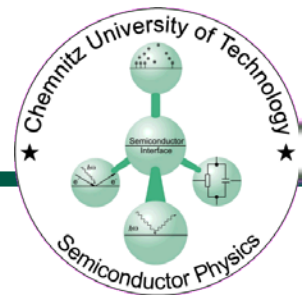




Photoemission spectroscopies

Inverse photoemission spectroscopies

Ellipsometry



MATTER \rightleftharpoons Radiation

Particle

Alpha, Beta (electrons), Neutrons, etc

Collisions elastic/ inelastic

Electromagnetic

Radio...IR, Visible, UV, X-Rays, gamma rays

Compton, photoelectric, pair production effects,
diffraction/refraction/reflection/scattering, polarization

Sample: solid, liquid, gas, plasma

Spectroscopy: Macro, micro , nano
depending on size of the samples

Nuclear

Nuclear emissions of unstable
nucleus
Alpha, Beta, Gamma, Neutrons, etc..

Atomic

Atomic transitions of electrons
IR-X-ray, Gamma rays & Auger
electrons

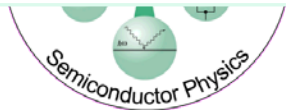
Molecular

Molecular vibrations
rotations
Visible, UV, IR

Structural

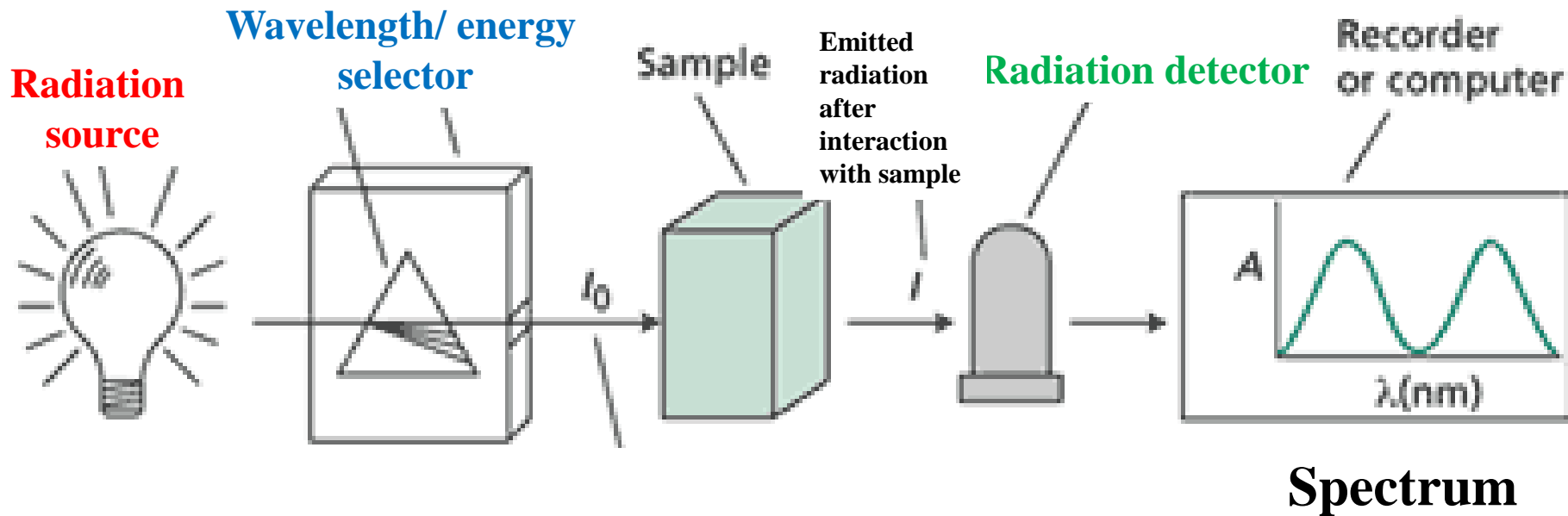
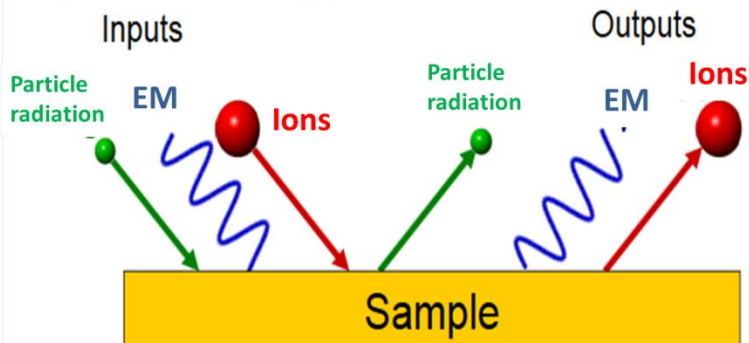
Crystal structure and
Crystal vibrations
rotations
Visible, UV, IR

Semiconductor Physics / Micro and Nano





Spectroscopy



Photoemission spectroscopies or **Photoelectron spectroscopies** refers to energy measurement of electrons emitted from solids, gases or liquids by the **photoelectric effect**, in order to determine the binding energies of electrons in a substance.

The term refers to various techniques, depending on whether the ionization energy is provided by an X-ray photon, EUV photon, or UV photon.

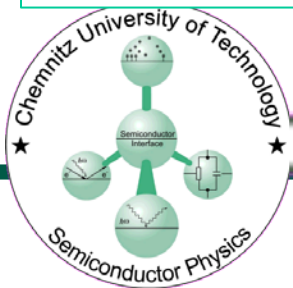
- XPS (ESCA)
- UPS
- 2PPE
- EUPS
- ARPES: Angle-resolved photoemission spectroscopy
- **IPS: Inverse Photoemission**
- **EELS**

The physics behind the PES technique:

The sample is exposed to a beam of **UV** or **XUV** light inducing **photoelectric ionization (photoelectric effect)**.

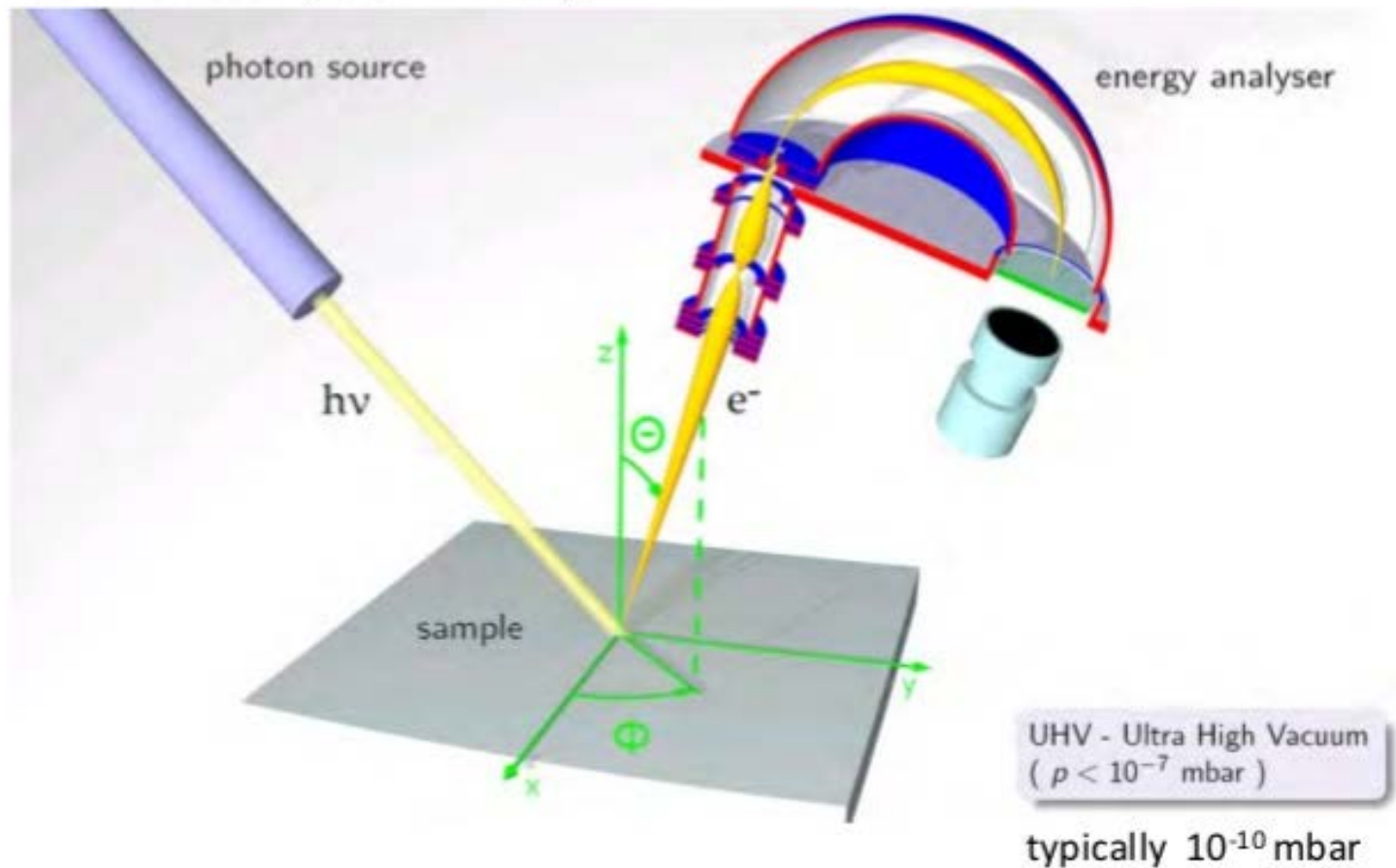
The energies of the emitted photoelectrons are characteristic of their **original electronic states**, and depend also on **vibrational state** and **rotational level**.

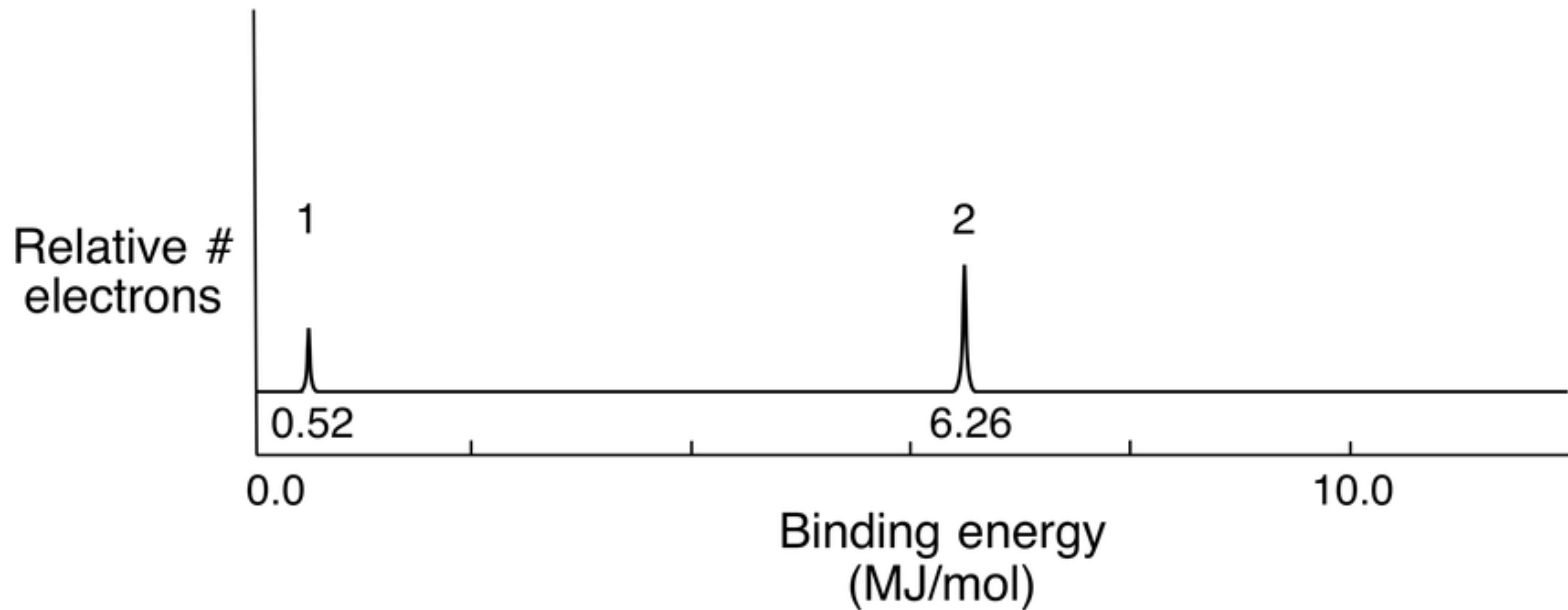
For solids, photoelectrons can escape only from a depth on the order of nanometers, so that it is the **surface layer which is analyzed**.



- rare gas discharge lamp (<40.2 eV)
- x-ray tube (1.256 and 1.486 keV)
- synchrotron radiation (10 eV ... 10 keV)

- hemispherical analyzer
- time of flight (TOF) analyzer





- The photoelectrons are collected, energy resolved, which results in a spectrum of electron intensity as a function of the measured kinetic energy.
- Because **binding energy values** are more readily applied and understood, the kinetic energy values, which are source dependent, are converted into binding energy values, which are source independent. Conversion performed using,

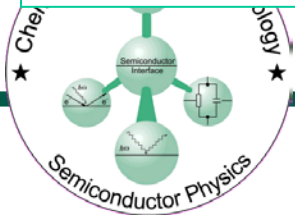
Einstein's relation:

$$E_k = h\nu - E_B$$

XPS = X-ray photoelectron spectroscopy was developed to study the energy levels of atomic core electrons, primarily in solids.

Originally also called **ESCA**: electron spectroscopy for chemical analysis because the core levels have small chemical shifts depending on the chemical environment of the atom that is ionized, allowing chemical structure to be determined.

Other names for this technique – **PESIS** & **PESOS**: photoelectron spectroscopy for inner/outer shells.



Ultraviolet photoelectron spectroscopy – **UPS** - is used to study **valence energy levels** and **chemical bonding**, especially the bonding character of molecular orbitals. The method was developed originally for gas-phase molecules. The technique was modified to use a UV laser to excite the sample, in order to measure the **binding energy of electrons**.

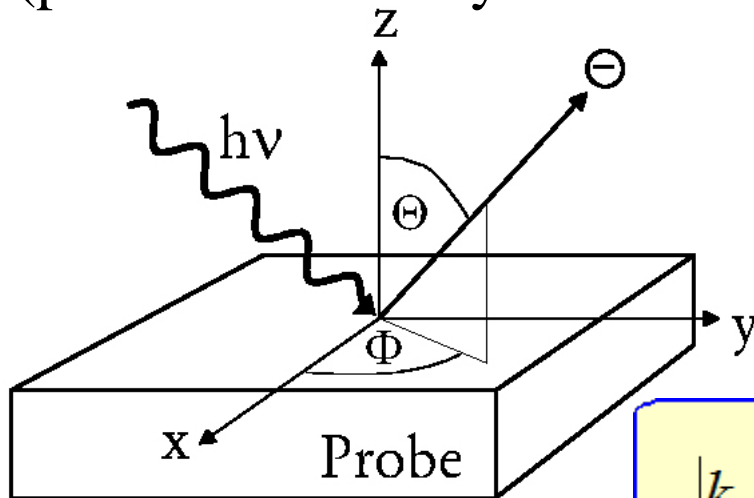
Two-photon photoelectron spectroscopy - **2PPE** - extends the UPS technique to **optically excited electronic states** through the introduction of a pump-and-probe scheme.

Extreme-ultraviolet photoelectron spectroscopy - **EUPS** - lies in between XPS and UPS. It is typically used to assess the **valence band structure**. Compared to XPS, it gives better energy resolution, and compared to UPS, the ejected electrons are faster.

- Delivers: number of electrons vs. KE (and BE)
- Direct measurement of density of occupied states $N(E)$
- Intensity of the bands in PES spectra depend on the cross-section of the atomic orbitals which contribute to the probed band and on (polarization) selection rules.

Angle Resolved (Valence Band) Photoemission (ARPES)

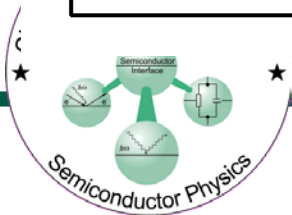
(probes the density of states (DOS))



➡ Single crystals

➡ Angle dependent detection of electrons → band dispersion

$$|k_{\parallel}| = \frac{\sqrt{2mE_{kin}}}{\hbar} \sin \theta = 0.512 \sqrt{E_{kin} (eV)} \sin \theta$$



Inverse photoemission spectroscopies are techniques used to study the unoccupied electronic structure of surfaces, thin films, and adsorbates.

Due to the low energy of the incident electrons, their penetration depth is only a few atomic layers, making inverse photoemission a particularly surface sensitive technique.

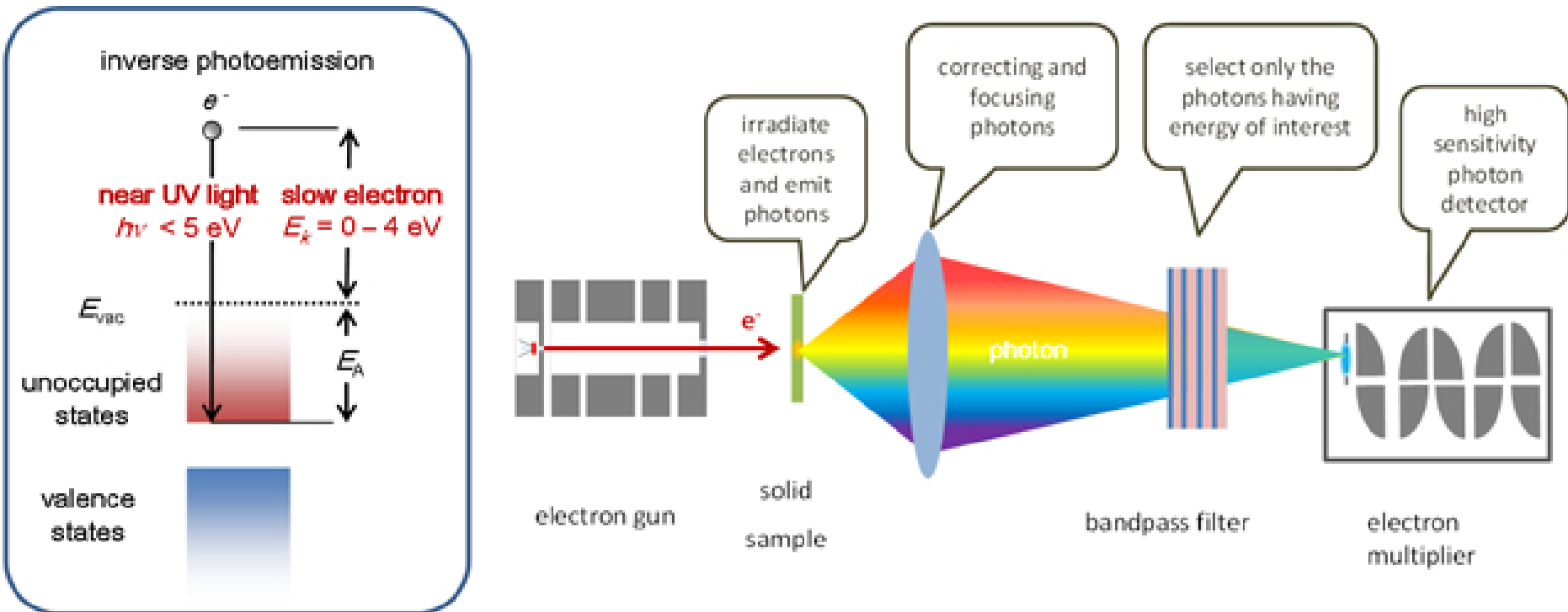
As inverse photoemission **probes the electronic states above the Fermi level of the system**, it is a complementary technique to photoemission spectroscopy.

A well-collimated **beam of electrons** of a well defined energy.

These electrons **couple to high-lying unoccupied electronic states and decay to low-lying unoccupied states**, with a subset of these transitions being radiative.

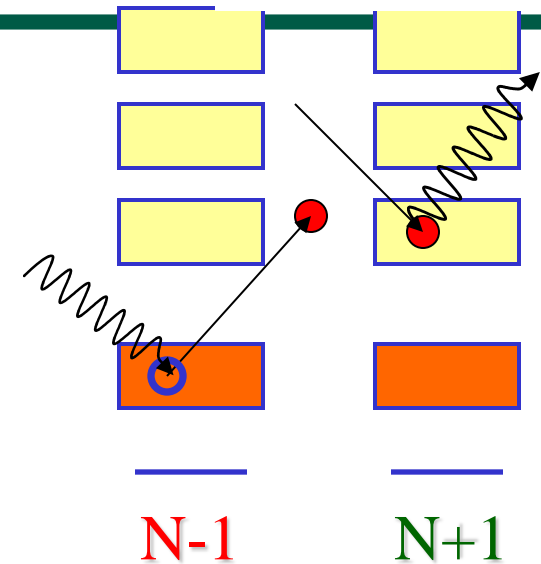
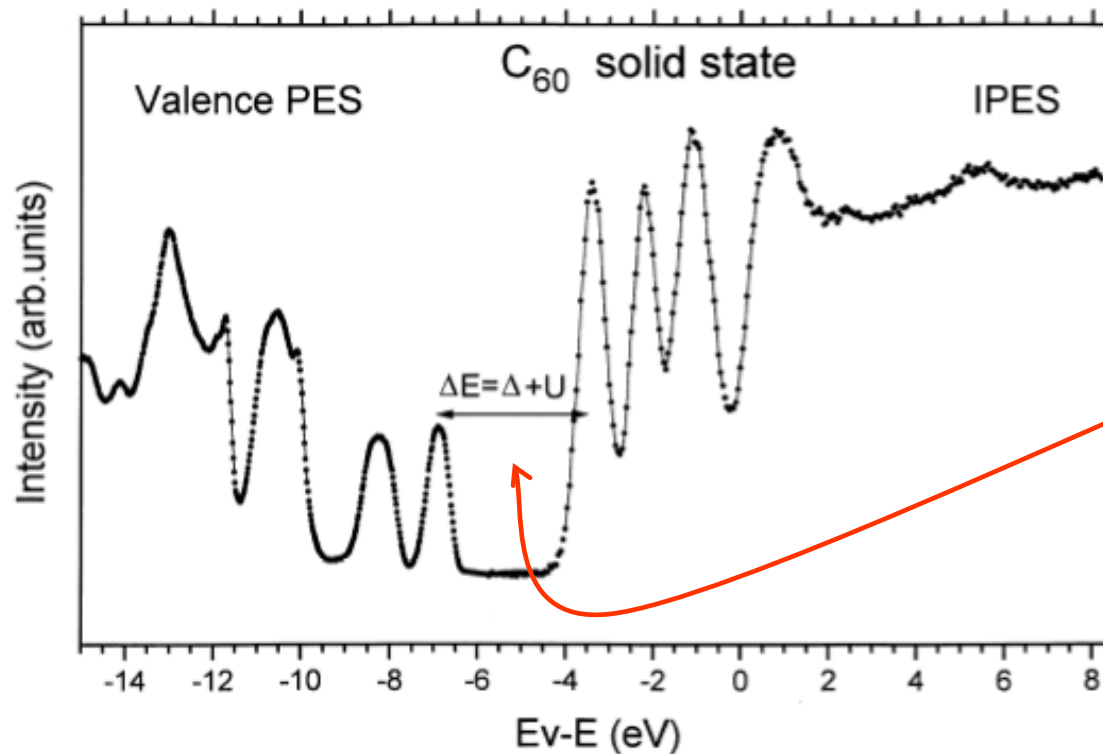
The photons emitted in the decay process are detected and an **energy spectrum, photon counts vs. incident electron energy**, is generated.

Principle of Operation



combination PES + IPES is powerful

- 1) metals
- 2) systems with gaps



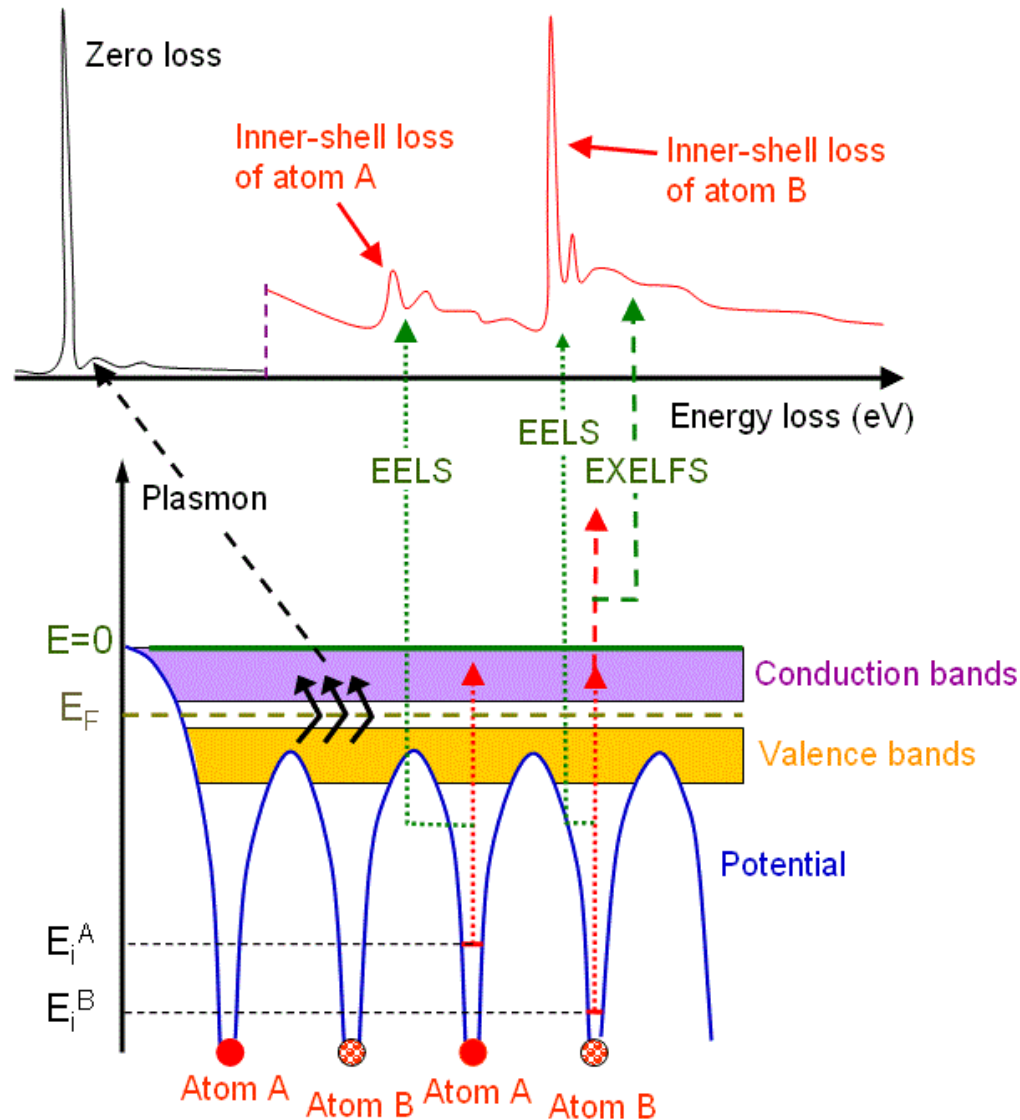
transport gap

.....cf. excitons
discussed later

EELS - Electron Energy loss Spectroscopy

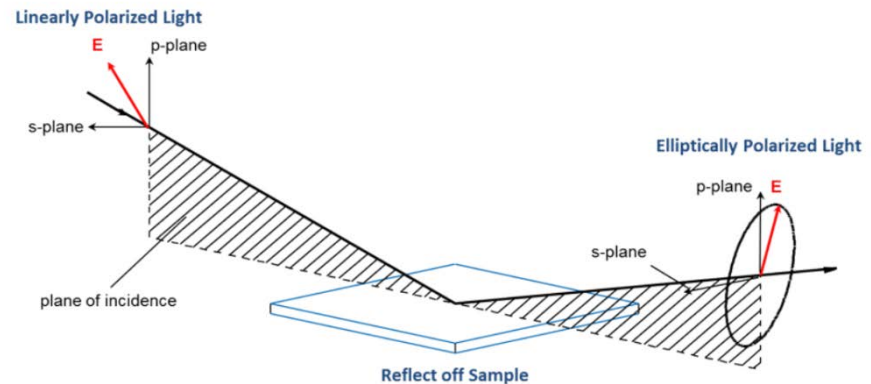
- the material is exposed to a **beam of electrons** with a known, narrow range of kinetic energies.
- Some of the electrons will undergo **inelastic scattering**, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be **measured via an electron spectrometer and interpreted in terms of what caused the energy loss**.
- Inelastic interactions: phonon excitations, inter- and intra-band transitions, plasmon excitations, inner shell ionizations, and Cherenkov radiation.

EELS spectra



Ellipsometry

- measures the change in polarization as light reflects or transmits from a material structure.
- The polarization change is represented as an **amplitude ratio, Ψ** , and the **phase difference, Δ** .



- The measured response depends on optical properties and thickness of individual materials.

Ellipsometry is primarily used to determine film thickness and **optical constants**. However, it is also applied to characterize **composition**, **crystallinity**, **roughness**, **doping concentration**, and other material properties associated with a change in optical response.

Two values are used to describe the optical properties which determine how light interacts with a material. They are generally represented as a complex number.

$$\tilde{n} = n + ik$$

The **complex refractive index** consists of the index (n) and extinction coefficient (k).

Alternatively, the optical properties can be represented as the **complex dielectric function**:

$$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$$

With the following relation between conventions: $\tilde{\epsilon} = \tilde{n}^2$

The index describes the phase velocity of light as it travels in a material compared to the speed of light in vacuum, c:

$$v = \frac{c}{n}$$

Light slows down as it enters a material with higher index. Because the **frequency of light waves remains constant**, the **wavelength will shorten**.

The **extinction coefficient** describes the loss of wave energy to the material. It is **related to the absorption coefficient**:

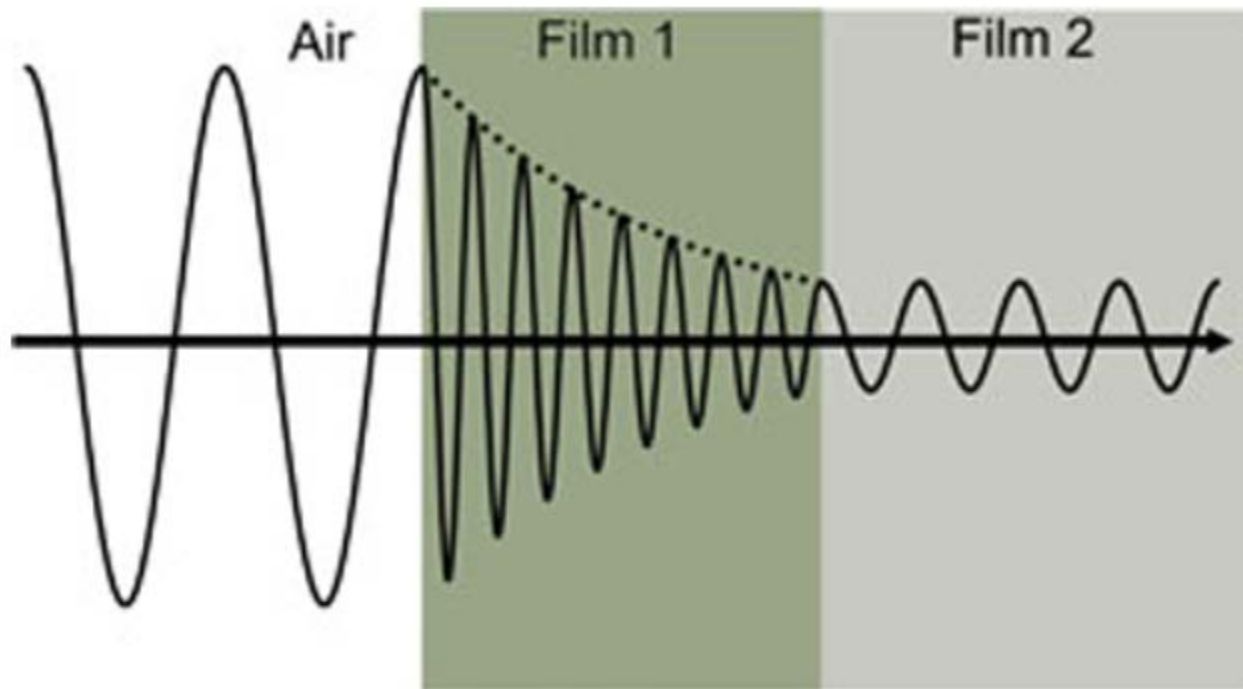
$$\alpha = \frac{4\pi k}{\lambda}$$

Light loses intensity in an absorbing material according to **Beer-Lambert Law**:

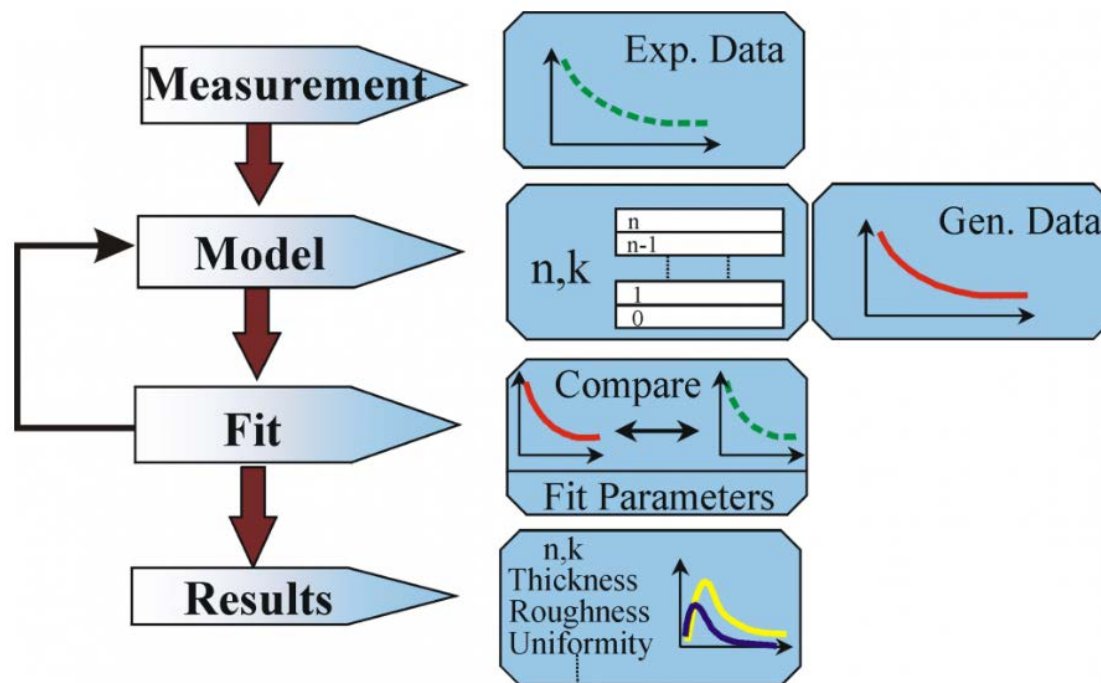
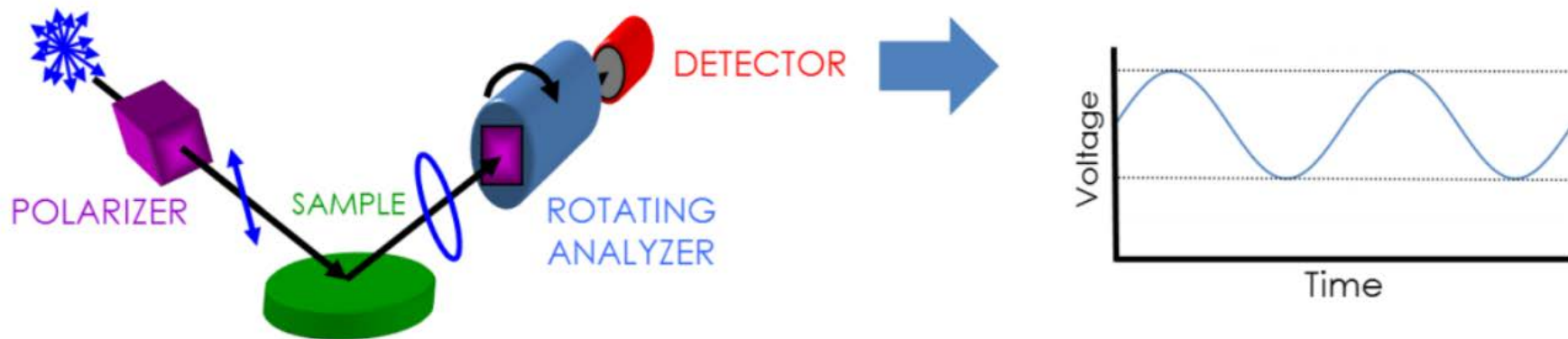
$$I(x) = I_0 e^{-\alpha x}$$

Thus, the **extinction coefficient** relates to **how quickly light vanishes in a material**.

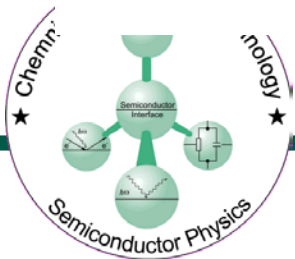
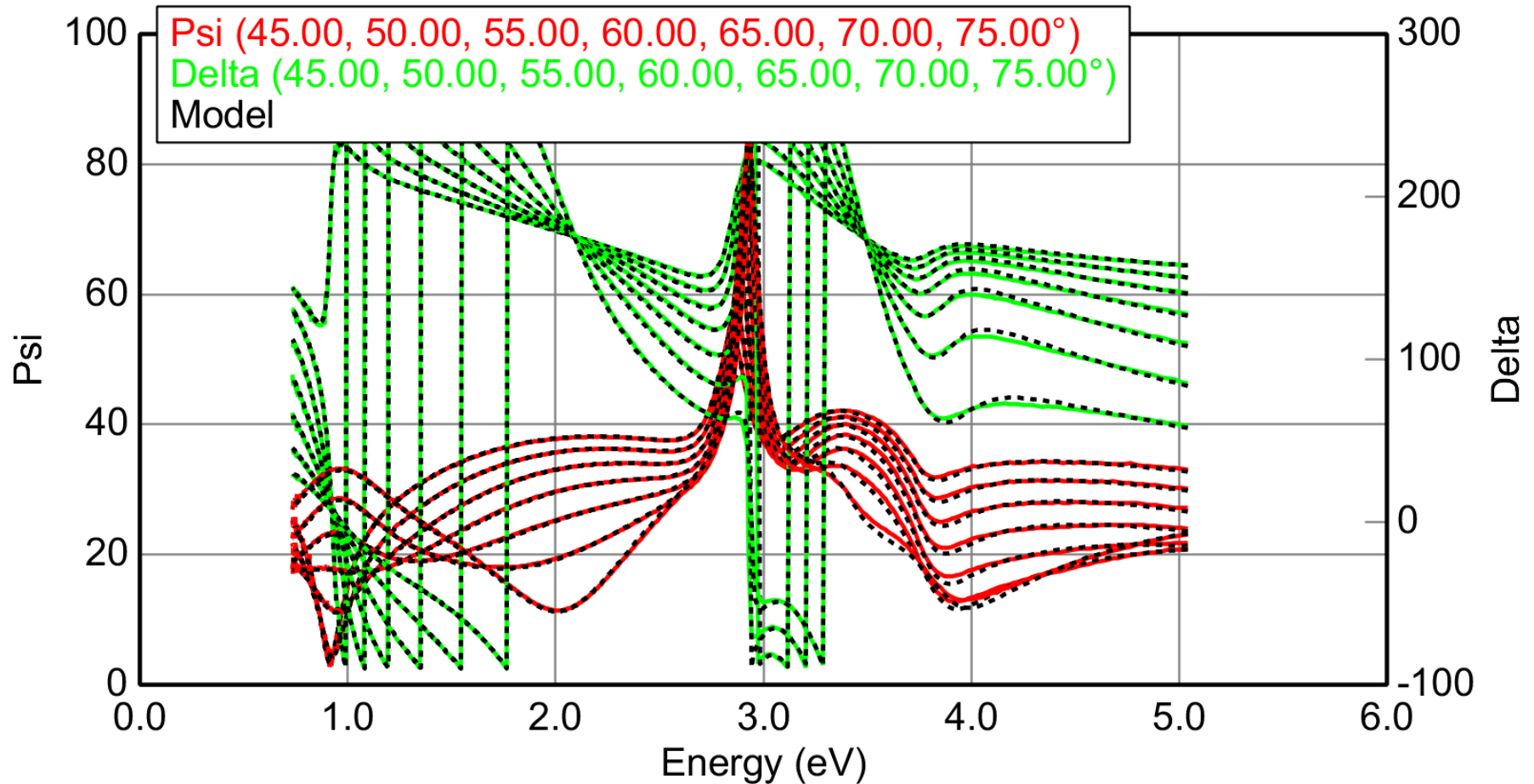
These concepts are demonstrated in the figure where a light wave travels through two different materials of varying properties before returning to Air.



Wave travels from air into absorbing Film 1 and then transparent Film 2. The phase velocity and wavelength change in each material depending on index of refraction (Film 1: $n=4$, Film 2: $n=2$).

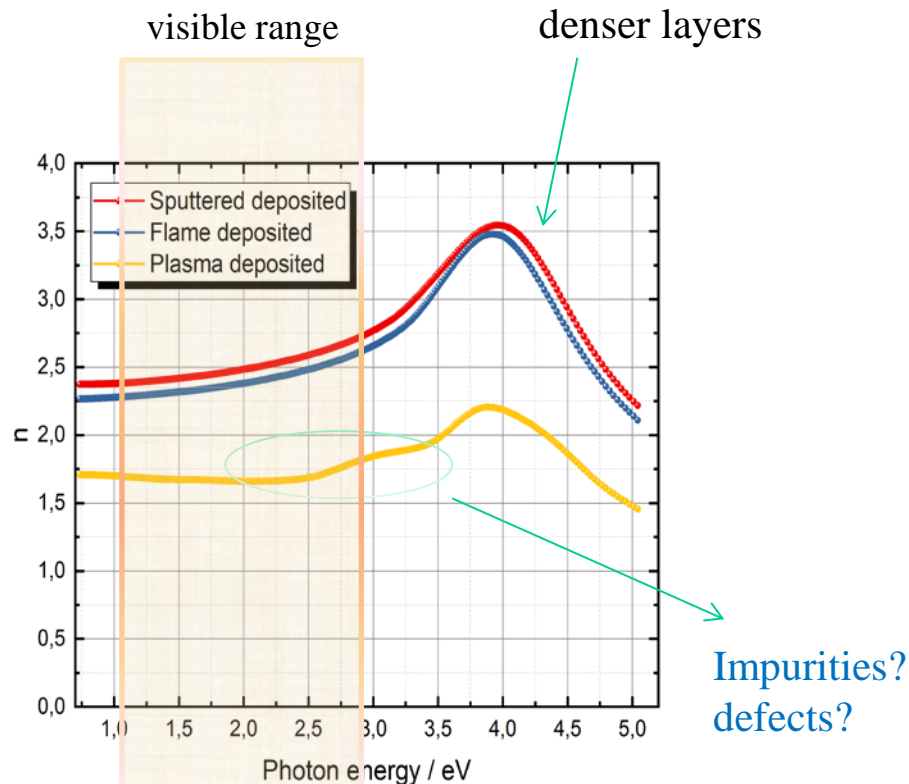


Variable Angle Spectroscopic Ellipsometric (VASE) Data



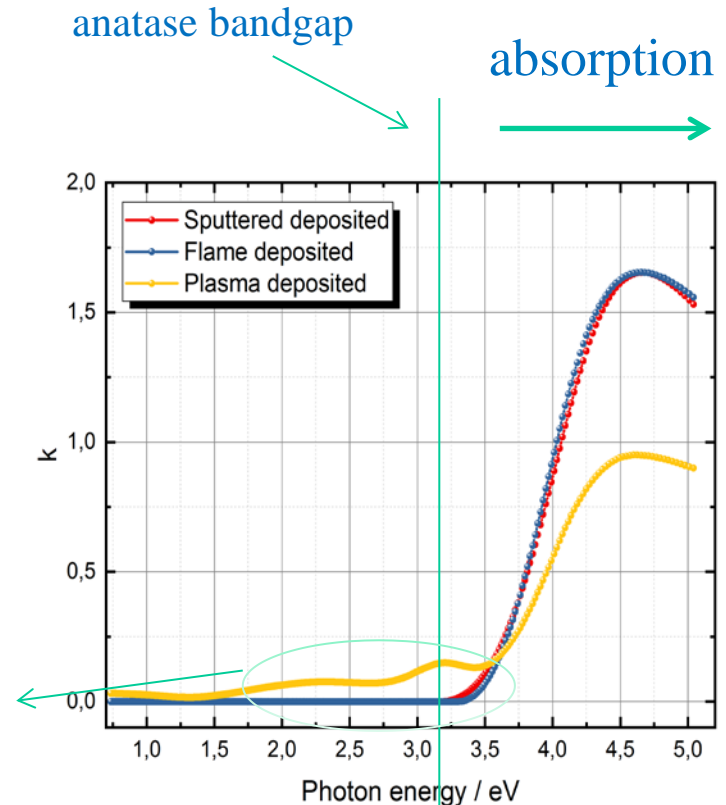


Determination of n



Comparison of refractive index (n) of TiO_2 deposited with three different deposition technique.

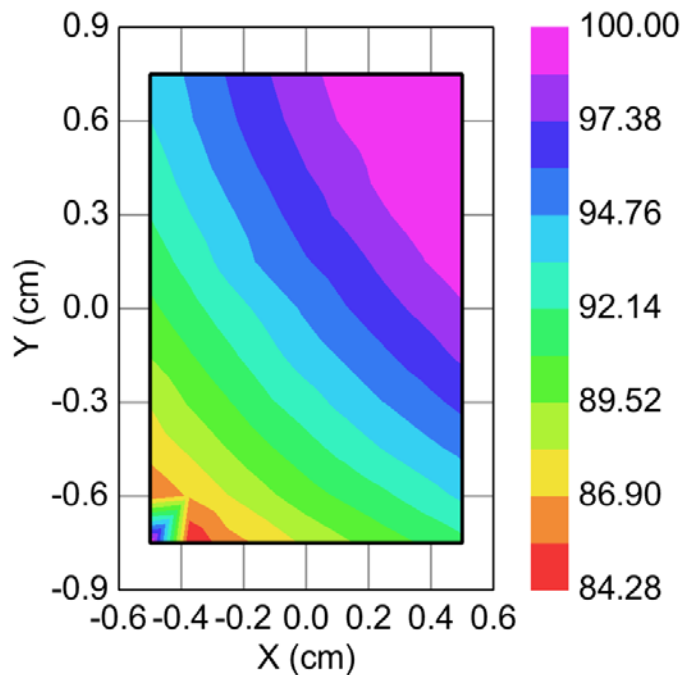
Determination of k



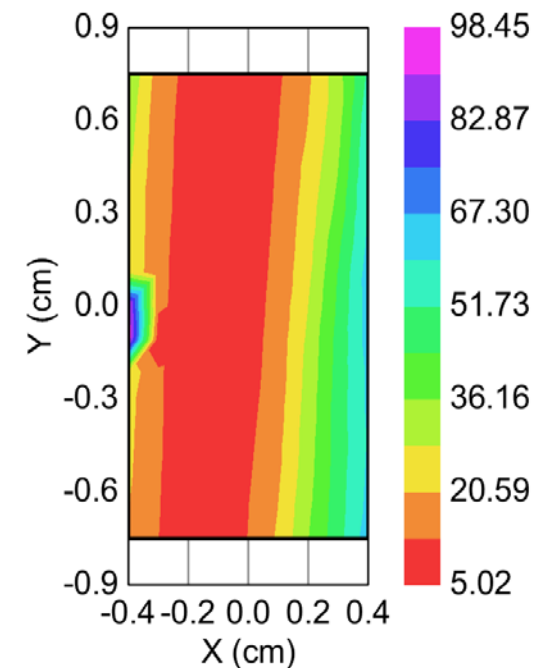
Comparison of extinction coefficient (k) of TiO_2 deposited with three different deposition techniques.



Sputter deposition



Flame deposition



Next Lecture

The Nanoworld

From Micro to Nanospectroscopy

Surfaces and Heterostructures

