlinear least squares regression analysis will be performed using the theoretical parameters.



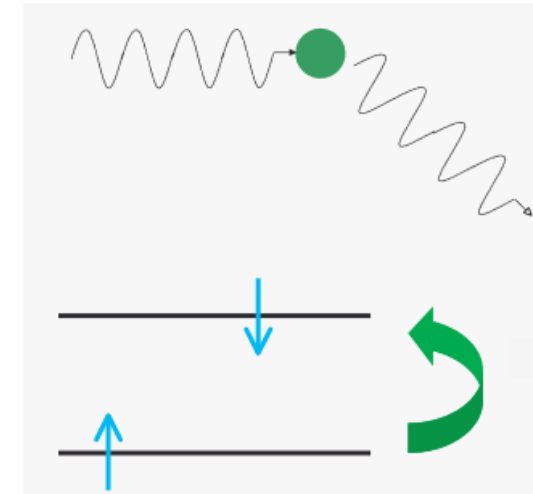
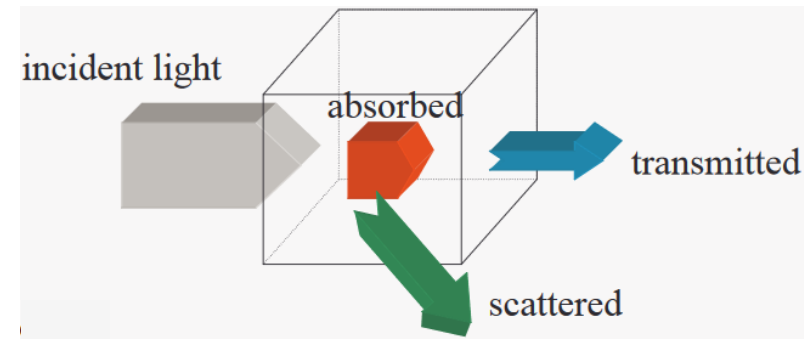
# Spectrophotometry: reflectance



# Transmission/Absorption

When a beam of light **incident on a material**, it can be **scattered, absorbed, or transmitted**

- **Transmitted light:** light emerges propagating in the **same direction** as the incident light
- **Absorbed light:** energy from light is absorbed in the volume of the material
- **Scattered light:** light emerges in a different direction from the incident light
- Absorption and scattering take place at the molecular and atomic level
  - For energy from light to be absorbed, it must **match available energy states** in the atoms or molecules, or it can scatter from the molecule, atom, or electrons
  - **Probability** that the light (photon) is removed (absorbed or scattered) from the incident beam is related to the **cross section  $\sigma$**





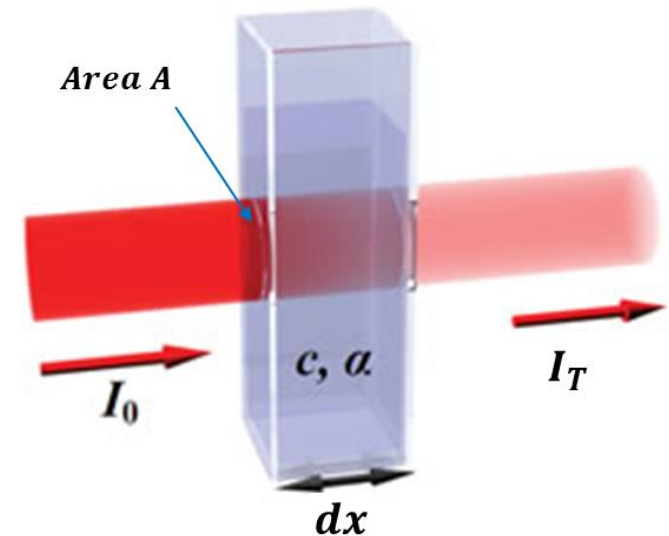
# Beer-Lambert law

- Consider light incident on a material with area  $A$  and thickness  $dx$  and concentration of molecules  $C$  (i. e.  $\#/cm^3$ )
- Number of molecules illuminated by light of incident intensity  $I_x$  is  $CA dx$
- Probability that the light is absorbed (scattered) is

$$-\frac{dI_x}{I_x} = \frac{\sigma CA}{A} dx$$

$$\int_{I_0}^{I_T} \frac{dI_x}{I_x} = - \int_0^x \sigma C dx$$

$$I_T = I_0 e^{-\sigma C x} = I_0 e^{-\alpha x}$$



- The coefficient  $\alpha = \sigma C$  is the **linear attenuation coefficient**
- Ignoring scattering,  $\alpha$  is the **absorption coefficient** and is related to the **extinction coefficient** by  $\alpha = \frac{4\pi k}{\lambda}$
- The absorption coefficient is wavelength dependent so that:

$$I_T(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)x}$$

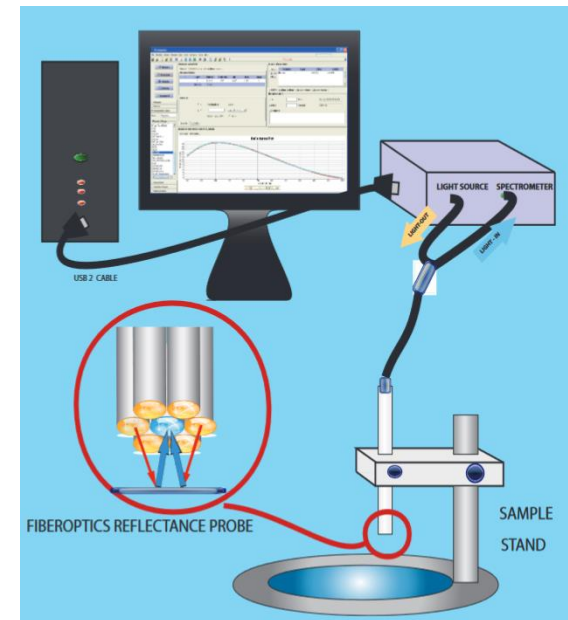
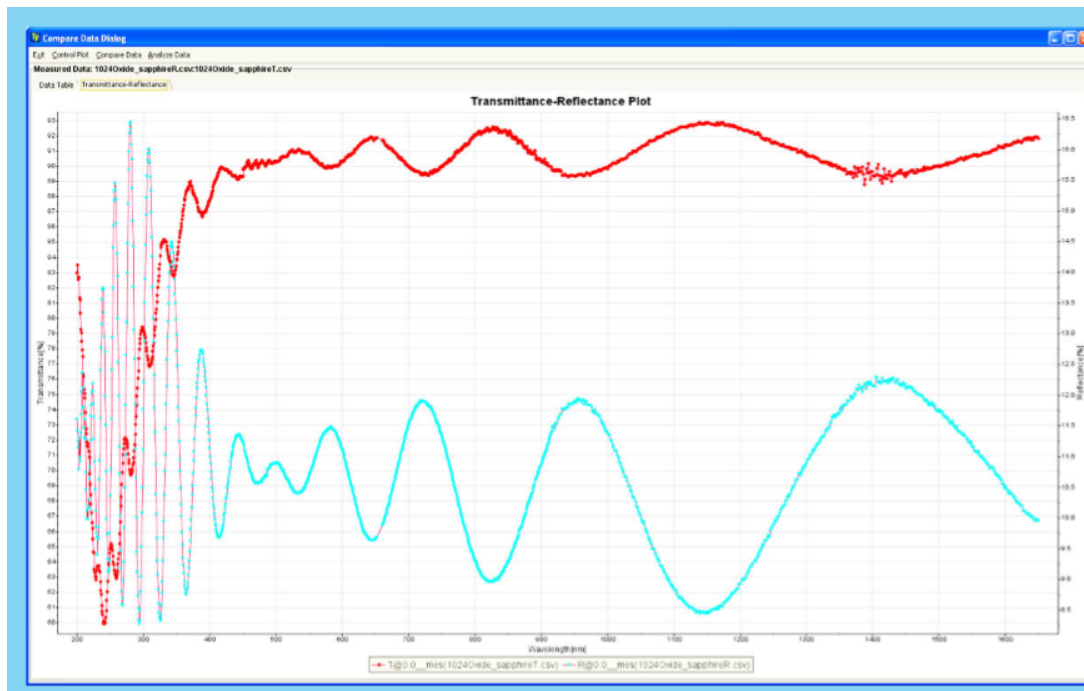


# Transmission/Absorption

- Transmittance is defined as  $T = \frac{I_T(\lambda)}{I_o(\lambda)}$
- A quantity called **absorbance**  $A$  is commonly used (by **chemists**)

$$A = \log_{10} \left( \frac{I_o(\lambda)}{I_T(\lambda)} \right) = \log_{10}(e^{\alpha x})$$

$$A = \alpha x \log_{10}(e) = 0.434 \alpha x$$



Semiconsoft Mprobe UVVis-NIR

# Transmission/Absorption

- Similar to the case of reflection, **oscillatory features** in the transmission spectrum can also be used to determine sample **thickness**

- Oscillation maxima occurs at

$$d = \frac{m\lambda_o}{2n}; d = \frac{(m+1)\lambda_1}{2n} \dots; d = d = \frac{(m+i)\lambda_i}{2n}$$

$$m = \frac{i\lambda_i}{\lambda_o - \lambda_i}$$

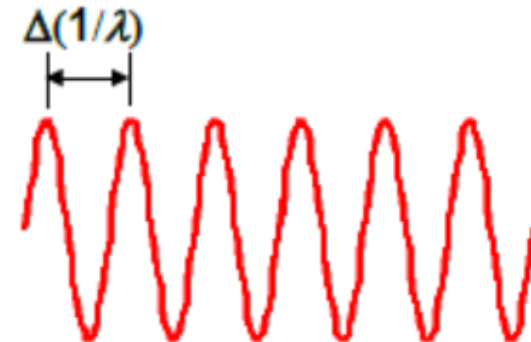
$$d = \frac{i\lambda_o\lambda_i}{2n(\lambda_o - \lambda_i)} = \frac{i}{2n(1/\lambda_i - 1/\lambda_o)}$$

- More often, transmission and reflection data are combined to find the absorption coefficient  $\alpha(\lambda)$

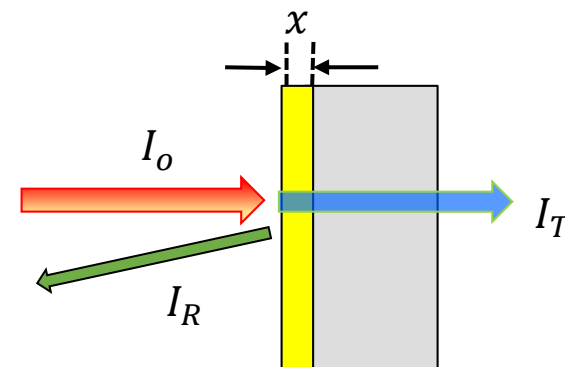
$$I_T(\lambda) = (I_o(\lambda) - I_R(\lambda))e^{-\alpha(\lambda)x}$$

$$\alpha(\lambda) = \frac{1}{x} \ln \left( \frac{I_o(\lambda) - I_R(\lambda)}{I_T(\lambda)} \right)$$

- From the absorption coefficient of a solid (thin film), the electronic properties can **be derived**.



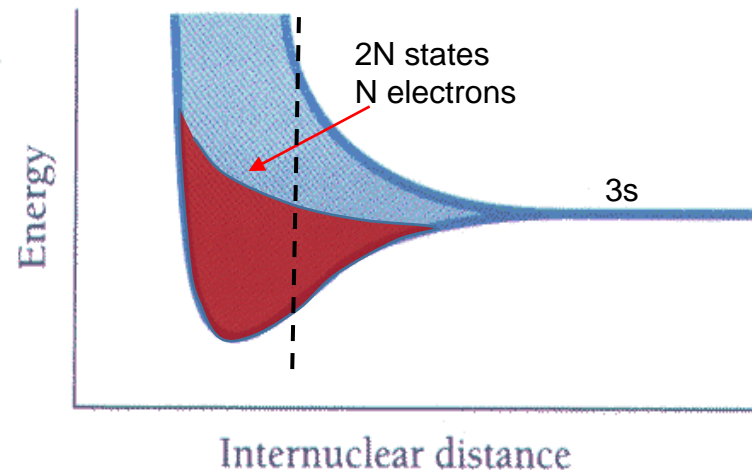
$1/\lambda$ : Wave number



Assuming that the substrate is **transparent** to the incident light

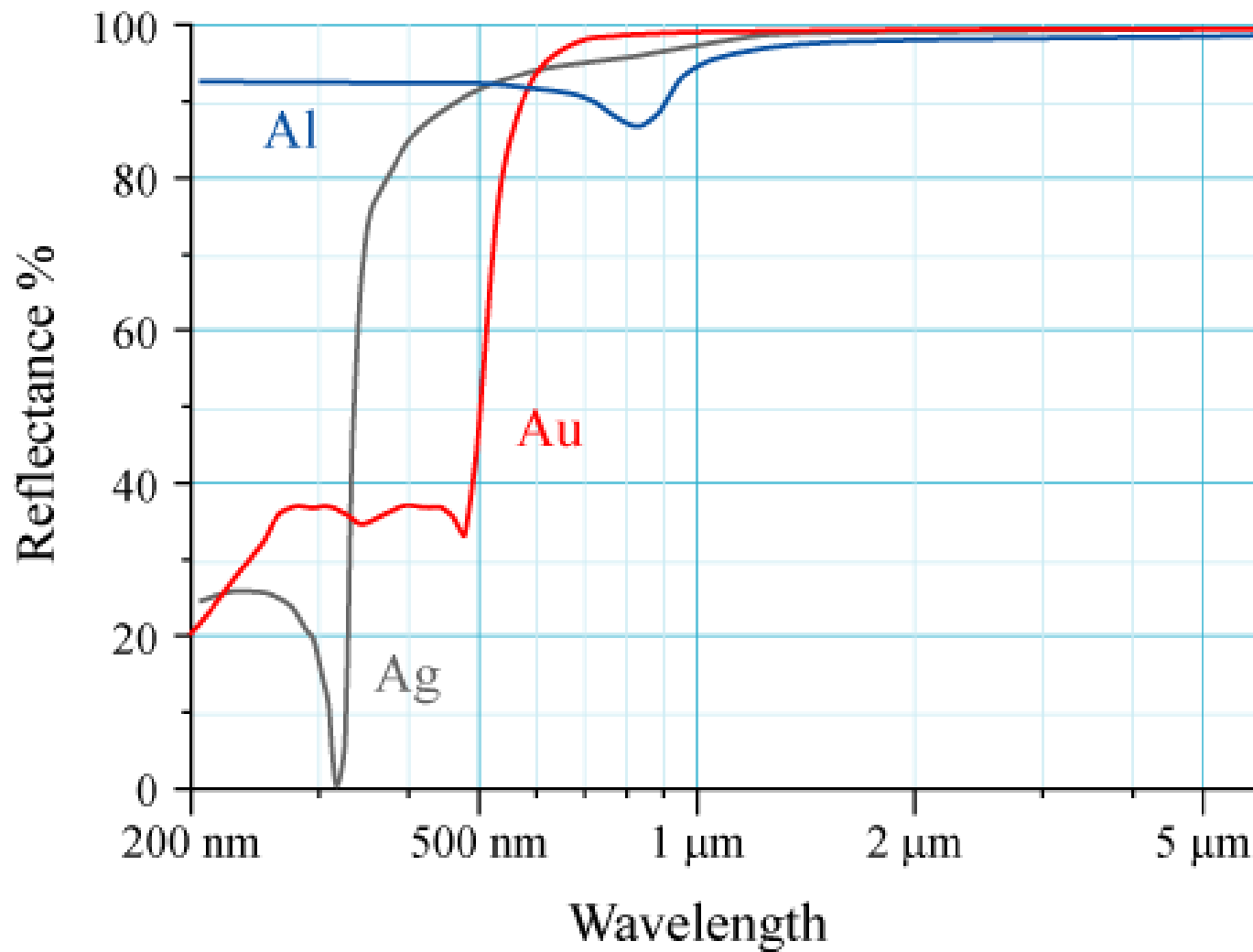
# Transmission/Absorption: metal

- In terms of energy bands, metals do not have an energy gap
- Since there is a very high concentration of electrons, practically all the light is absorbed within about  $0.1\mu\text{m}$  of the surface
- The excited atoms in the surface layers of metal atoms relax again, emitting a photon.
- The energy lost by the descending electron is the same as that of the originally incident electron
- So metal reflects the light very well – about 95% for most metals



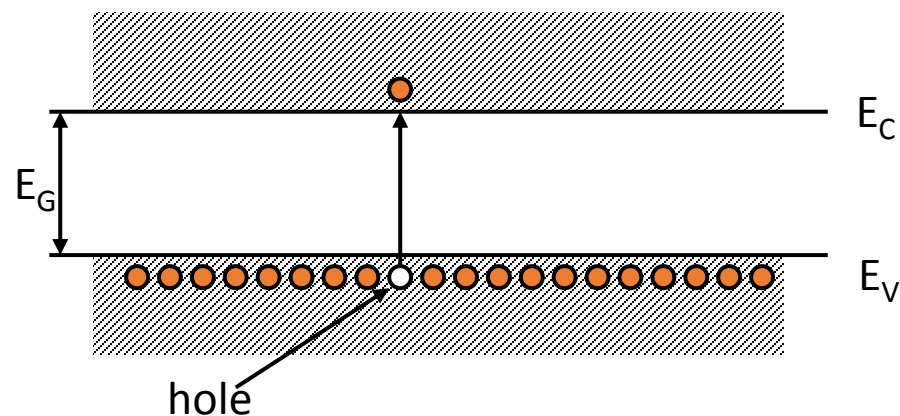
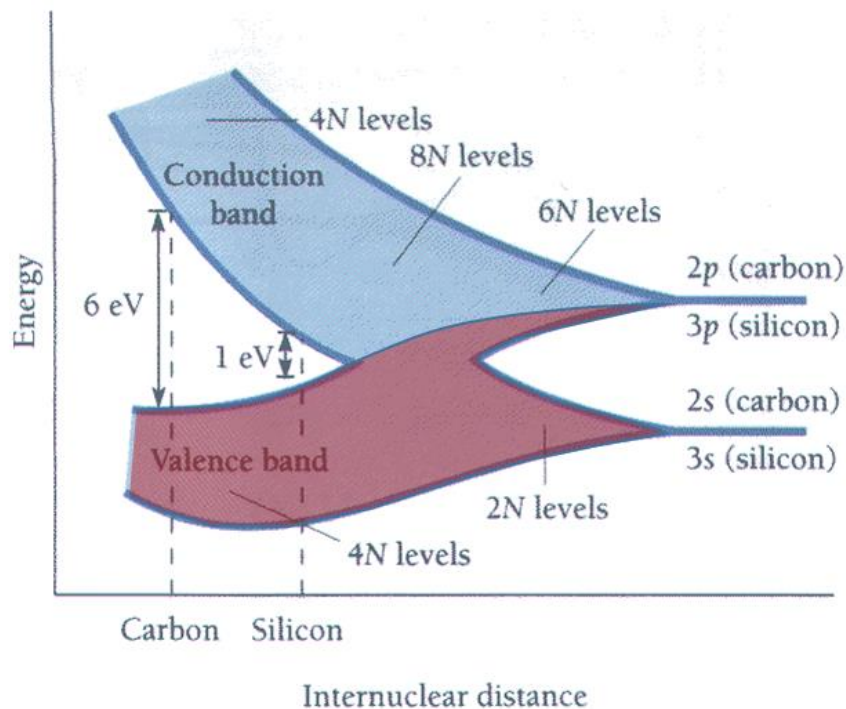
**Metal**

# Reflectance: metal

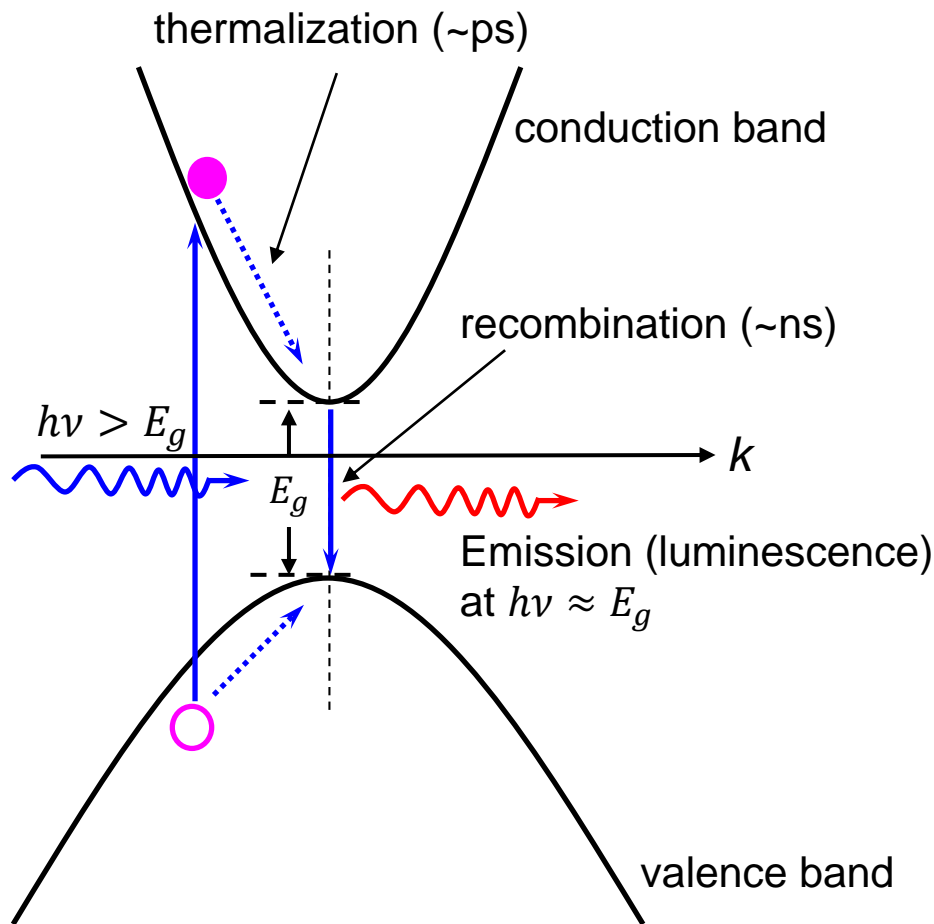


# Transmission/Absorption: non-metals

- **Dielectrics** and semiconductors behave essentially the same way, the only difference being in the size of the bandgap
- We know that photons with energies greater than  $E_g$  will be absorbed by giving their energy to electron-hole pairs which may or may not re-emit light when they relax.<sup>20</sup>



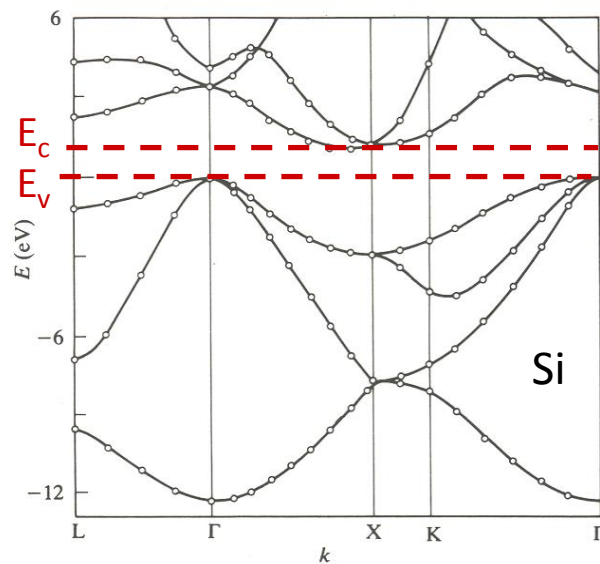
# Semiconductors and insulators: Absorption and Emission



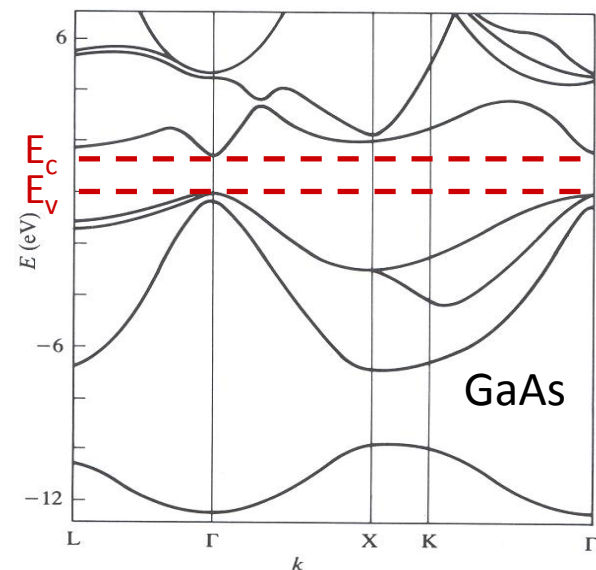
- The most important absorption process involves the transition of electrons from the valence to the conduction band. The process is referred to as **fundamental absorption**.
- In fundamental absorption, an electron absorbs an incident photon and jumps from the valence into available states in the conduction band.
- The photon energy  $h\nu$  must be equal to or larger than the energy gap  $E_g$
- In an absorption process, both energy and **momentum** must be **conserved**.

# Direct and Indirect Gap Semiconductors

- The 3-D band structures for semiconductors Si and GaAs



Indirect band gap  
( $\Delta k_{\text{gap}} \neq 0$ )



Direct band gap  
( $\Delta k_{\text{gap}} = 0$ )

- In a direct gap semiconductor, conduction band minimum  $E_C$  and valence band maximum  $E_V$  occurs at the same  $k$  value
- For an indirect gap semiconductor, the conduction band minimum  $E_C$  and valence band maximum  $E_V$  occurs at different  $k$ .



# Absorption: direct and indirect band gap

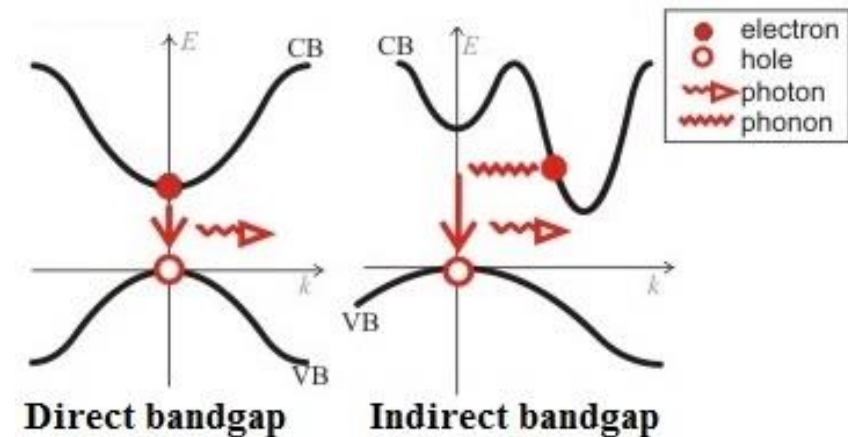
- For a **direct gap** materials, photons can excite electrons across the minimum band gap without a change in momentum — efficient process involving only two particles: a photon and an electron
  - Absorption coefficient is high  
 $\alpha > 10^4 - 10^5 \text{ cm}^{-1}$
- For an **indirect gap** material, a phonon is required to conserve momentum.
  - The phonon energy  $\hbar\Omega$  is typically tens of meV,  $\ll E_g$
  - Phonons cause nearly horizontal transitions
  - Such three-particle process is less likely than the two-particle process so that  $\alpha_{\text{direct}} \gg \alpha_{\text{indirect}}$  (on the order of  $10^3 \text{ cm}^{-1}$ )
- The absorption coefficient  $\alpha$  can be related to the band gap by:

$$(\alpha \hbar\nu)^{1/n} = A(\hbar\nu - E_g)$$

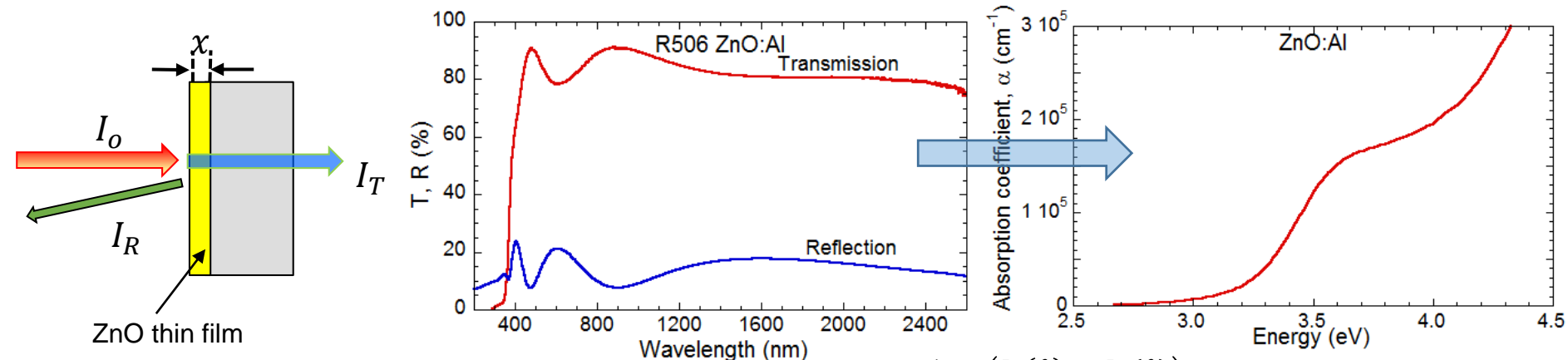
$\hbar\nu$  is the photon energy,  $E_g$  is the bandgap, A is a proportionality constant and

For direct allowed transition:  $n = 1/2$

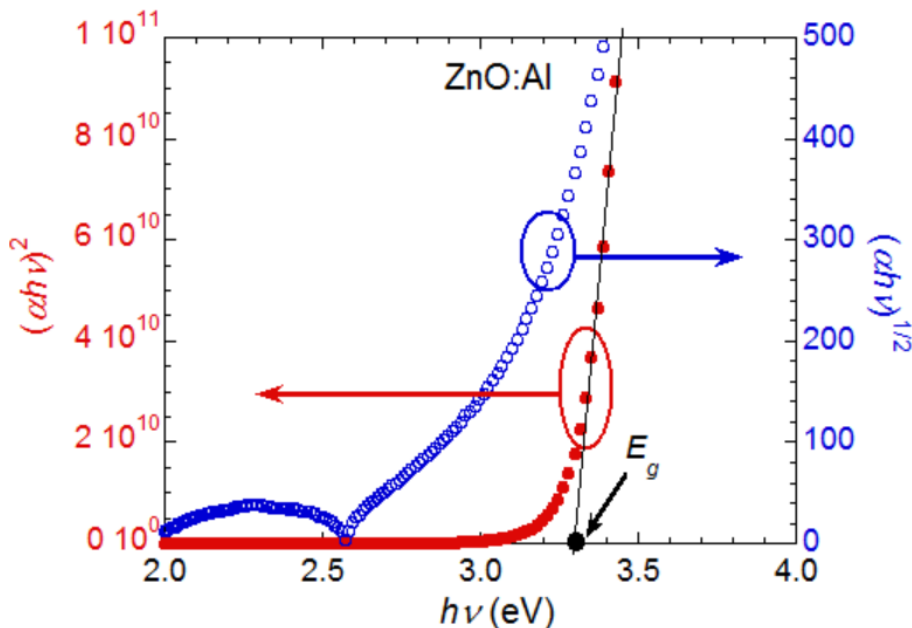
For indirect allowed transition:  $n = 2$



# Optical Absorption Measurement



$$\alpha(\lambda) = \frac{1}{x} \ln \left( \frac{I_o(\lambda) - I_R(\lambda)}{I_T(\lambda)} \right)$$



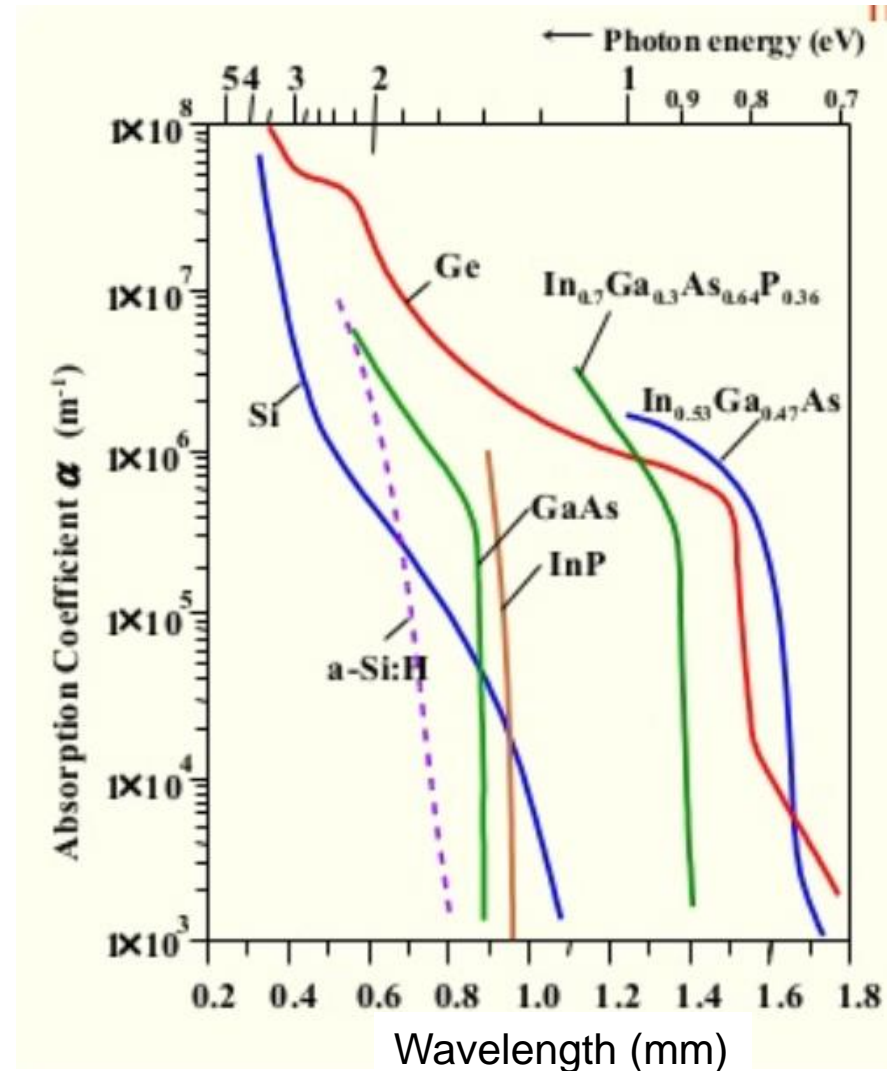
$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

To determine if the material has a direct or indirect gap

- plot  $(\alpha h\nu)^{1/n}$  vs.  $h\nu$
- Notice that we can **linearly extrapolate**  $(\alpha h\nu)^2$  vs.  $h\nu$  ( $n = 1/2$ ) to obtain a band gap  $E_g = 3.3$  eV
- $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  ( $n = 2$ ) does not result in a straight line
- ZnO is a direct gap material.

# Absorption coefficient $\alpha$

- Take the indirect gap Ge, for example,
  - the rise of  $\alpha$  at the minimum band gap energy of 0.66 eV (1.878  $\mu\text{m}$ ) to a value of only  $10^4 \text{ m}^{-1}$  ( $100 \text{ cm}^{-1}$ )
  - A second sharp rise up  $10^6 \text{ m}^{-1}$  ( $10^4 \text{ cm}^{-1}$ ) occurs at higher energies where direct transitions become possible ( $>0.8 \text{ eV}$ )
- Another indirect gap material Si
  - the indirect gap of 1.1 eV (1127 nm) and direct gap is at  $>3 \text{ eV}$
- For direct gap semiconductors, e.g. GaAs,  $\alpha$  is significantly larger,  $>10^5 \text{ m}^{-1}$  ( $>10^4 \text{ cm}^{-1}$ )



# Spectrophotometry: strengths and weaknesses

## ▪ Strength:

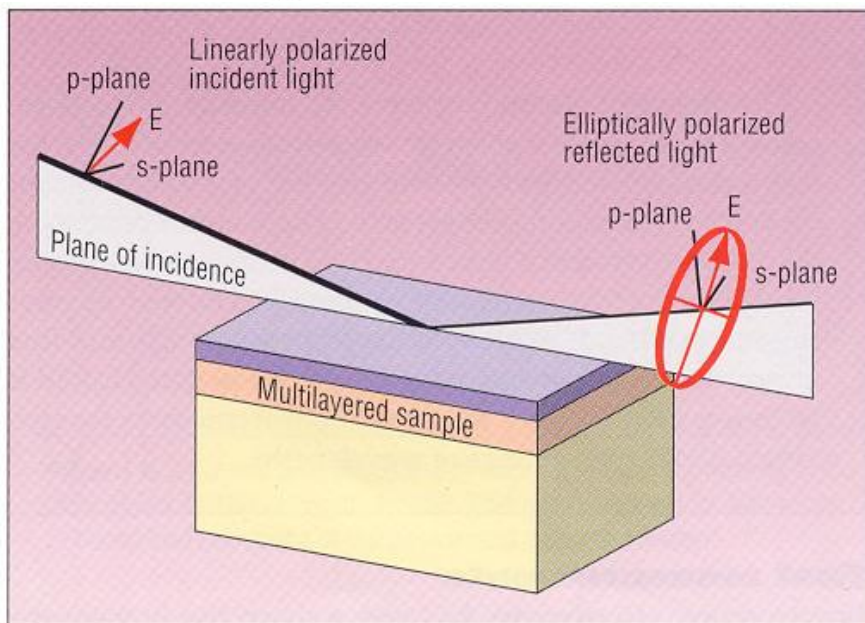
- Very little to no sample preparation.
- Simplicity of use and data interpretation
- Short acquisition time, for most cases.
- Non destructive.
- Broad range of photon energies, typically from 150 nm to 3500 nm.
- Relatively low equipment cost, from <20k USD to 60k USD.

## ▪ Weaknesses:

- For transmission measurements, substrate has to be transparent to the beam.
- Sample surface has to be smooth, otherwise a more expensive integrating sphere collecting all diffused light is needed.
- Limited spatial resolution.

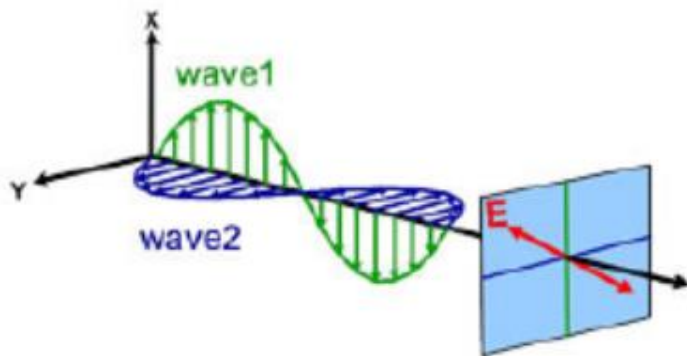
# Spectroscopic ellipsometry (SE)

Ellipsometry is an optical technique for investigating the **dielectric properties** (complex refractive index or dielectric function) of thin films. Ellipsometry measures the **change of polarization** upon reflection or transmission and compares it to a model.

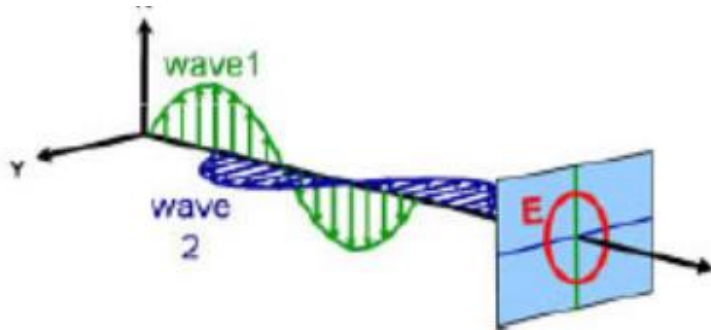


- Optical constant  $n$  and  $k$  can be deduced from the result.
- It can be used to characterize **composition, roughness, thickness** (depth), **crystalline nature, band gap**, doping concentration, electrical conductivity and other material properties.
- It is very sensitive technique measuring films **down to Å thickness**. It is an absolute measurement: do not need any reference.
- It is an **indirect method**: does not give directly the physical parameters of the sample, it requires using a **model** to describe the sample.

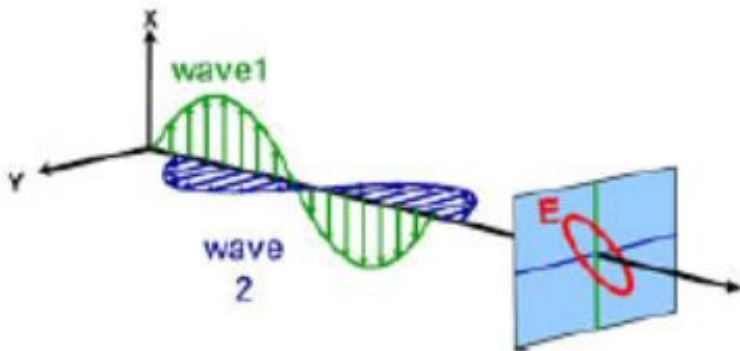
# Polarized light



When two orthogonal light waves are in phase, the resulting light will be linearly polarized. The relative amplitudes determine the resulting orientation



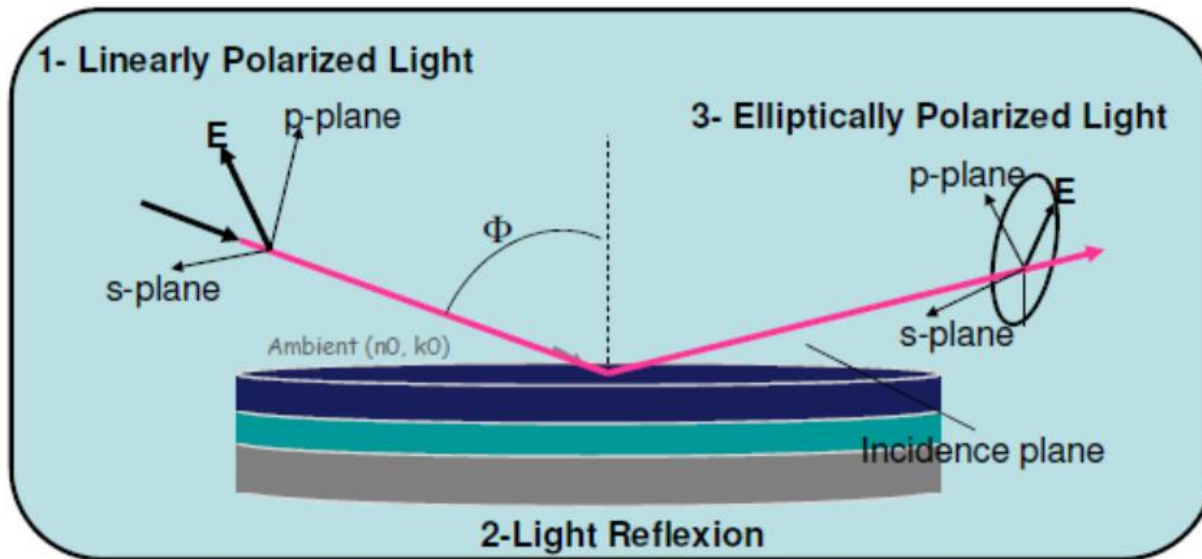
When two orthogonal light waves are  $90^\circ$  out-of-phase and equal in amplitude, the resulting light is circularly polarized.



When two orthogonal light waves are of arbitrary amplitude and phase, then the resulting light will be elliptical. Ellipsometry measures the “shape” of this “ellipse” as the light is reflected from a sample surface, hence the name ellipsometry



# Spectroscopic ellipsometry (SE)



The sample has a layered structure and each layer  $i$  has optical constants ( $n_i, k_i$ ) and a thickness  $t_i$ .

- The measured signal is the **change in polarization** as the incident radiation (in a known state) interacts with the material structure of interest (reflected, absorbed, scattered, or transmitted).
- The polarization change is quantified by the **amplitude ratio,  $\Psi$** , and the **phase difference,  $\Delta$** .

$$\rho = \frac{R_p}{R_s} = \tan \Psi e^{i\Delta} = f(n_i, k_i, t_i)$$

where  $\frac{R_p}{R_s}$  is the Fresnel reflection coefficient

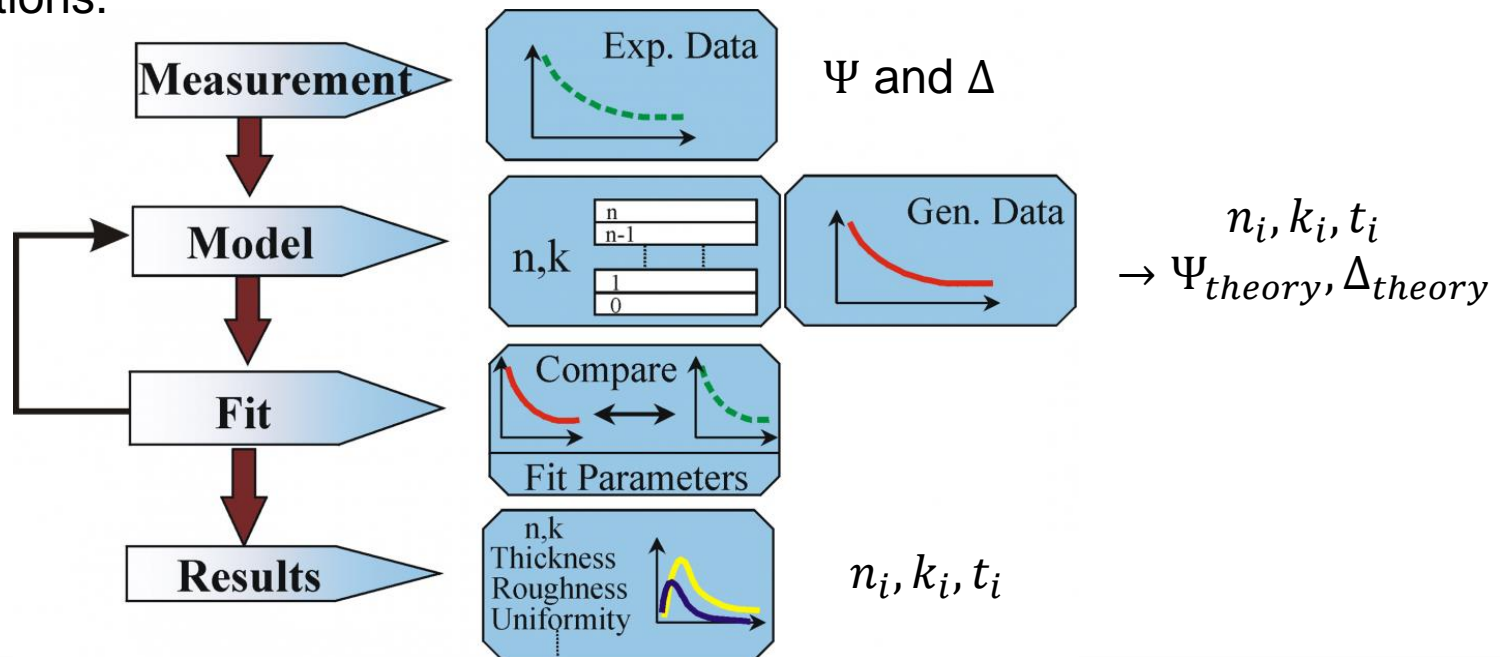
$$R_p = \frac{E_p(\text{reflected})}{E_p(\text{incident})}; R_s = \frac{E_s(\text{reflected})}{E_s(\text{incident})}$$



# SE data analysis

Ellipsometry is an **indirect method**, i.e. in general the measured  $\Psi$  and  $\Delta$  cannot be converted directly into the optical constants of the sample. Normally, a model analysis must be performed.

- First, a **layer model** must be established, which considers the optical constants and thickness parameters of all individual layers of the sample including the correct layer sequence.
- Using an iterative procedure unknown optical constants and/or thickness parameters are varied, and  $\Psi$  and  $\Delta$  values are calculated using the Fresnel equations.



# SE data analysis: models for $n$ , $k$

- The dielectric function and the optical constants are related by

$$n(\lambda) + ik(\lambda) = \sqrt{\tilde{\epsilon}} = \sqrt{\epsilon_1(\lambda) + i\epsilon_2(\lambda)}$$

$$\epsilon_1 = n^2 - k^2; \epsilon_2 = 2nk$$

- Cauchy model** for transparent materials

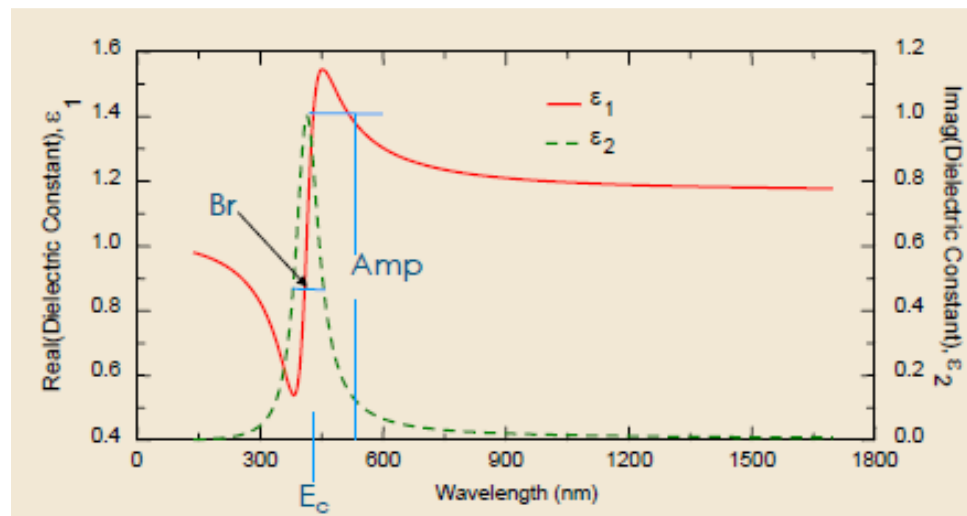
$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}; k(\lambda) = 0$$

- Oscillator model** for absorbing materials

- Lorentz, Gaussian, Harmonic, Tauc-Lorentz, etc.
- Common to all oscillator models is that they all have **3 common parameters**: amplitude (Amp) or strength, broadening (Br) or width, center energy ( $E_c$ ) or position.
- The Lorentz oscillator can be written as:

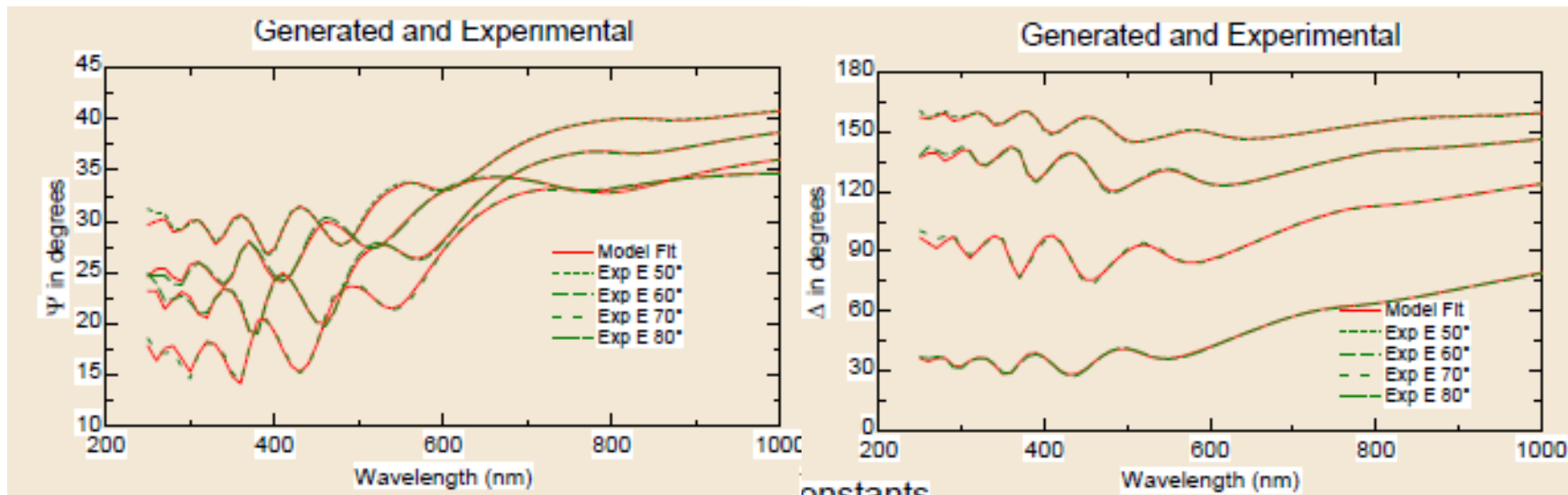
$$\tilde{\epsilon} = \epsilon_{1,\text{offset}} + \frac{AE_c}{E_c^2 - E^2 - iBE}$$

- The dielectric function can be modeled as a sum of various oscillators



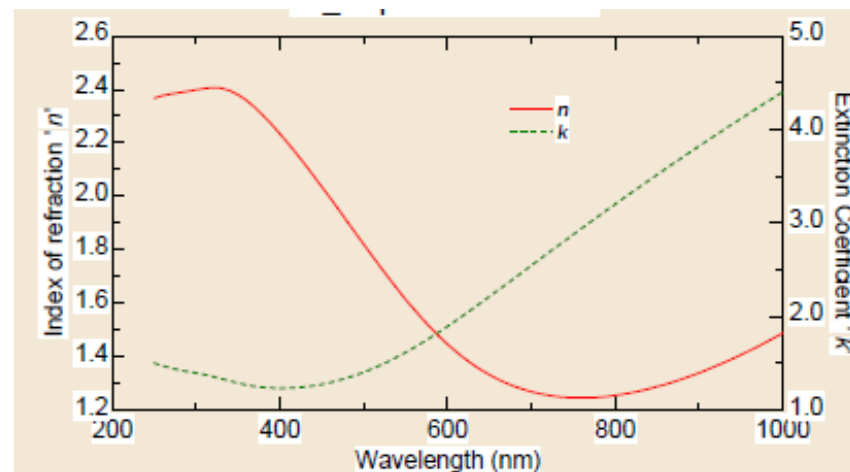
# Example: thin metal film on oxide

TiN thin film on SiO<sub>2</sub> on Si



Best fit results in layer structure and optical constants of TiN

2	tin_l	55.128 nm
1	sio2_jaw	627.46 nm
0	si_jaw	1 mm

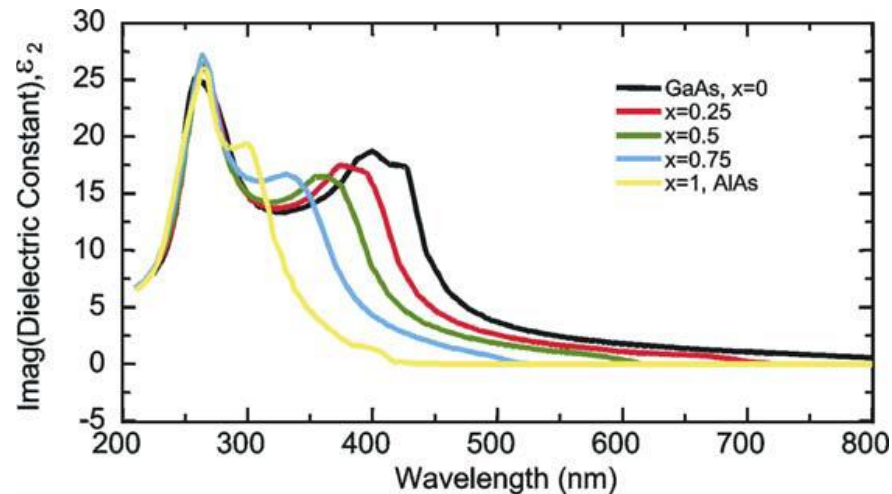


R. Synocicki, J. A. Woollam Co., Inc., Dec 2010.

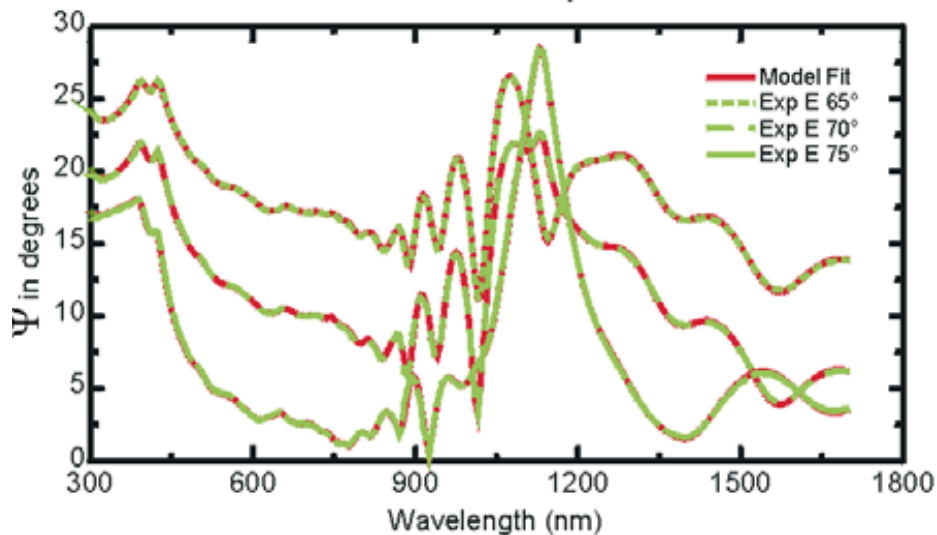
# Example: $\text{Al}_x\text{Ga}_{1-x}\text{As}$ multilayer

9	GaAs Oxide	19.9 Å
8	GaAs	3348.1 Å
7	AlGaAs $x=0.365$ (Coupled to 5)	995.6 Å
6	GaAs	849.3 Å
5	AlGaAs $x=0.365$	995.6 Å
4	GaAs	852.9 Å
3	AlGaAs $x=0.274$	866.5 Å
2	GaAs	843.3 Å
1	AlGaAs $x=0.168$	742.5 Å
0	GaAs Substrate	1 mm

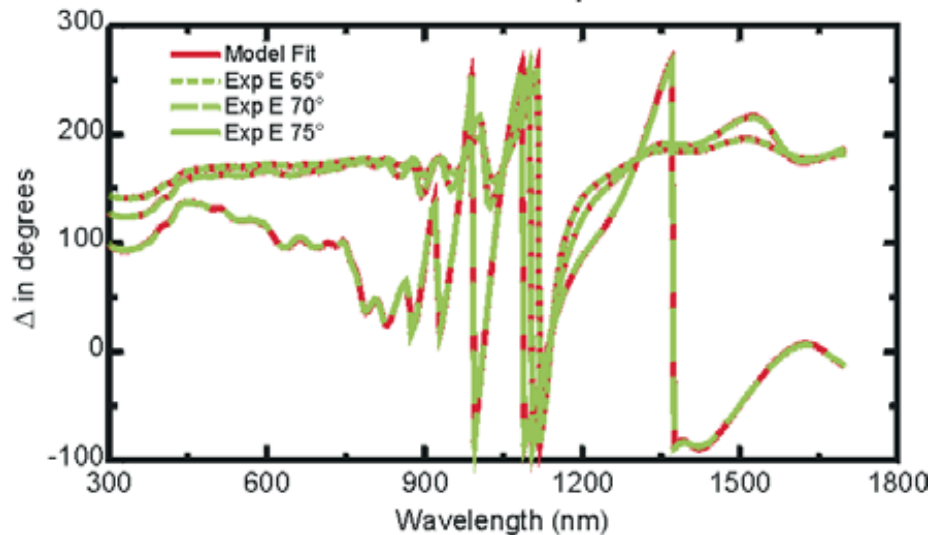
2  
3  
3



Generated and Experimental



Generated and Experimental



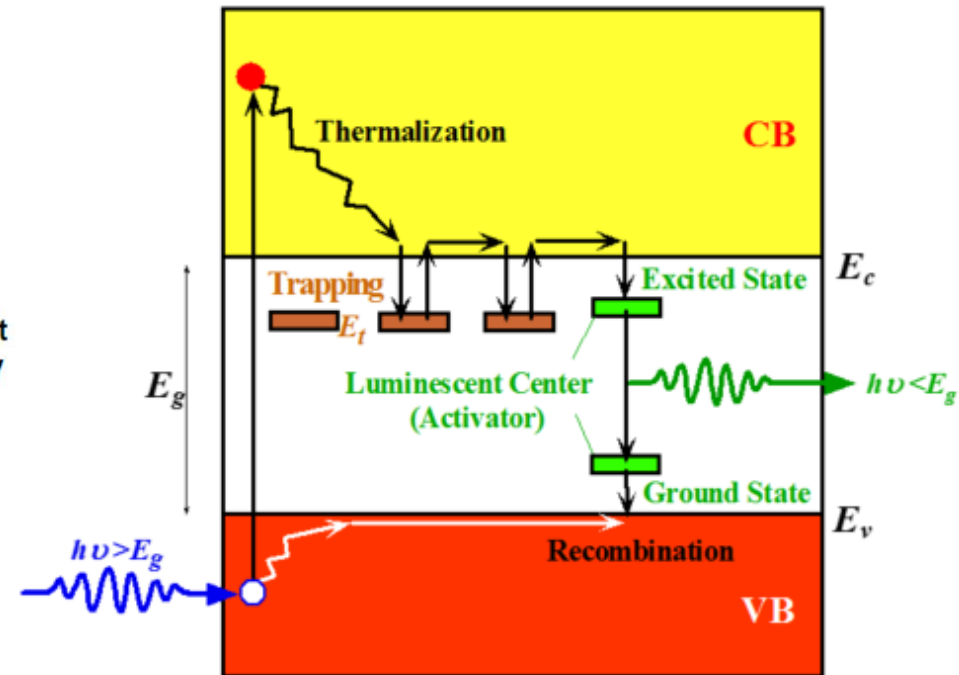
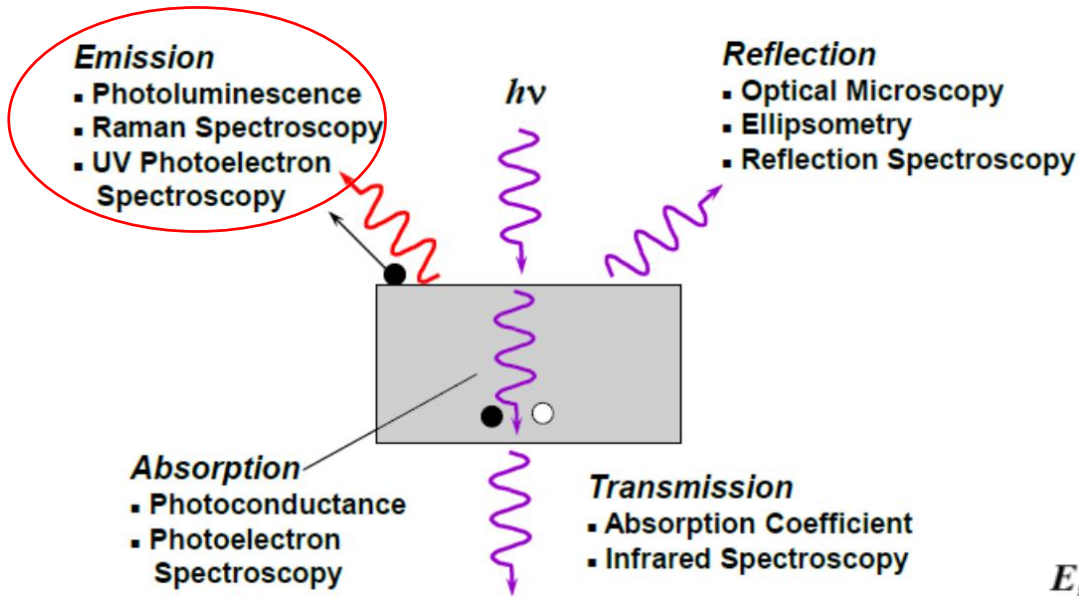
B. Johs, et al., SPIE Proc. Vol CR72, (1999) pp. 50-51.

# SE: advantages and limitations

- **Non-destructive** technique
- Film thickness measurement, can measure down to  $<1$  nm
- Can measure optical constants  $n$  and  $k$  for unknown materials
  - Absorption coefficient, band gap, carrier concentration, mobility, effective mass, etc.
- Can also measure film composition, porosity and roughness
- Absolute measurement: do not need any reference.
- Rapid measurement: get the full spectrum (190nm up 1700nm) in few seconds
- Can be used for *in-situ* analysis
- Small equipment footprint: do not require a lot of lab space
- Can only measure flat, parallel and reflecting surfaces
- Some knowledge of the sample is required: number of layers, type of layers, etc.
- SE is an **indirect** measurement: does not give directly the physical parameters
- A realistic physical model of the sample is usually required to obtain useful information

# Luminescence

Luminescence refers to the emission of light by a material due to the relaxation of the material from an excited state.



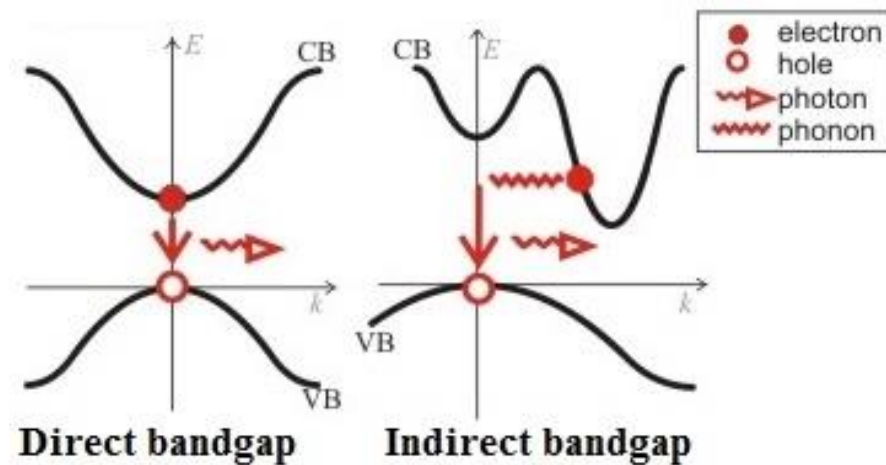
The material can be excited by:

- Photons (typically a laser): Photoluminescence (PL)
- Electrons: Cathodoluminescence (CL)
- Electric field: Electroluminescence (EL)



# Photoluminescence spectroscopy (PL)

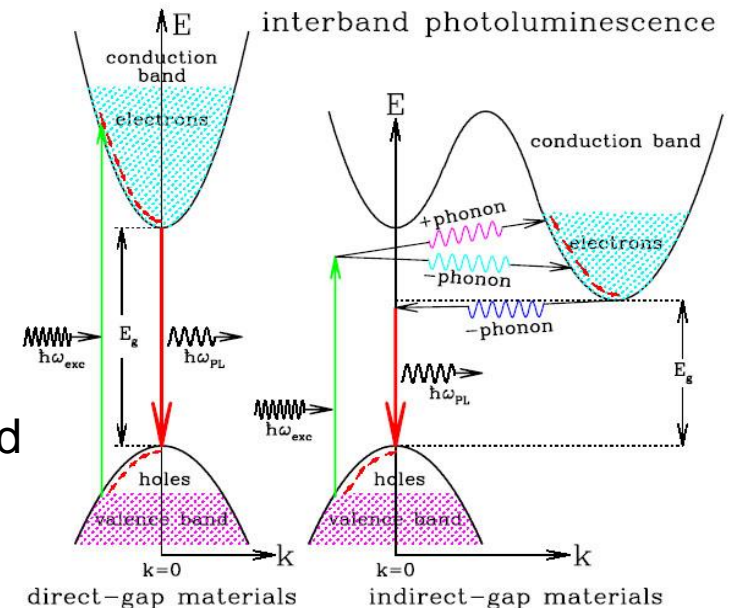
- Photoluminescence (PL) narrows this down to any emission of light that results from **optical stimulation**.
- The impinging light promote electrons from the less energetic levels to excited levels, forming **electron-hole pairs**. As the electrons and holes recombine, they may release some of the energy as photons. The emitted light is called **luminescence**.
- The detection and analysis of this emission is widely used as an analytical tool due to its sensitivity, simplicity, and low cost
- Depth sensitivity of PL is restricted by the optical penetration depth and carrier diffusion length ( $\sim 0.05$  to several mm).
- PL can give information on many inorganic solids: impurities, defects, surface damage; dopants and electronic band structures in semiconductors; structural imperfection in crystals...



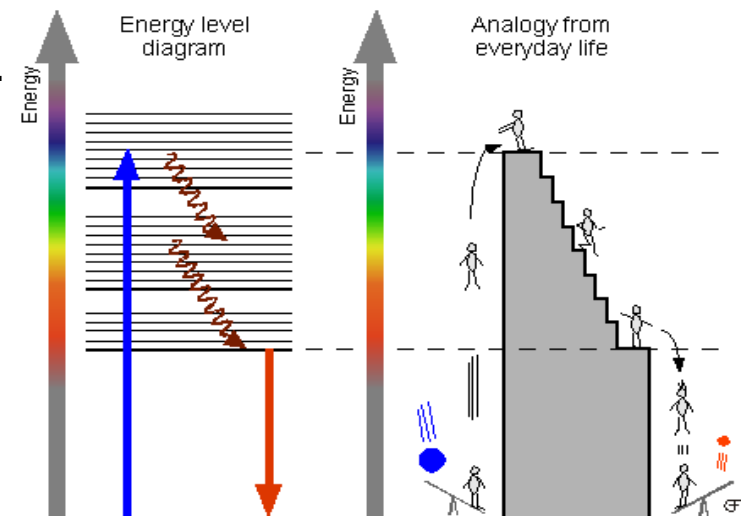


# PL: basics

- In **PL** a material gains energy by absorbing light at some wavelength, promoting an electron from a low to a higher energy level.
- This may be described as making a transition from the ground state to an **excited state** of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal (electron-hole pair creation).
- The system then undergoes a **nonradiative internal relaxation** to a more stable excited level, such as the bottom of the conduction band or the lowest vibrational molecular state.
- The system will return to the ground state through emission of light—**radiative**.
- The wavelength (energy) of this emission is longer (lower) than that of the incident light.
- The time dependence of the emission provide information about energy level coupling and lifetimes.

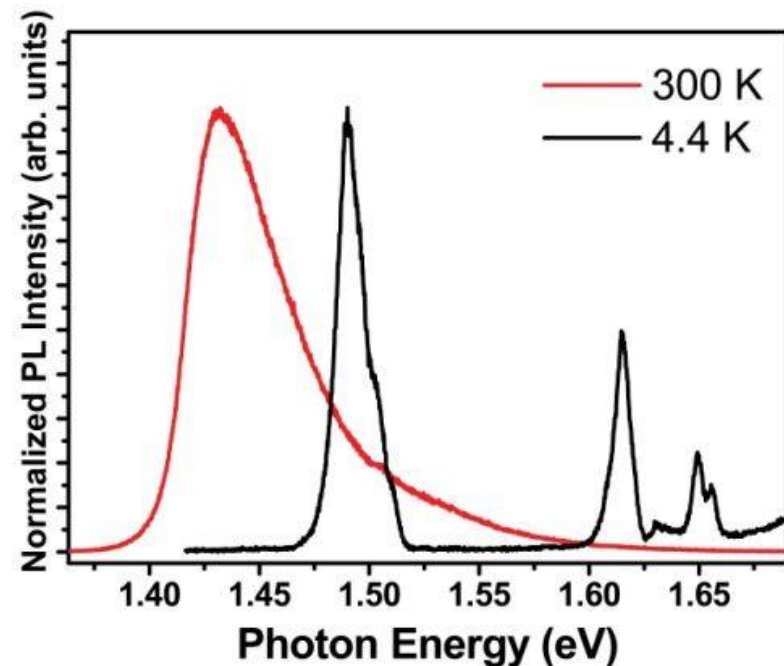


**Absorption, Nonradiative Relaxation and Luminescence**  
 Making **heat** and 1x **red** out of 1x **blue**



# PL: basics

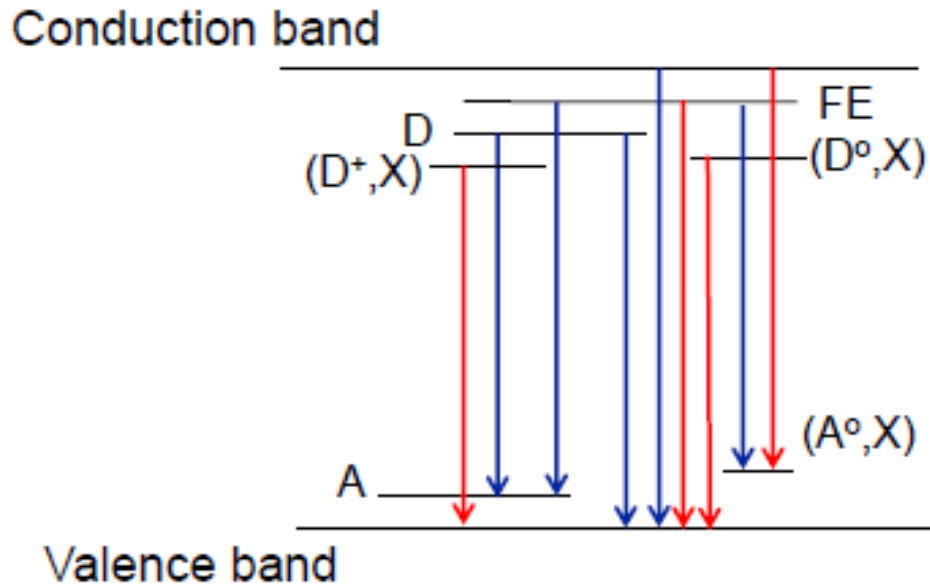
- The light involved in PL excitation and emission usually is in the range 0.6-6 eV (roughly 200-2000 nm), typically using a laser.
- At room temperature, PL emission is **thermally broadened**. As the temperature is lowered, features tend to become sharper, and PL is often stronger due to fewer nonradiative channels.
- Low temperatures are typically used to study phosphorescence in organic materials or to identify particular impurities in semiconductors.
- PL is generally most useful in semiconductors if their band gap is direct.
- Applications of PL are varied, including compositional analysis, trace impurity detection, spatial mapping, structural determination (crystallinity, bonding, layering), and the study of energy-transfer mechanisms.



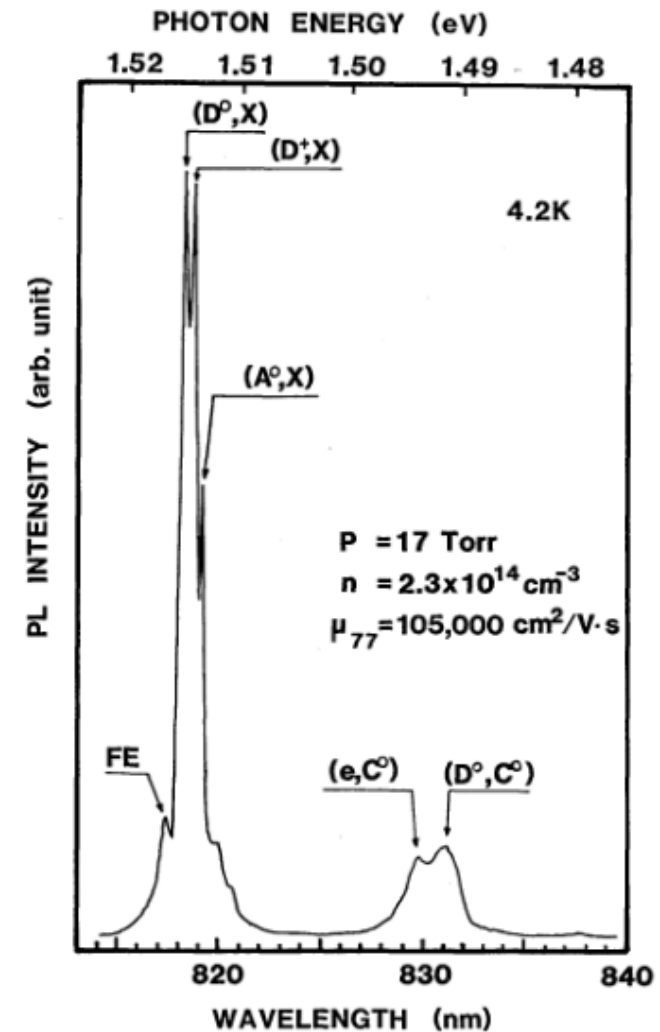
Room and low (4.4 K) temperature  $\mu$ -PL emission spectra from a single GaAs/AlGaAs core-shell NW (Zhou et al., 2009).

# PL: example

High purity GaAs epitaxial layer

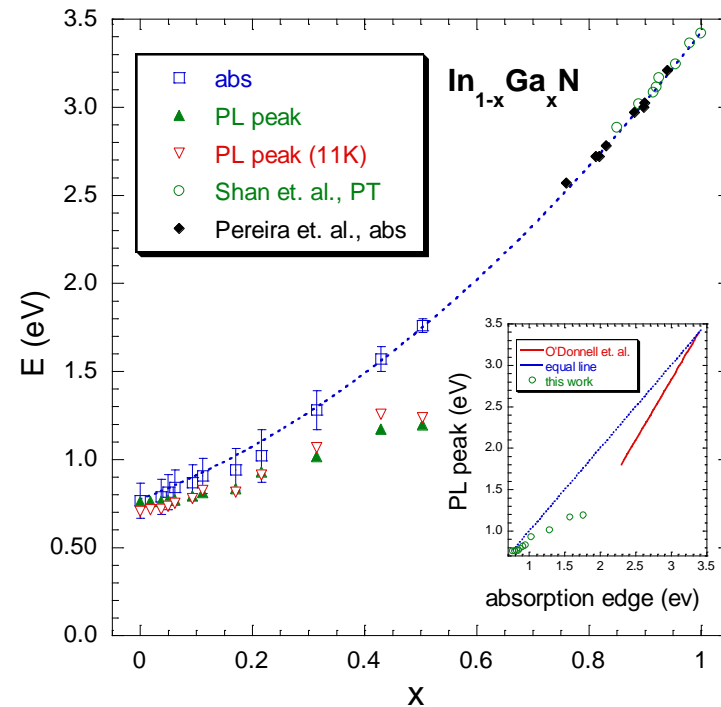
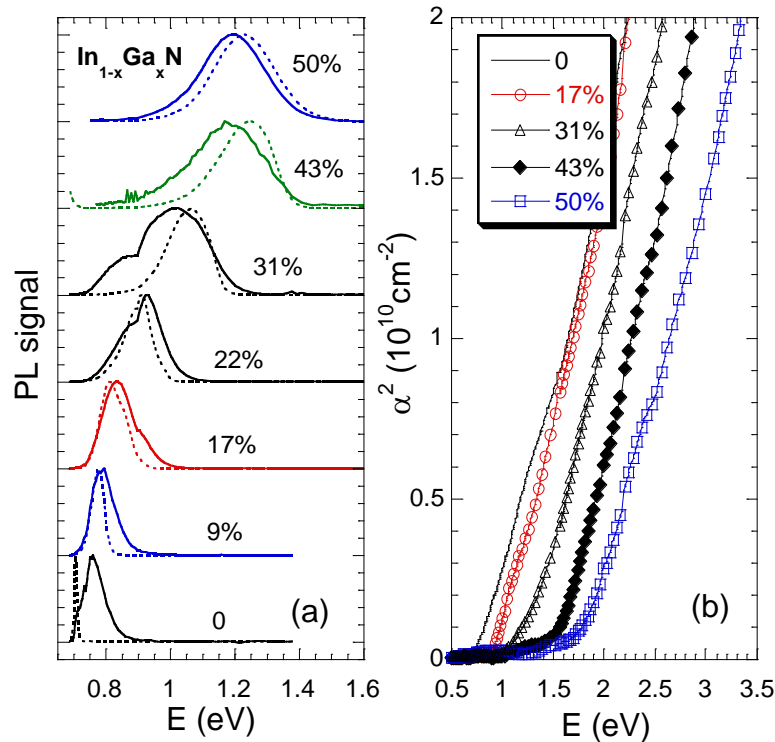


- Learn about the various impurities and their associated energy levels in a crystal
- Deduce the bandgap of a semiconductor



Takagishi and Mori, Jpn. J. Appl. 23, L100 (1984).

# Example: composition dependence of bandgap in InGaN

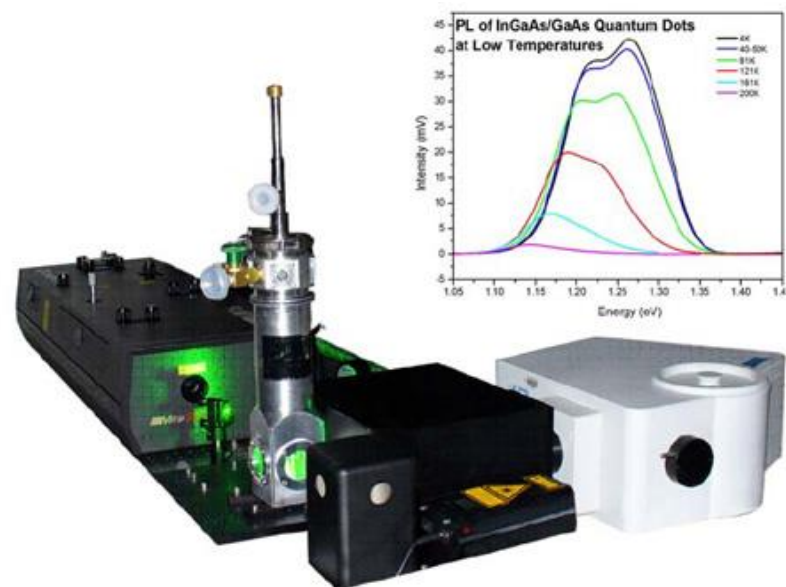
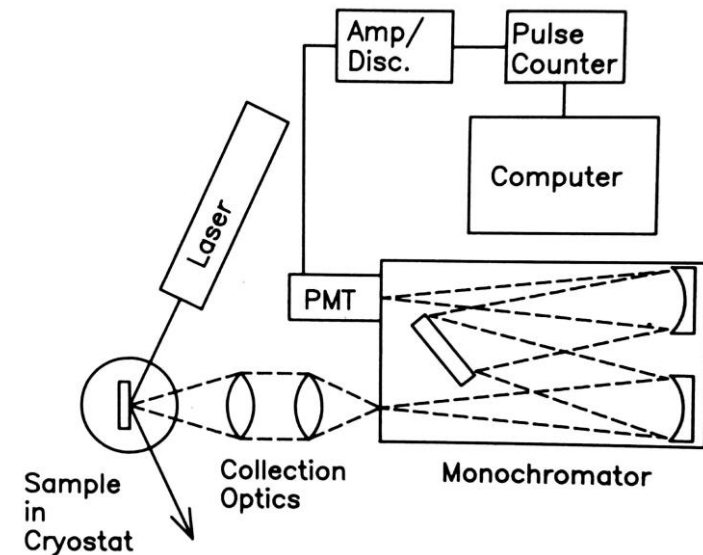


Wu et al. Appl. Phys. Lett. 80, 4741 (2002).

- PL was used to investigate the band gap of alloy semiconductor thin films as a function of alloy composition.
- Alternatively if the composition dependent bandgap of a certain alloy system is known, alloy composition of a sample can be obtained from its PL peak position

# PL: material parameters

Spectral feature	Material parameter
Peak energy	Compound identification
	Band gap/electronic levels
	Impurity or exciton binding energy
	Quantum well width
	Impurity species
	Alloy composition
	Internal strain
	Fermi energy
Peak width	Structural and chemical quality
	Quantum well interface roughness
	Carrier or doping density
Peak intensity	Relative quantity
	Polymer conformation
	Relative efficiency
	Surface damage
	Excited state lifetime
	Impurity or defect concentration



# PL: strengths and weaknesses

## ■ Strengths:

- Very little to none sample preparation
- Non destructive technique
- Very informative spectrum
- Rapid data acquisition

## ■ Weaknesses

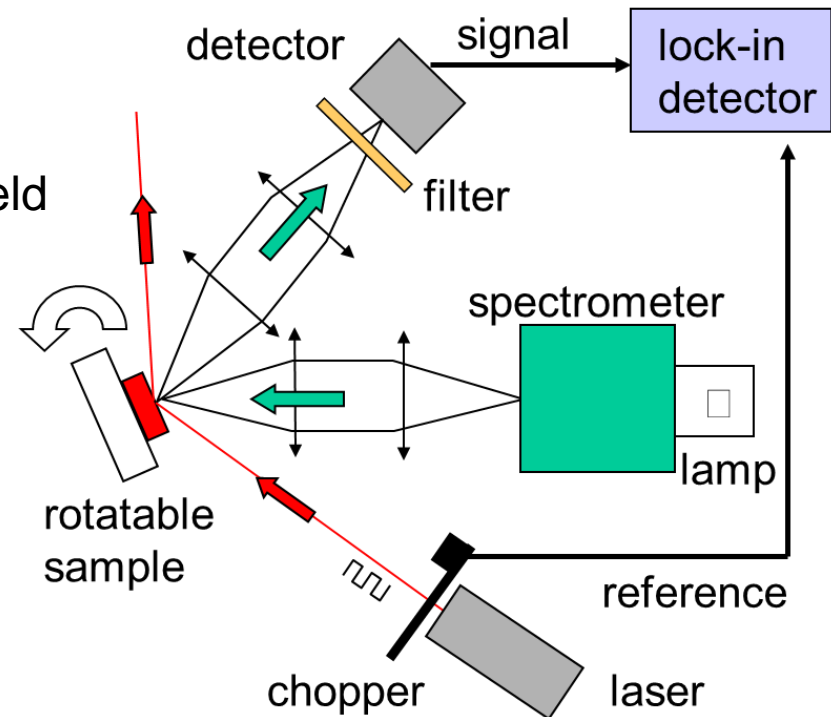
- Often requires low temperature (down to LHe).
- Data analysis may be complex (many transition levels).
- Laser with different wavelengths may be needed as probe.
- Many materials have weak luminescence intensity

# Modulation spectroscopy

**Modulation Spectroscopy** is an analog method for taking the derivative of an optical spectrum (reflectance or transmittance) of a material by modifying the measurement conditions in some manner. This procedure results in a series of **sharp, derivative-like** spectral features in the photon energy region corresponding to **electronic transitions** between the filled and empty quantum levels of the atoms that constitute the bulk or surface of the material. Using Modulation Spectroscopy it is possible to measure the photon energies of the interband transitions to a high degree of **accuracy and precision**.

The modulation is applied by periodical changes of one of the system parameters:

- Electric field: modulation of the electric field by
  - applying a periodic bias: **Electroreflectance**
  - applying a periodic light probe: **Photorefectance (PR)**
- Temperature: **thermoreflectance (TR)**
- Strain: **piezoreflectance**

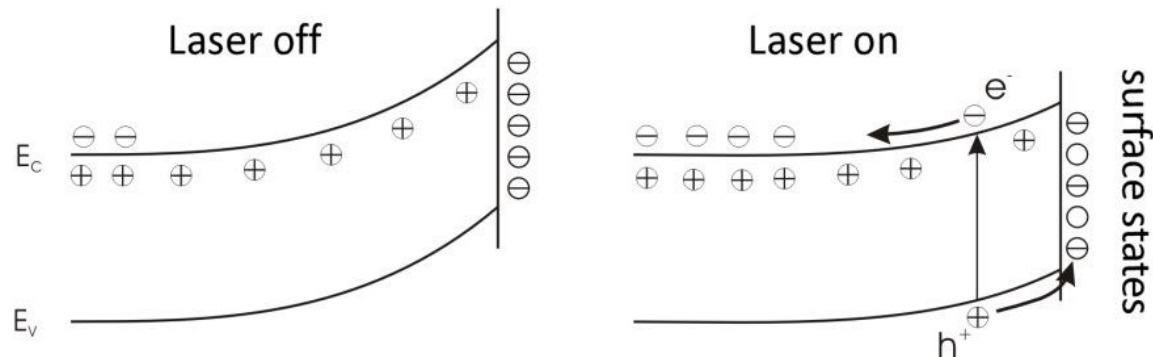




# Photoreflectance (PR)

Photoreflectance (PR) spectroscopy is the simplest approach to **modulate the internal electric field** of a sample by an additional light source and measure the reflectance of the sample. PR has many advantages:

- **contactless** and hence no special sample preparation needed
- **non-destructive**
- low cost, fast measurement
- The light beam (usually periodically **chopped laser** light with energy higher than the material bandgaps) generates electron-hole pairs in the structure causing the change in the occupation of the surface states



- In PR the relative changes of the reflectivity are measured:

$$\frac{\Delta R}{R} = \frac{R - R'}{R}$$

where  $R$  and  $R'$  are the reflectivity with the laser light off and on, respectively

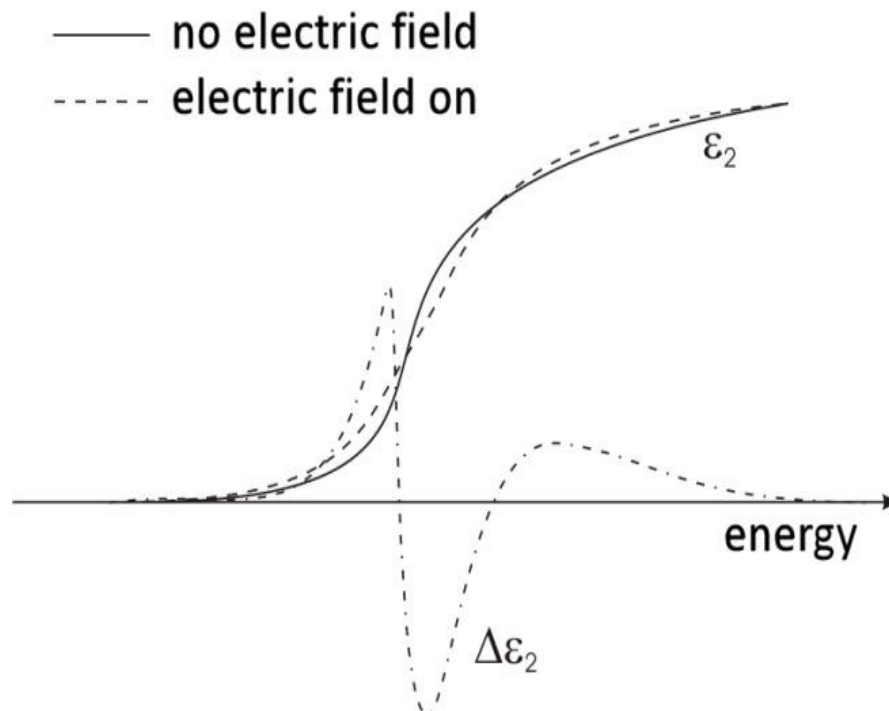
# Photoreflectance: principles

- Changes in reflectivity  $\frac{\Delta R}{R}$  can be related to the **perturbation** of the **dielectric function** of the material,  $\varepsilon = \varepsilon_1 + i\varepsilon_2$ :

$$\frac{\Delta R}{R} = \alpha(\varepsilon_1, \varepsilon_2)\Delta\varepsilon_1 + \beta(\varepsilon_1, \varepsilon_2)\Delta\varepsilon_2$$

where  $\alpha$  and  $\beta$  are the **Seraphin coefficients**,  $\Delta\varepsilon_1$  and  $\Delta\varepsilon_2$  represent photo-induced changes of the real and imaginary parts of the dielectric function, respectively.

- The imaginary part  $\varepsilon_2$  changes slightly in electric field, resulting in a sharp resonance  $\Delta\varepsilon_2$  exactly at the energy of the optical transition.
- It can be shown that in a case of the bulk crystal, the shape of dielectric function changes is of the **third derivative** of the unperturbed dielectric function.



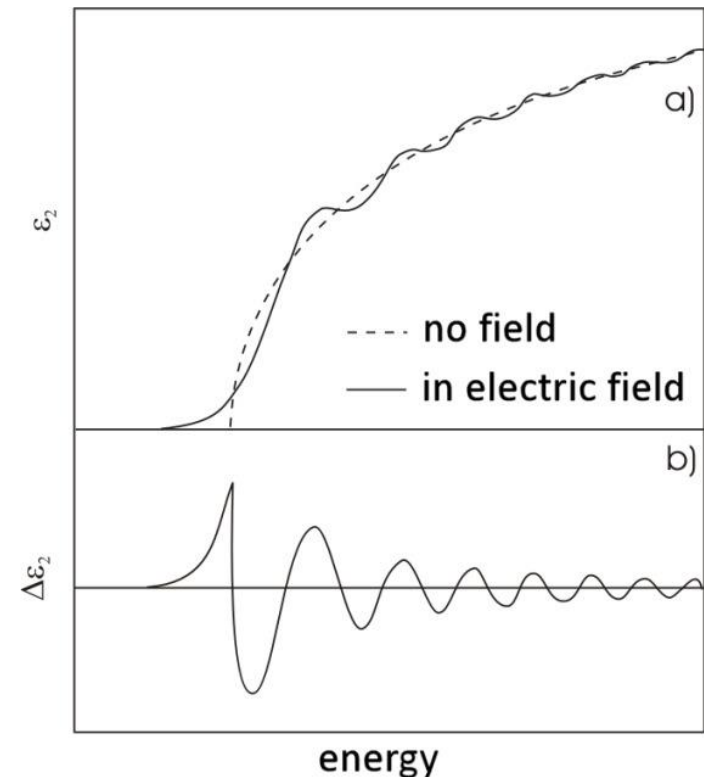
# Photoreflectance: principles

The reflectivity change under an electric field modulation can be expressed in a general form:

$$\frac{\Delta R}{R} = \text{Re} \left[ A e^{i\varphi} (E - E_g + i\Gamma)^{-n} \right],$$

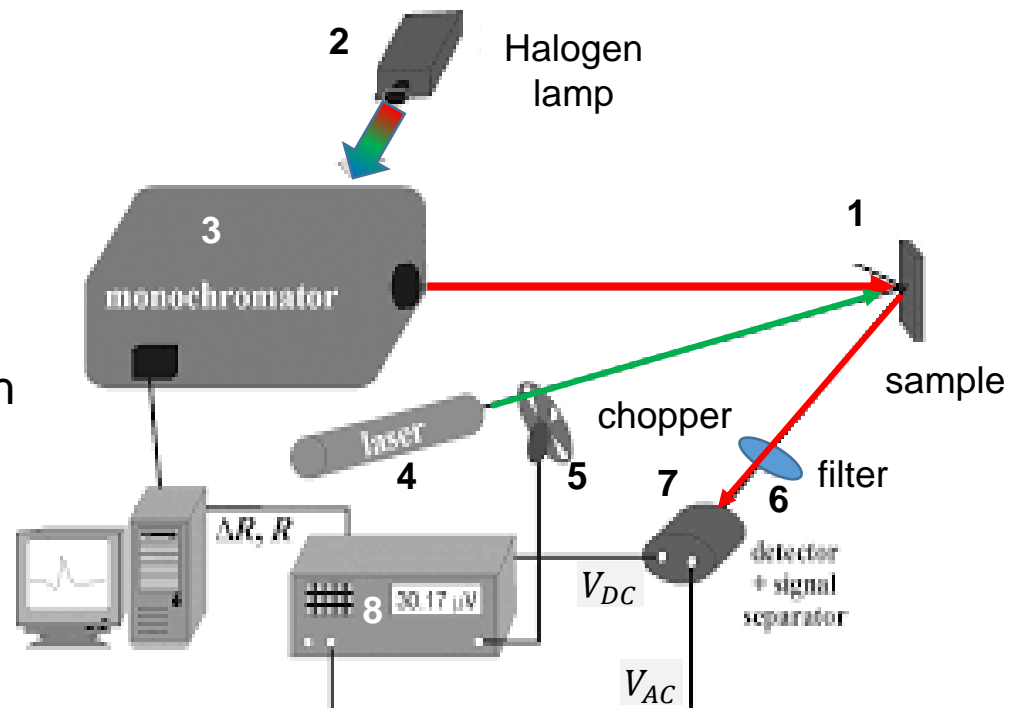
where  $A$  is the amplitude of the signal,  $\varphi$  is the phase angle with respect to the modulating factor,  $E$  is the photon energy,  $E_g$  is the energy gap, and  $\Gamma$  is the broadening parameter of the spectral line.

- The  $n$  parameter determines the critical point type – for three dimensional system (e.g. straight energy bandgap in GaAs)  $n = 2.5$ , and for the two dimensional critical point  $n = 3$ .
- For sufficiently high built-in electric fields the spectrum can display an oscillatory behavior above the band gap; these are called **Franz-Keldysh oscillations** (FK oscillations)
  - The electric field intensity in the structure can be determined from the period of the FK oscillations.

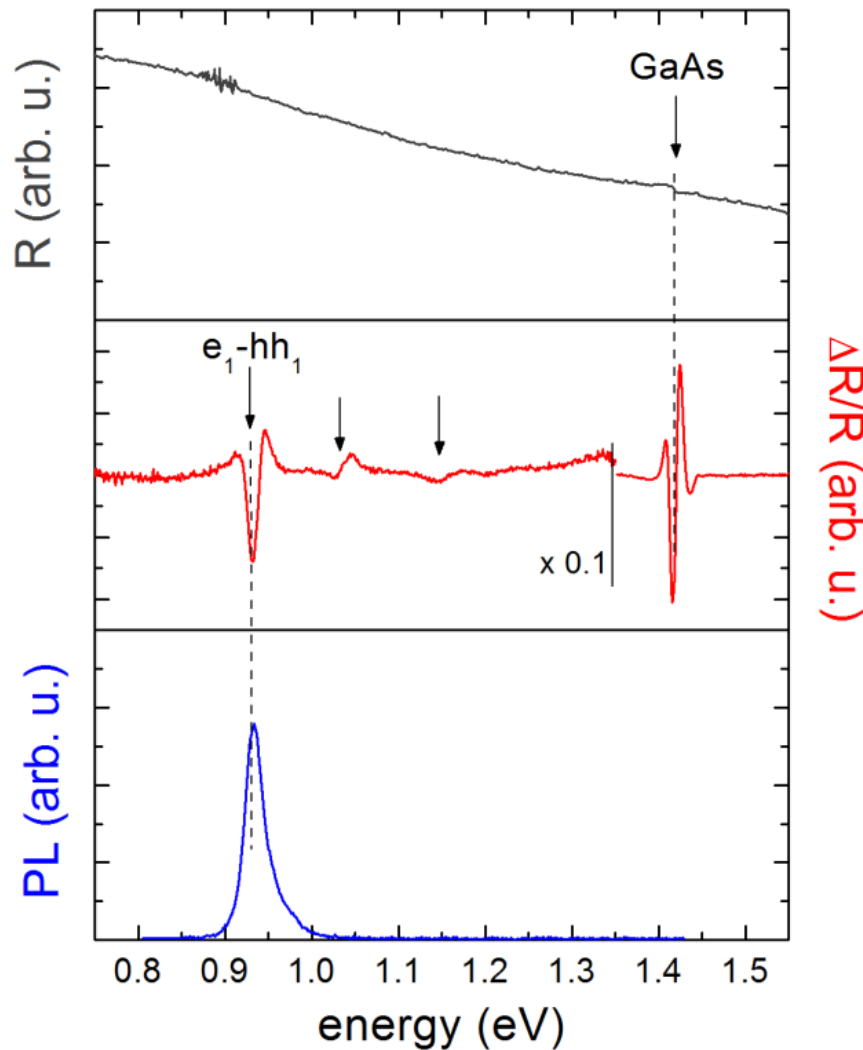


# PR operation

- The sample (1) is mounted on a sample holder (or into a cryostat for low temperature measurement)
- The sample is illuminated by monochromatic light from a halogen lamp (2) passing through a monochromator (3).
- A laser beam (4) with energy higher than the band gap is chopped by a mechanical chopper (5) provides the modulation.
- A filter (6) is placed in front of the detector to block the laser light.
- The reflected signals are collected by a photodetector (7) and processes by a lock-in amplifier (8).
- The chopper is also connected to the lock-in providing the reference frequency.



# PR: quantum well



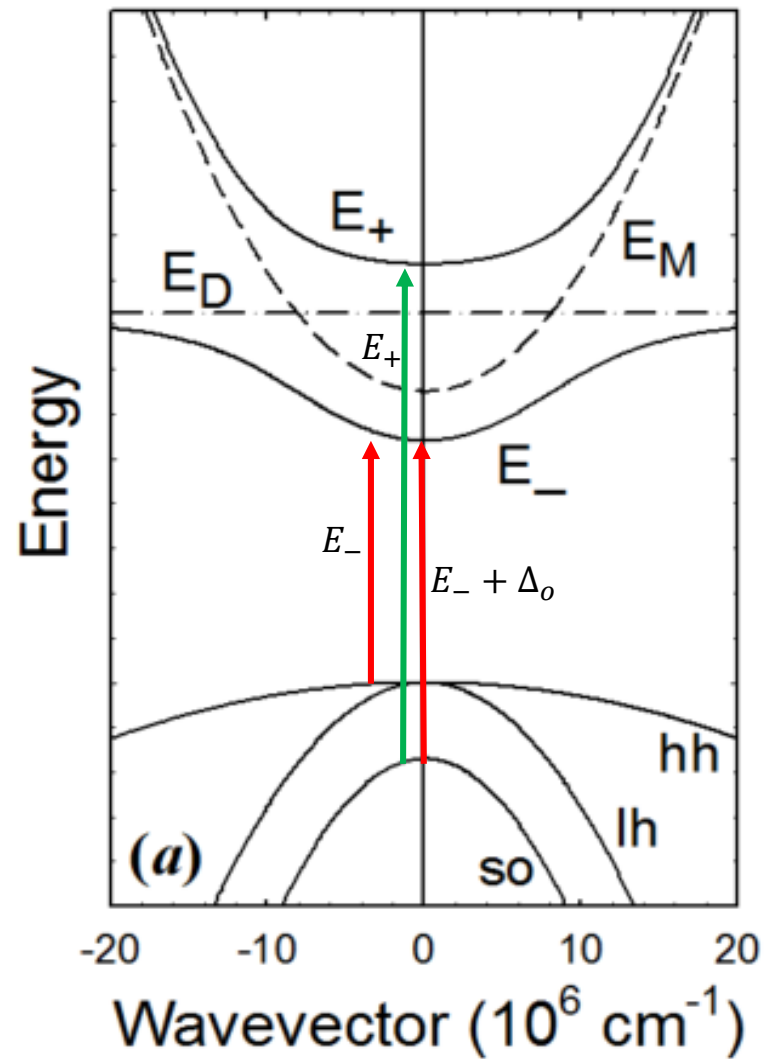
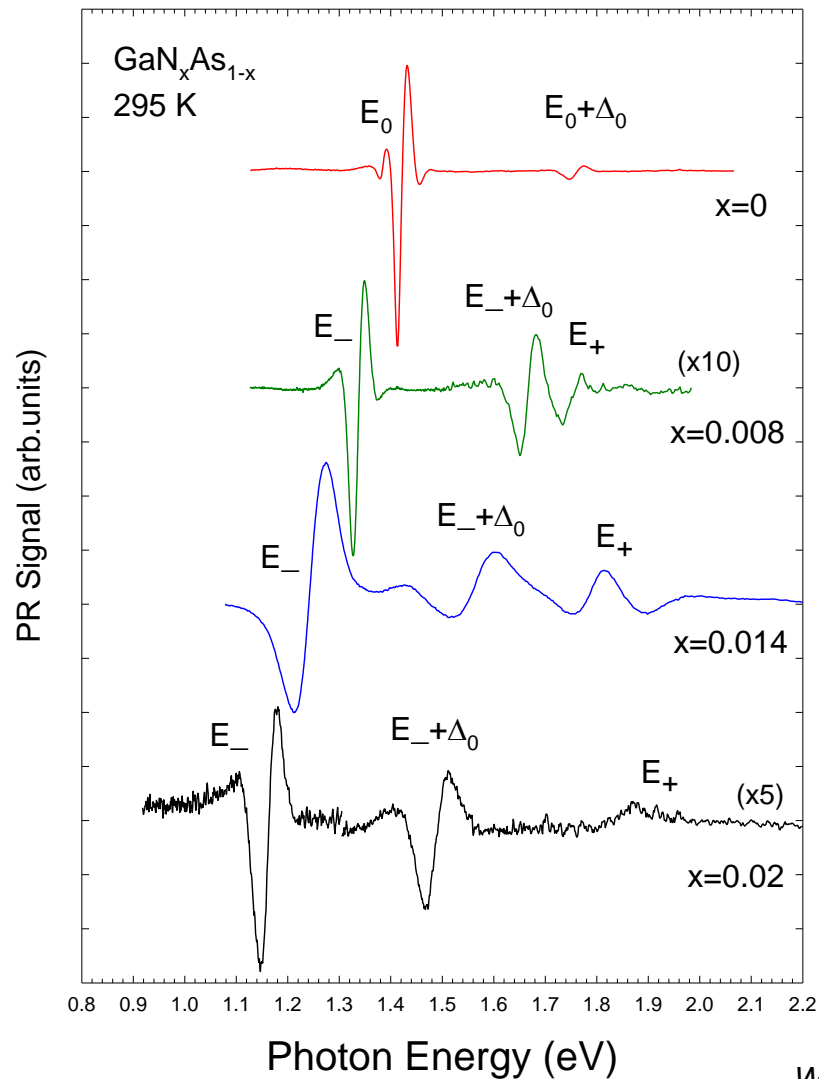
Room temperature on InGaAsN/GaAs quantum well

Kudrawiec, Wroclaw University of Technology, 2004.

A single quantum well of InGaAsN/GaAs

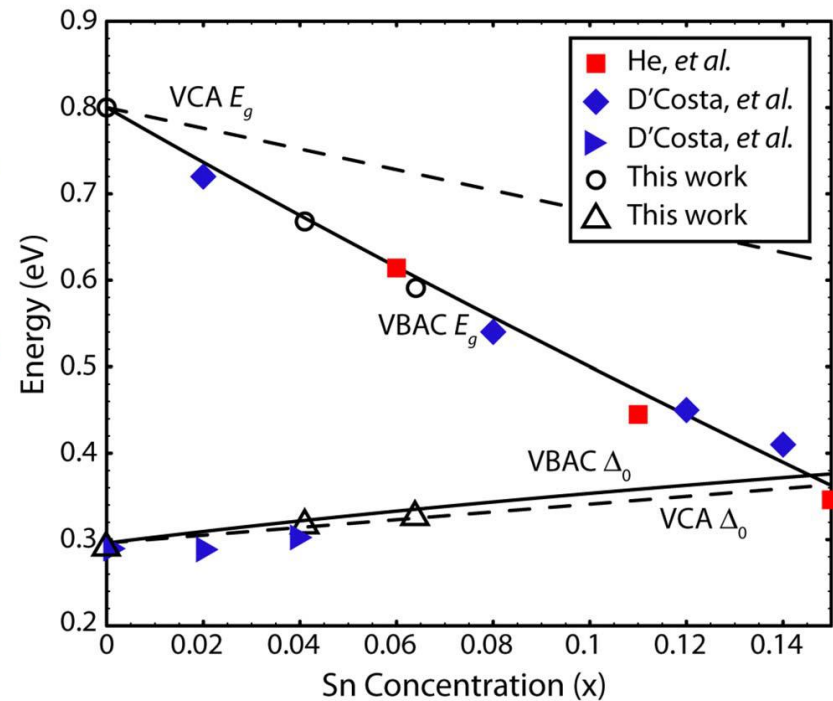
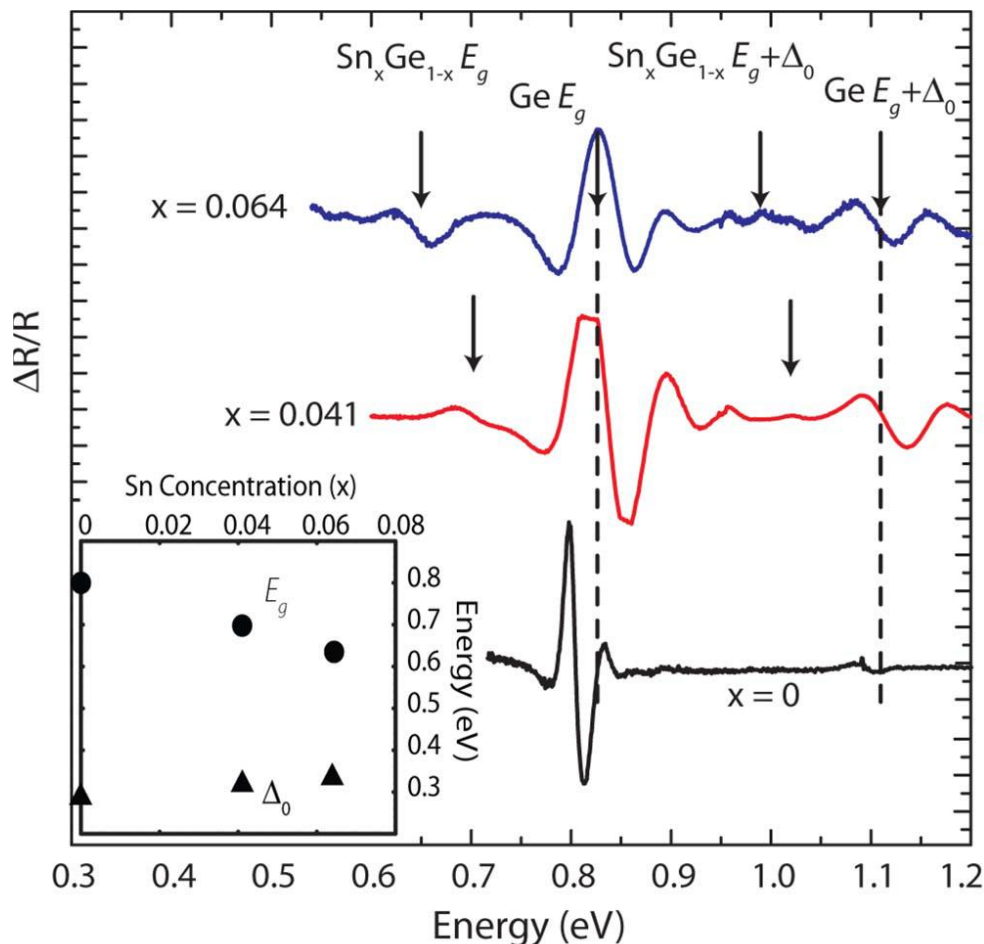
- The reflectivity spectrum ( $R$ ) exhibits only a very weak feature related to the bulk-like part of the structure (GaAs) at energy of 1.42 eV (GaAs band gap energy).
- Photoluminescence spectrum (PL) clearly indicates the energy of the ground state transition of the system (transition between first electron and first heavy hole levels in the quantum well) at the energy 0.93 eV.
- Photoreflectance spectrum  $\Delta R/R$ , has a more complex structure –all the critical transitions are observable both present the previously observed transitions (ground state and excited states in the quantum well).

# PR: $\text{GaN}_x\text{As}_{1-x}$



W. Walukiewicz et al., in *Dilute Nitride Semiconductors*, edited by M. Henini (Elsevier, Oxford, UK, 2005) Chapter 10, p. 325-392.

# PR: $\text{Sn}_x\text{Ge}_{1-x}$ grown on Ge



Alberi et al., Phys. Rev. B 77, 073202 (2008).

Alloying Sn in Ge results in restructuring of the valence band, giving rise to a strong decrease of the direct gap of the alloy