

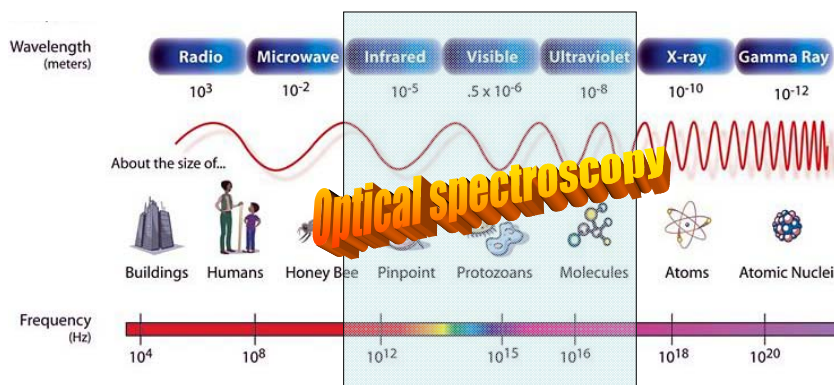


Optical Characterisation Techniques

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Where is our "playground"?



Ref: www.wikipedia.org



- Light interaction with matter can result in:
 - Absorption
 - Reflectance
 - Change in polarization
 - Inelastic scattering
- The optical spectroscopic techniques make use of light interaction with matter:
 - UV-VIS-NIR spectrophotometry, Spectroscopic ellipsometry, Fourier Transform Infrared (FTIR), Raman



Optical Spectrophotometry

- How spectrophotometry work?
- Instrumentation
- What we measure?
- Practical guide for optical spectrophotometry



Optical Spectrophotometry: *UV-VIS-NIR- 175nm-3300nm*

- *One of the oldest techniques known*
- Typical samples:
 - Bulk samples:
 - Solids
 - Liquids
 - Powders
 - Thin films
 - Optical coatings
 - Transparent conductive oxides
 - Semiconductors, Dielectrics
- Nanomaterials: information on electronic property of tubes (metallic, semiconductive)
- Many industrial applications
 - Pharmaceutical and food industry (e.g.drugs)
 - Cosmetics and Sun Protection Products
 - Flat Panel Displays, Optical Component Measurements, Fiber Optic Filters
 - Inks, Dyes, Pigments, Paints
 - Architectural Glass Coatings and Compounds

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- Optical Spectrophotometry involves the use of a spectrophotometer.
- A spectrophotometer is a **photometer** (a device for measuring light intensity) who measure intensity as a function of the wavelength of light
- The spectrophotometer measures quantitatively the fraction of light that passes through or is reflected by a sample
- Measurable quantities are expressed in terms of:
 - Percent transmission (%T)
 - Percent reflectance (%R)

Note:

- *Measurable quantities (%T and %R) are reported to some references*
- Measurements are in general simple to do and straightforward

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OPTICAL SPECTROPHOTOMETRY

Most common information obtained:

- » *Transparency (direct measurement)*
- » *Reflectivity (direct measurement)*
- » *Chemical composition or intermixing*
- » *Color*
- » *Thin film thickness*
- » *Optical constants*
- » *Optical band gap and interband transitions*

Require building an optical model.



- Measurement strategy: air/thin film/substrate/air - Two configuration available, *T* and *R*



NOTE:

- *T* and *R* are complex function: $T(\lambda, n_s, k_s, n_f, k_f, d_f)$, $R(\lambda, n_s, k_s, n_f, k_f, d_f)$
- no direct inversion *T* and *R* possible to obtain n_f , k_f and d_f for you thin film
- do not forget that for oblique incidence $T/R (>10^\circ)$ **inherent instrument polarisation** kick-in



Practical guide for optical spectrophotometry:

Optical constants determination

- Optical constants are expressed as a complex dielectric function, $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$
or as complex refractive index $\tilde{n} = n + ik$
- Simultaneous determination of the refractive index, n and absorption coefficient, k , for a thin film, require minimum two set of data, T and R
- A brief reminder...
 - ✓ Achieving highly accurate R measurements is not really straightforward
 - ✓ Absorption coefficient, k is the most sensitive to experimental errors

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Spectroscopic ellipsometry

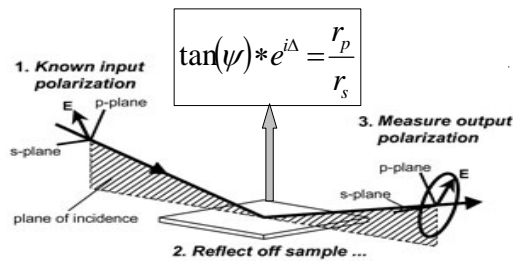
- Applications
- What information can be provided?
- How the ellipsometry work?
- Creating an optical model that describe your sample
- Fitting procedure

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What is ellipsometry?

- Ellipsometry measure the change in polarization of light reflected from sample
- Uses the p-(parallel) and s-(perpendicular) coordinate system, relative to the sample plane of incidence
- Ratio of p/s reflectivity is quantified by Ψ and Δ parameters



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Ellipsometric advantages

- Repeatabile and Accurate
 - Self-referencing (single-beam experiment) measure the ratio of orthogonal components E_p/E_s
 - Reduced problems with light source fluctuation
- Sensitive
 - phase term Δ is very sensitive to film thickness
- Measure two parameters
 - more information are available

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What are the ellipsometry applications?

- Thin films (ranging from monolayers to micron thick films):
 - *Semiconductors*
 - *Metals*
 - *Dielectrics*
 - *Polymers, organic films*
- Bulk materials
- *Note: Optical spectrophotometry can be more useful in the case of microns-thick thin films*

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What parameter can be determined by SE ?

- *Optical constants*
- *Thickness*
- *Optical band gap and interband transitions*
- *Surface or interfacial roughness*
- *Chemical composition or intermixing*
- *Crystallinity (polymorphs identification)*
- *Micro-porosity*
- *Anisotropy or birefringence*

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Optical spectroscopy myths

- Contrary to most advertising there is no optical experiment which directly measure layer thicknesses or optical constants, or any other useful structural or optical parameter of a sample.

• *This apply also to ellipsometry !*



Data analysis

- For bulk material the equations derived for a single reflection can be directly inverted to provide the “pseudo” optical constants from the ellipsometry measurement, ρ :

$$\langle \varepsilon \rangle = \sin^2(\varphi) \left[1 + \tan^2(\varphi) \left(\frac{1-\rho}{1+\rho} \right) \right]$$

- *Note: it not take into account any surface layer (roughness, superficial oxide etc)*
- When we need to include these effects or when we are dealing with thin films is not possible to achieve a direct inversion of ellipsometric equation:

$$\rho = \frac{r_p}{r_s} = \tan(\psi) * e^{i\Delta}$$

- *We need to do a more complex data analysis...*

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Ellipsometric data analysis: building a model

Substrate [$n_0(\lambda), k_0(\lambda)$]

↓

Thin film [$d=?$, $n_1(\lambda)=?$, $k_1(\lambda)=?$]

Substrate [$n_0(\lambda), k_0(\lambda)$]

↓

Surface roughness [$d_2=?$, $n_2(\lambda)=?$, $k_2(\lambda)=?$]

Thin film [$d_1=?$, $n_1(\lambda)=?$, $k_1(\lambda)=?$]

Substrate [$n_0(\lambda), k_0(\lambda)$]

Use know optical constants tabulated from literature/databases

NEVER extrapolate optical constants/dispersion laws beyond their reported spectral range

Use tabulated data or dispersion law , (e.g.Cauchy, Sellmeier, Tauc Lorentz....)

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A good fit can be misleading...

“...fitting of parameters is not the end-all of parameter estimation. To be genuinely useful, a fitting procedure should provide (i) parameters, (ii) error estimates on the parameters, and (iii) a statistical measure of goodness-of-fit. When the third item suggests that the model is an unlikely match to the data, then items (i) and (ii) are probably worthless. Unfortunately, many practitioners of parameter estimation never proceed beyond item (i). They deem a fit acceptable if a graph of data and model “looks good.” This approach is known as *chi-by-eye*. Luckily, its practitioners get what they deserve.”

W. H. Press , S. A. Teukolsky , W. T. Vetterling, B. P. Flannery and M. Metcalf,
Numerical Recipes (2nd ed. Cambridge, 1992), Ch.15, pg.650

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Infrared spectroscopy

A molecule may absorb infrared radiation of the appropriate frequency to excite it from one vibrational or rotational level to another.

When a beam of infrared energy, covering a broad frequency range, passes through a sample, the energy at certain frequencies is absorbed by the sample. The spectrum is characteristic of the particular molecule and its molecular motions.

In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the permanent dipole.

For small molecules, bond lengths and angles can be determined from infrared spectra. For large molecules, the pattern of absorbances in the spectrum is characteristic of the functional groups in the molecule. The spectrum can be thought of as "fingerprint" of that chemical species, and therefore, infrared spectroscopy can be used to identify molecules (i.e., qualitative analysis).

Region	Range (cm ⁻¹)	Range (μm)
Near-infrared	13300 - 4000	0.75 - 2.5
Mid-infrared	4000 - 400	2.5 - 25
Far-infrared	400 - 10	25 - 100

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Fourier Transform Infrared spectroscopy

Powerful techniques for organic and inorganic chemistry

Versatile technique allowing measurements of sample in any form, gas, powders, liquid and thin film

Highly sensitive down to monolayer level

Depending on the sample presentation measurements can be done:

- Transmission
- Reflection
- Attenuated Total Reflection (ATR)
- Diffuse reflection

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Raman spectroscopy

Raman spectroscopy is a light scattering technique, and can be thought of in its simplest form as a process where a photon of light interacts with a sample to produce scattered radiation of different wavelengths.

Raman spectroscopy relies on inelastic scattering, or Raman scattering of monochromatic light upon interaction with the sample.

The Raman lines at frequencies higher than that of the Rayleigh line are known as anti-Stokes lines, and those at lower frequencies are known as the Stokes lines. The frequency shifts of the Raman lines from the Rayleigh lines correspond to the vibrational energies associated with excited states (or levels) of the sample molecule.

A molecular polarizability change, or amount of deformation of the electron cloud, with respect to the vibrational coordinate is required for the molecule to exhibit the Raman effect. The amount of the polarizability change will determine the Raman scattering intensity, whereas the Raman shift is equal to the vibrational level that is involved.

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Raman spectroscopy

- Powerful techniques for organic and inorganic chemistry
- Versatile technique allowing measurements powders, liquids and thin film
- Sensitive down to monolayer level (e.g. Surface Enhanced Raman Spectroscopy, graphene)
- Complimentary to FTIR
- More easy to do mapping than in the case of FTIR, offer a more local information (spot size typically 1 micron compared with typically 1cm for FTIR)
- Highly sensitive to crystalline structure and stress (microelectronics)

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Thank you !

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