4. Experimental methods

4.3 Diffuse reflection

Last week: Mainly homogenous solutions

- Reminder on energy states, transitions
- Light absorption in solutions
- Measuring absorption spectra for solutions and (some) films, scattering

- Fluorescence, lifetimes and quantum yields
- Measuring fluorescence and quantum yields (lifetimes will be treated later)

Topics of this lecture:

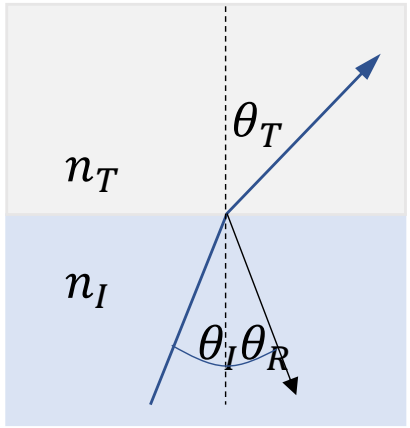
Opaque systems and powders

- Reminder on specular reflection
- Scattering media
- Absorption/reflection by scattering media
- Measuring absorption spectra for powders and (some) films

Thin films

- How to measure optical constants of films: ellipsometry
- Basic principles and experimental setup
- Ellipsometry versus conventional absorption measurements
- Data analysis

Specular vs. diffuse reflectance



- So far, we have treated absorption/reflection by non-continuous media
- Absorption/reflection by a specular (mirror-like) ***smooth*** surface

$$I_0 = I_R + I_A + I_T \qquad 1 = T + R + \mathcal{A} \qquad R = \frac{I_R}{I_0}$$

- Specular reflectance **<u>at small incidence angles</u>** for **<u>absorbing</u>** media:

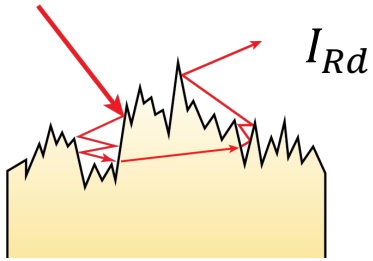
$$\mathrm{R} = |r_\perp|^2 = |r_\parallel|^2 = \frac{(n_{rel}-1)^2 + {k_{rel}}^2}{(n_{rel}+1)^2 + {k_{rel}}^2}$$

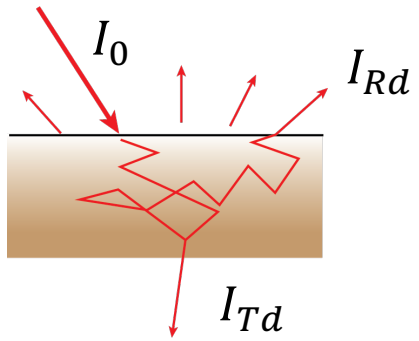
Relative refractive index: $\tilde{n}_{rel} = \frac{\tilde{n}_T}{n_I} = n_{rel} + ikr_{el}$ with $n_{rel} = \frac{n_T}{n_I}, k_{rel} = \frac{k_T}{n_I}$

However, if:

- Loss of surface smoothness
- Grains/scattering centers
- Decreasing particle size

→ Decrease in specular reflection
→ *Appearance of diffuse reflection*

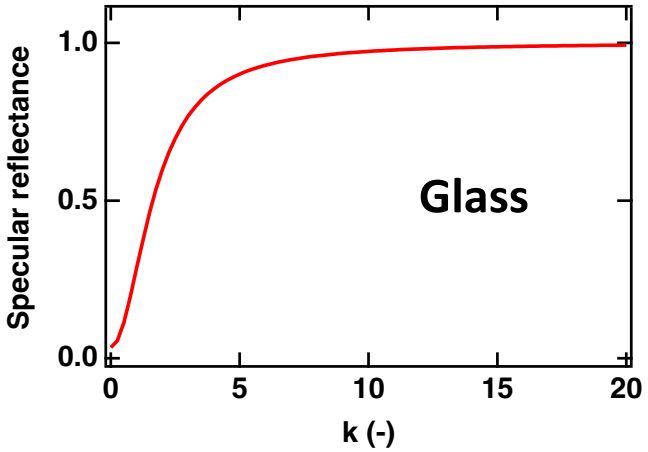


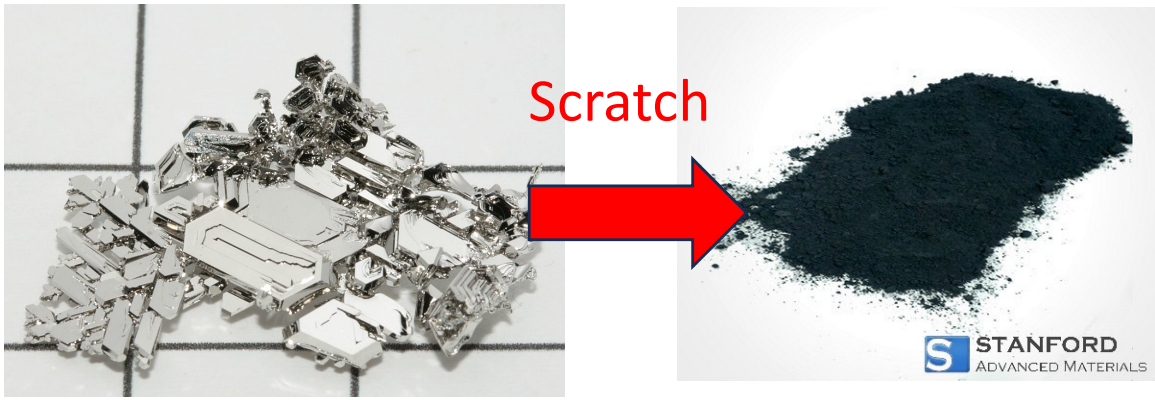


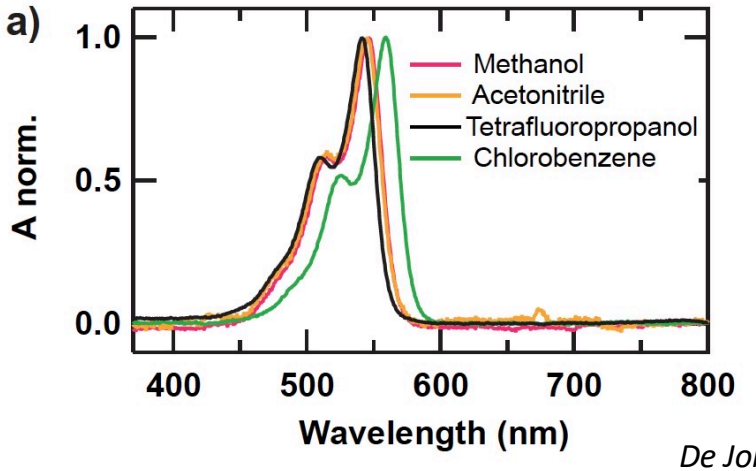
Reminder on Fresnel's law

Important consequence of Fresnel's law at planar interfaces:

Strong reflection in wavelength regions where the medium absorbs strongly ($k_{rel} \geq 1$)







De Jonghe, EPFL Thesis

But… What happens when there is no planar interface?

Scattering media

The color of powders will be dependent on the particle size…

Note: The chromophore concentration in the particles remains constant!

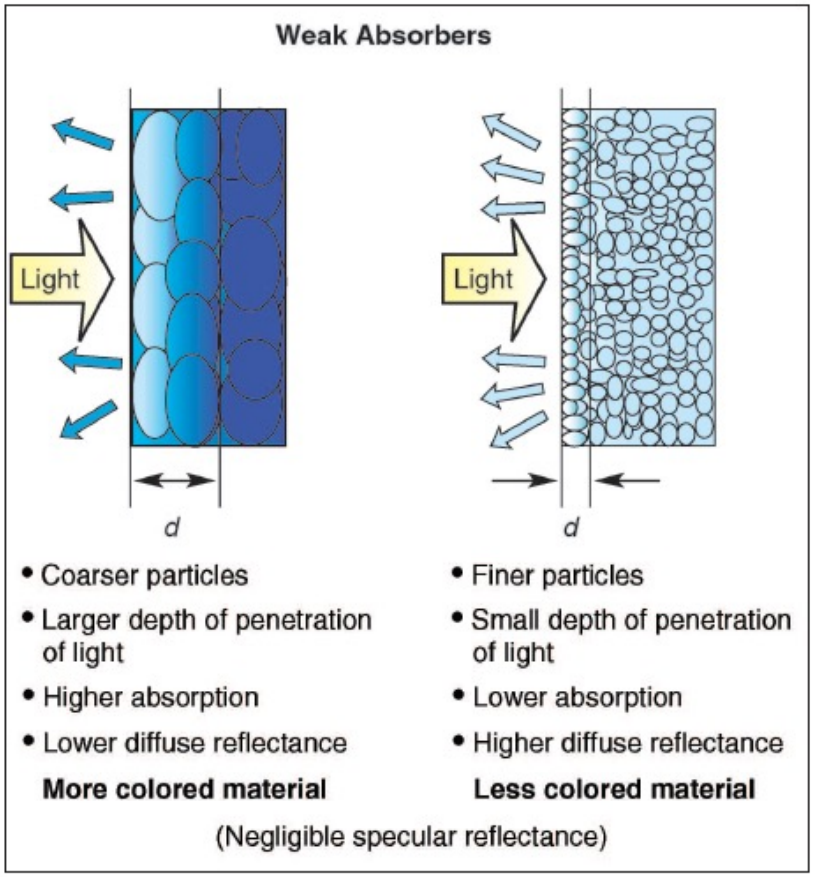
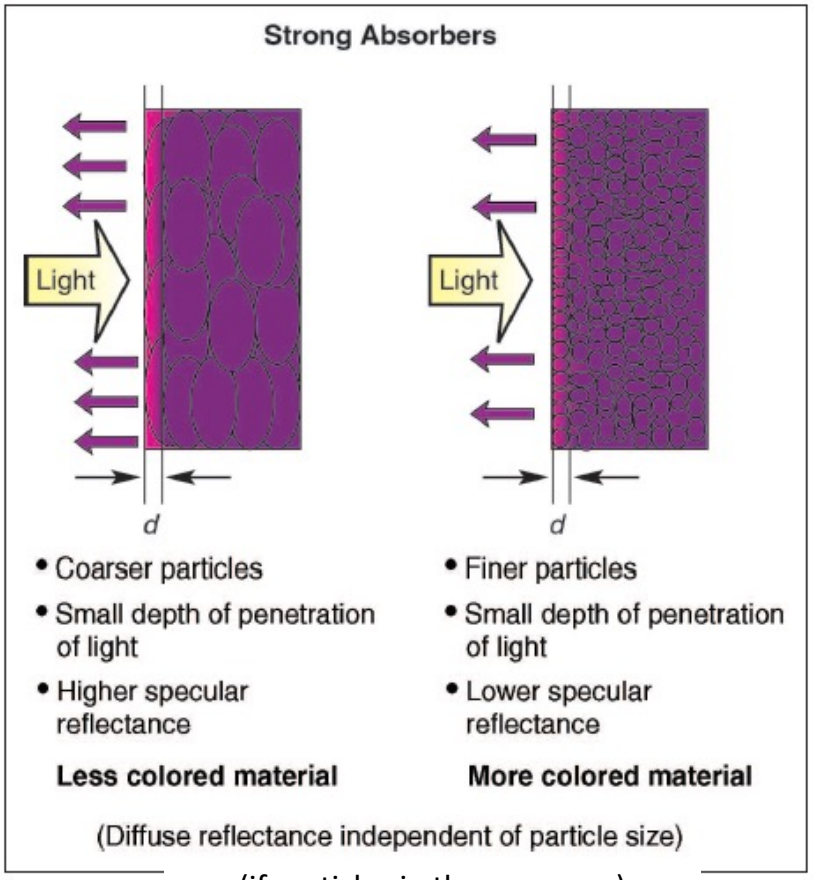


Figure 1. Pictorial description of the light penetration as a function of the particle size for a weak absorber. Light reflectance is primarily due to diffuse reflection.



(if particles in the um range)

Figure 2. Pictorial description of the light penetration as a function of the particle size for a strong absorber. Light reflectance is primarily due to specular reflection.

Scattering media

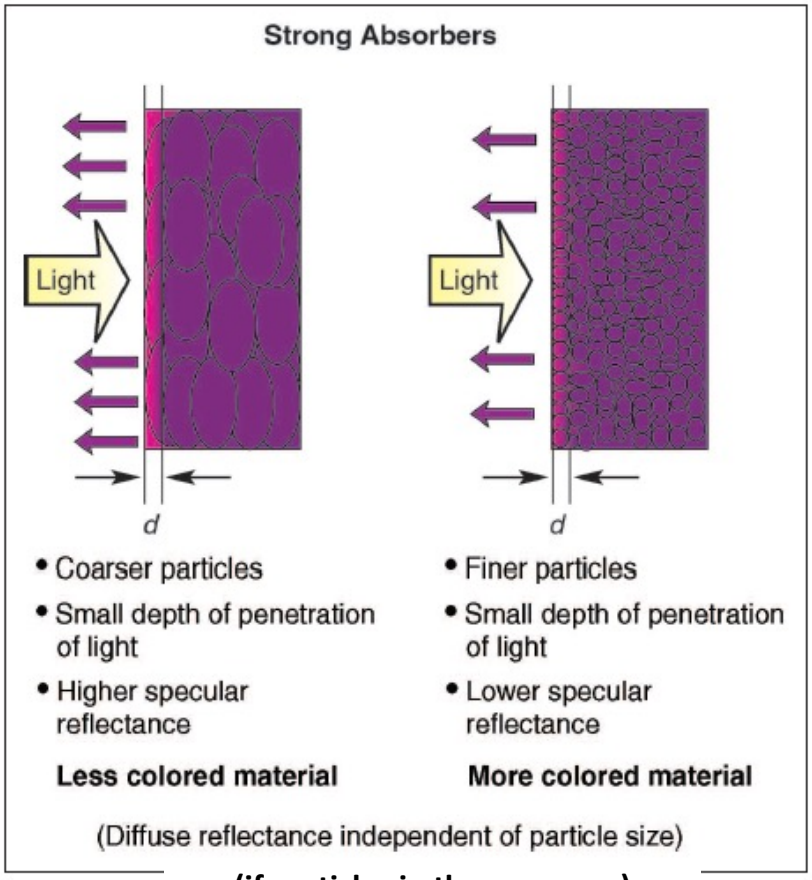
The color of powders will be dependent on the particle size…

Note: We assume the chromophore concentration in the particles remains constant.

Note: For very strong absorbers, the depth of penetration of light is so small that the R_d becomes almost independent of particle size

=

Changes in particle size for a strongly absorbing material do not result in significant changes in the depth penetrated by light, except if the particles are very small!

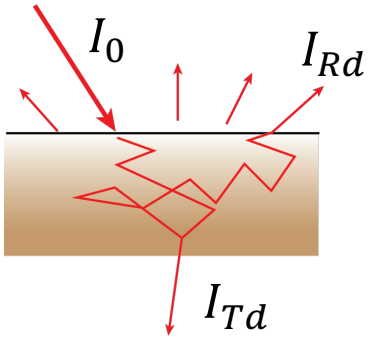


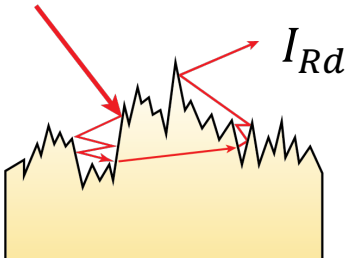
(if particles in the um range)

Figure 2. Pictorial description of the light penetration as a function of the particle size for a strong absorber. Light reflectance is primarily due to specular reflection.

Absorption/Reflection by scattering media: Schuster-Kubelka-Munk theory

$$I_0 = I_{Rd} + I_A + I_{Td}$$





$$-dI =$$

$$dJ =$$

Phenomenological extinction constants

$k_s\ [cm^{-1}]\ absorption$

s $[cm^{-1}]\ scattering$

$$k_{s,s\to 0} = -\frac{1}{dx} ln \frac{I}{I_0}$$

$$s_{k\to 0} = -\frac{1}{dx} ln \frac{I}{I_0}$$

Note: This theory does not take into account specular reflection, so it is only applicable to the diffuse part of light reflection!

Kubelka and Kubelka-Munk equations

$$R_d = \frac{1 - R_g(a - b \cdot \coth(b \cdot 2s \cdot l))}{a + b \cdot \coth(b \cdot 2s \cdot l) - R_g}$$

$$T_d = \frac{b}{a \cdot \sinh(b \cdot 2s \cdot l) + b\cosh(b \cdot 2s \cdot l)}$$

with

$$a = 1 + \frac{k_s}{s}$$

$$b = \sqrt{a^2} - 1$$

$$R_g = background\ reflectance$$

Kubelka-Munk simplified equation, material completely opaque (= neglect T_d):

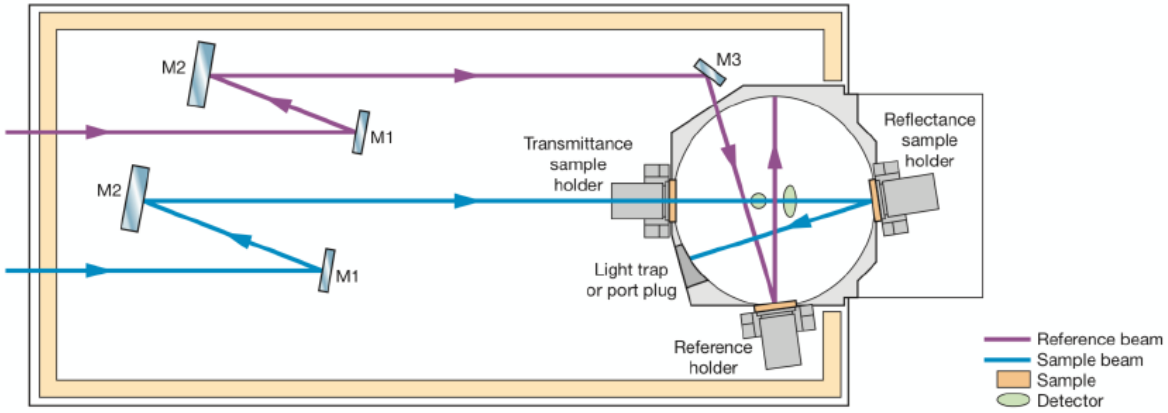
$$l \to \infty \qquad F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k_s}{s}$$

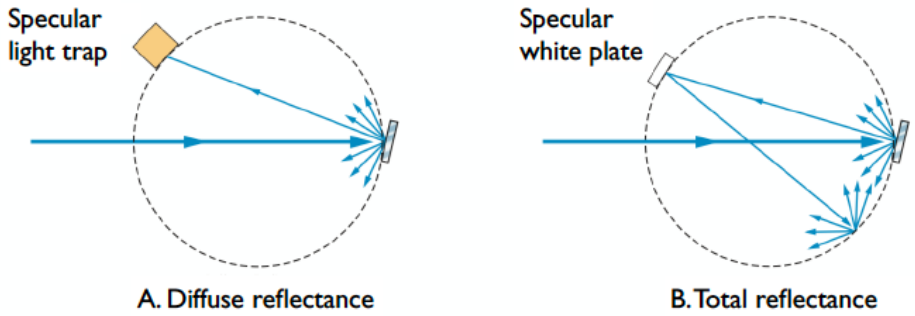
Absorber homogeneously dispersed in a scattering medium (powder):

$$k_s = \propto = \ln(10) \cdot \varepsilon \cdot c \qquad F(R_\infty) = \frac{k_s}{s} = \frac{\ln(10) \cdot \varepsilon \cdot c}{s}$$

Applications: Paints, papermaking, pharmaceutical industry, textiles…

Integrating sphere for diffuse reflectance spectroscopy





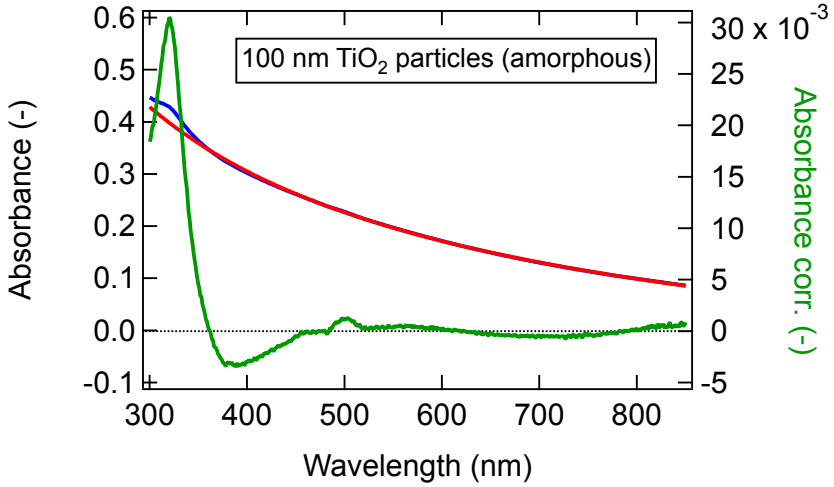
T: Measure all the transmitted light (use a specular light trap)
=
Specular transmittance + Diffuse transmittance

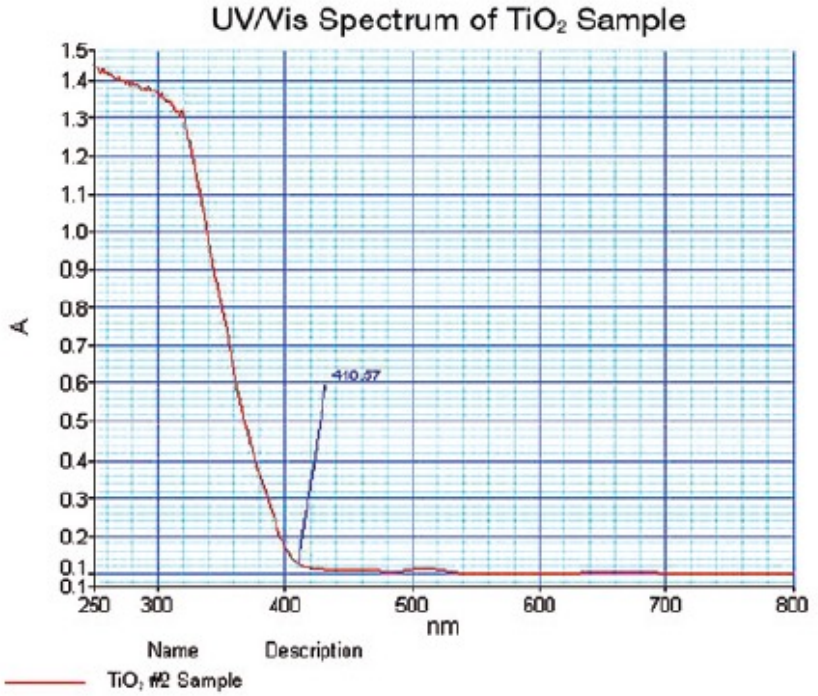
R: Measure all the reflected light (use a a specular white plate)
=
Specular reflectance + Diffuse reflectance

Specular = Total - Diffuse

- Some spectrophotometers offer to measure directly $F(R_\infty)$
- Need to **remove the specular part** if only interested in $F(R_\infty)$
- Entrance port of the integrating sphere is kept open to minimize specular reflection component - can cause fringes or noise at the extreme end of the range
- The accuracy level decrease as the size of the sphere gets smaller

Application:
Measure the bandgap of TiO_2 powders vs. colloidal solutions





We saw last week some corrections have to be implemented for scattering solutions!
(But resulting absorbance spectrum is still not great…)

- Use a powder sample press
- Sample in a holder is clamped on the external port of the integrating sphere
- Absorption edge can be more accurately determined!

4.4 Ellipsometry

Principles

- Optical technique that gives the optical constants (refractive index n and extinction coefficient k), dielectric function and absorption coefficient ($\propto$) of materials

- Can be used to characterize thickness (depth), roughness, composition, electrical conductivity, doping concentration, crystallinity…

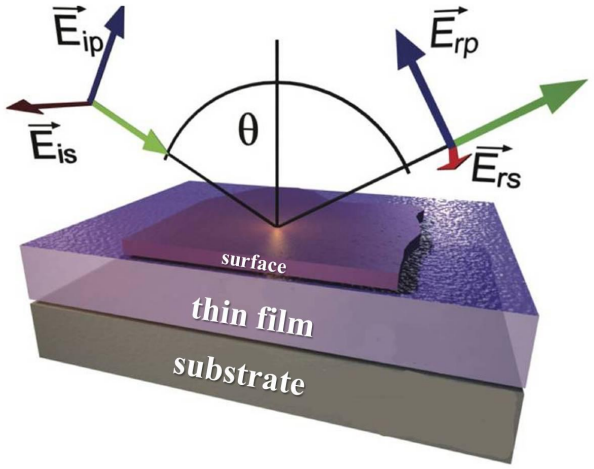
- **Contact-free**, non-destructive method to characterize layered nanostructures (size range < 1 nm to several µm)

- Applicable to almost any type of thin film materials: polymers, semiconductors, dielectrics, metals, alloys, even biological…

Example for photovoltaics:

- Characterize performance of light absorbing medium
- Characterize performance of anti-reflective coatings
- Characterize back-side reflections by a metal layer
- ***Determine band-gap!***

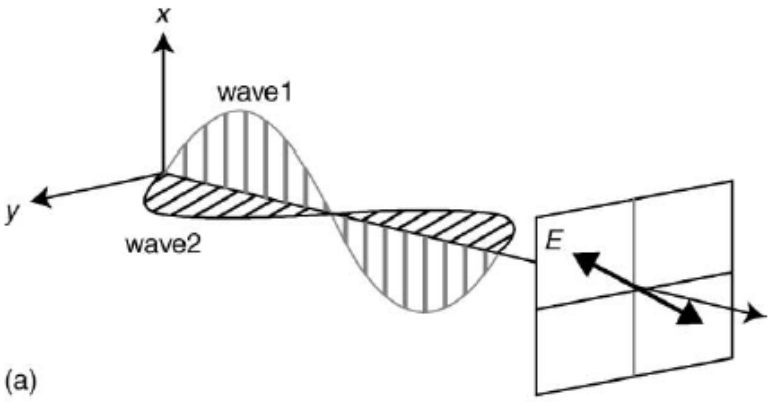
Note: Optical techniques are diffraction limited, but ellipsometry exploits phase information to achieve sub-nanometer resolution



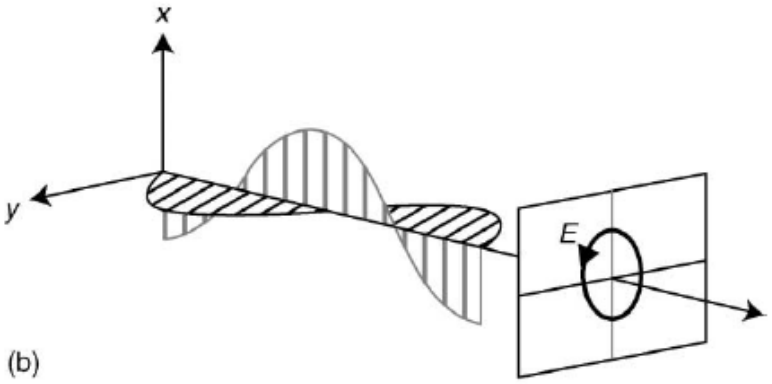
https://www.nffa.eu/offer/area/technique/?id=6339

Polarization: reminder

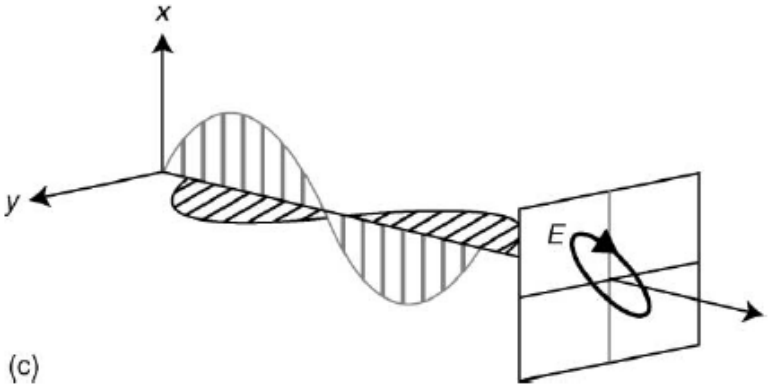
https://www.edmundoptics.com/knowledge-center/application-notes/optics/introduction-to-polarization/



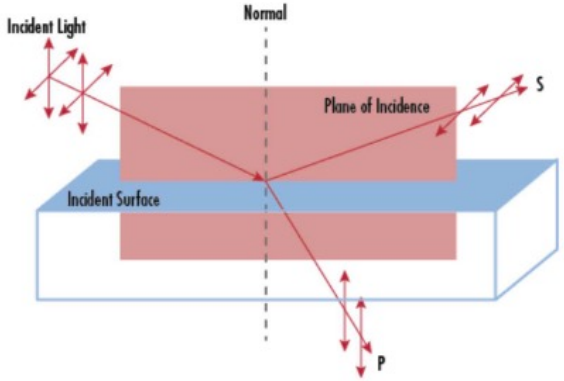
Orthogonal components in phase



Orthogonal components $\lambda/4$ out-of-phase



Orthogonal components ≠ $\lambda/4$ out-of-phase



Brewster's angle:
Only s-polarized light is reflected
Reflected beam is s-polarized
Transmitted beam partially p-polarized

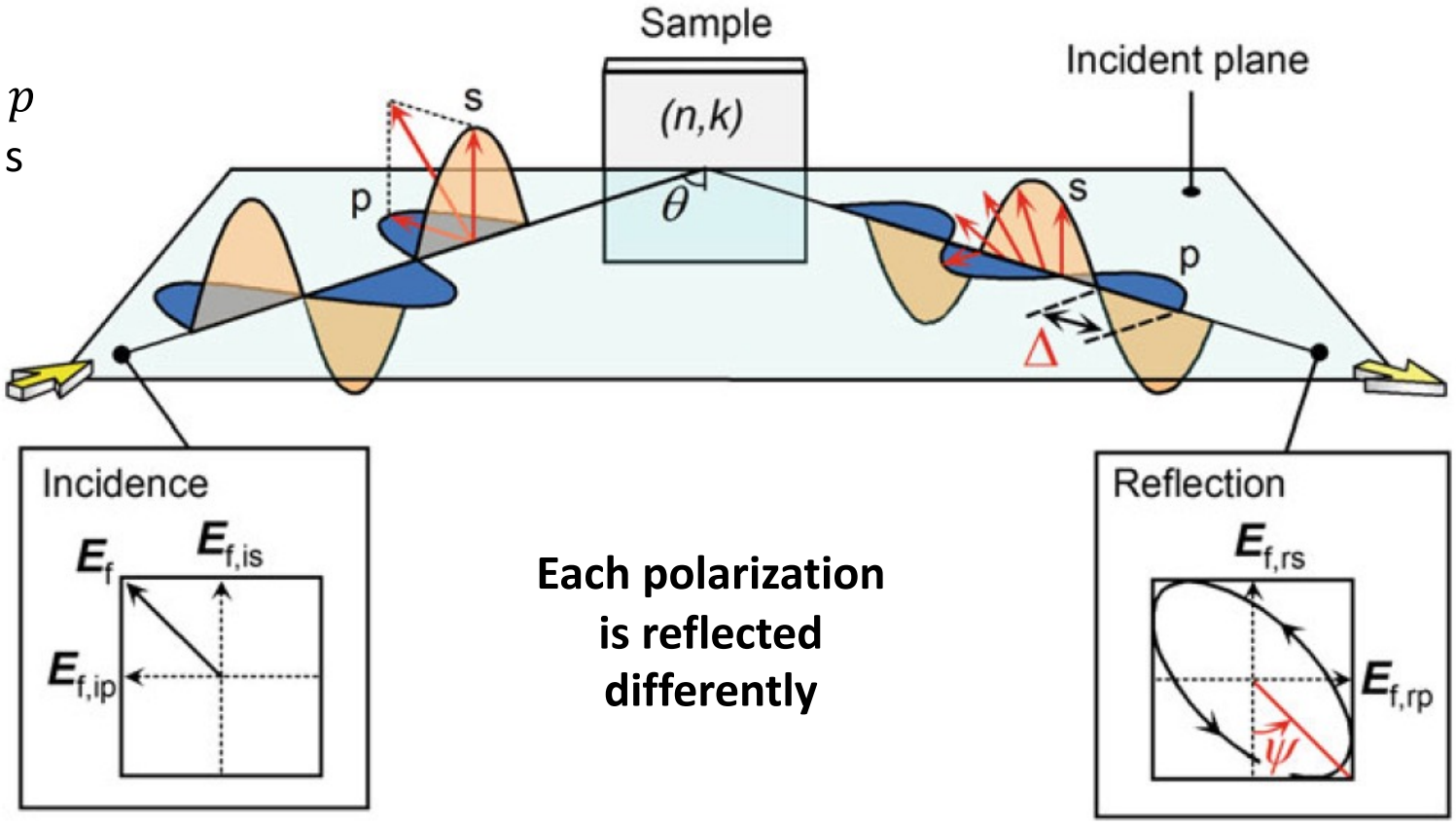
$\| = p$
$\perp$= s

Hilfiker, Woollam, Encyclopedia of Modern Optics, 2005, 297-307

Basic principle of ellipsometry

- Ellipsometry was developed over 100 years ago by Drude
- Determines optical constants of samples based on the change in light polarization upon light reflection, and does not requires a standard sample or reference beam

$\| = p$
$\perp$= s



Each polarization is reflected differently

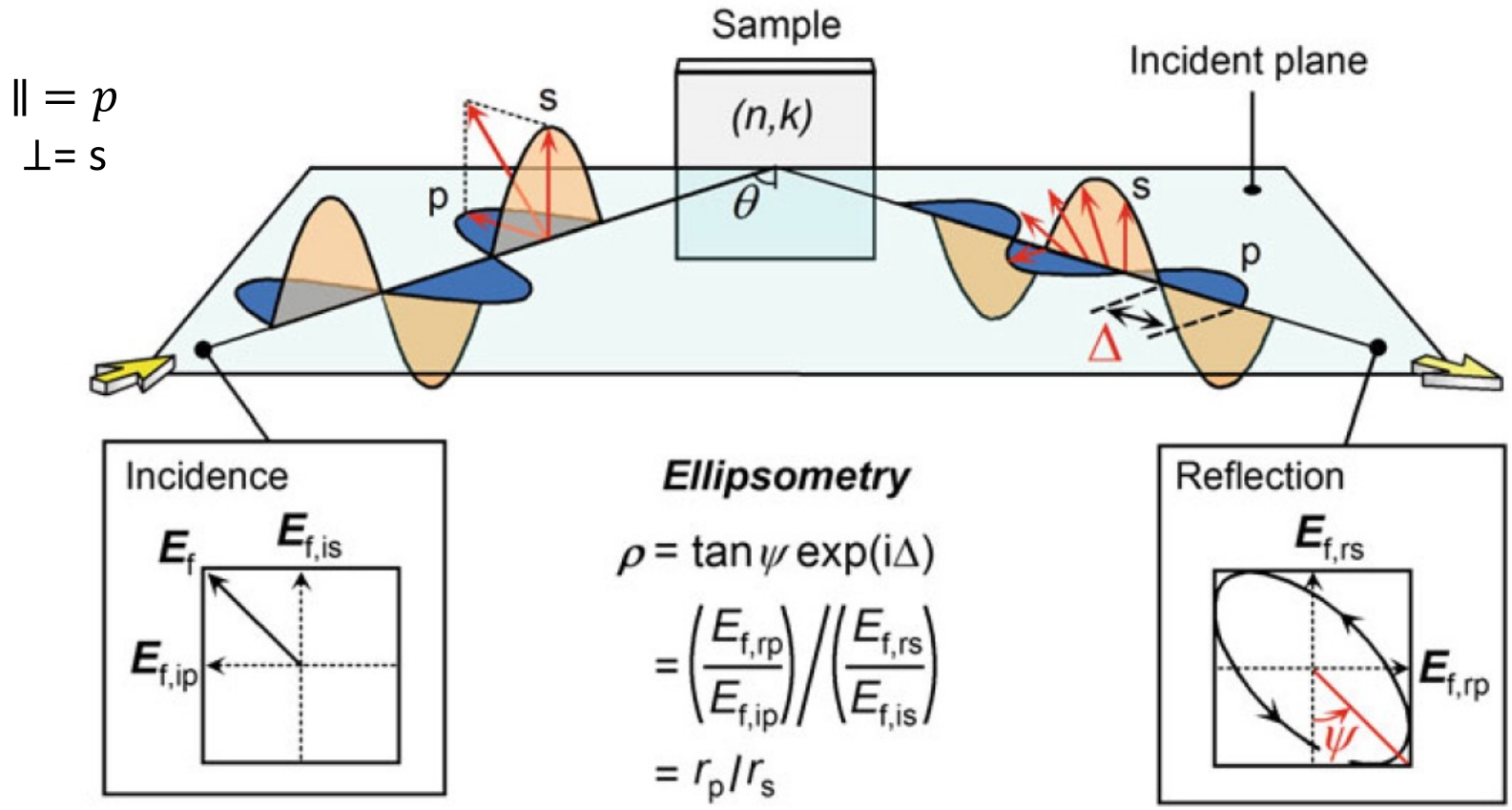
LINEAR POLARISATION

E_f oscillates in a plane inclined at 45° from the incident plane

ELLIPTICAL POLARISATION

Basic principle of ellipsometry

- Ellipsometry was developed over 100 years ago by Drude
- Determines optical constants of samples based on the change in light polarization upon light reflection, and does not requires a standard sample or reference beam



Amplitude of the ∥ - and ⊥-polarized waves and the phase between these polarizations change depending on the optical constants (n,k) and film thickness
The ellipsometry parameters (ψ, Δ) are defined by the amplitude reflection coefficients for ∥-polarization (r_p) and ⊥-polarization (r_s)

Experimental apparatus

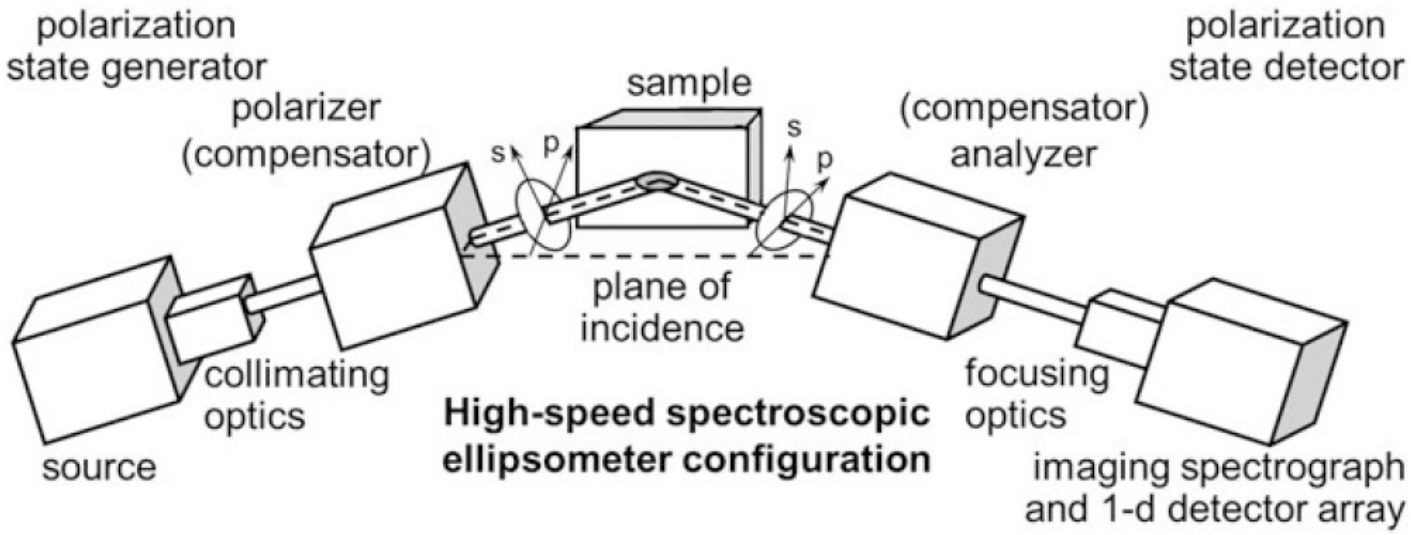
Polarizer:

- Produces a light beam in an identifiable polarization state starting from one or more sources of light

(Analysis of the beam prior to putting the sample must be done with an analyzer)

- May have to be adapted for different wavelengths

Example: Birefringent crystal or wire grid polarizer



Light source:

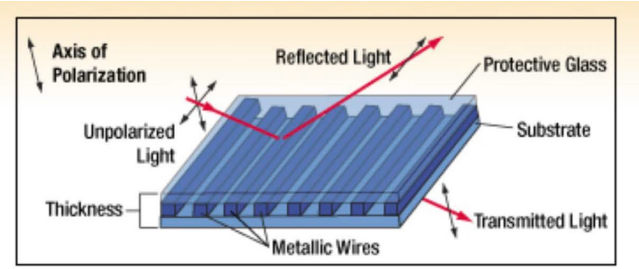
- Single wavelength from a laser
- Multiple wavelengths from one or more lasers
- Quasi-monochromatic light from a lamp and spectrometer
- Broadband source

Note on polarizers and retarders

Linear polarizers

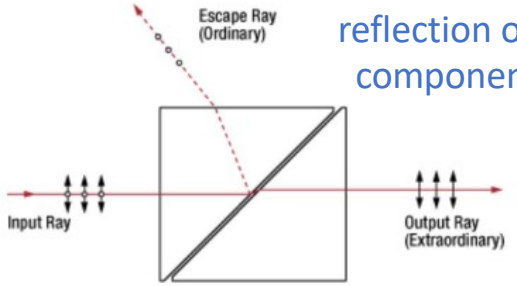
- Select unpolarized light and polarize it linearly
- Analyze the component along the polarizer axis

Thorlabs



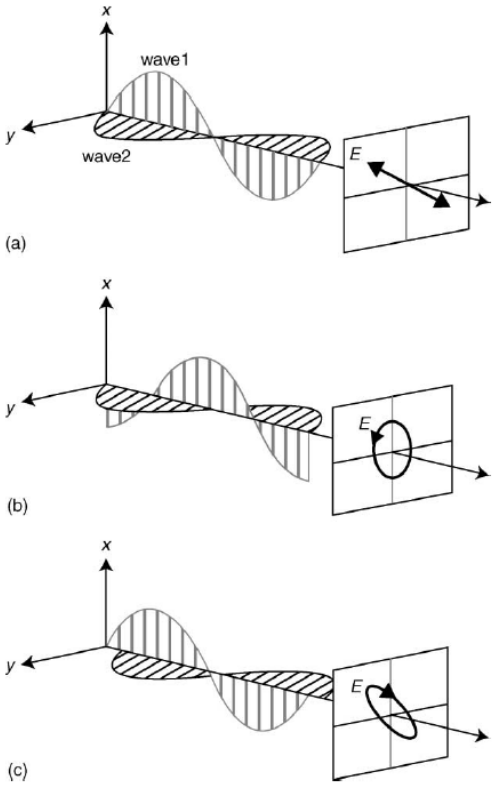
Wire grid polarizers

Total reflection of s component



Only the output ray (extraordinary ray) is highly polarized. A significant amount of reflected light escapes the polarizers through the side port, including all of the ordinary ray and some of the extraordinary ray. As such, the escape ray is not fully polarized.

Birefringent crystal



Retarders

$\lambda/2$-waveplate: Change polarization of linear beam (fast and slow axis)

λ /4 waveplates put at 45° with respect to incoming linear polarization → circular polarization

λ /4 waveplates put at other angles than 45° with respect to incoming linear polarization → elliptical polarization

Experimental apparatus

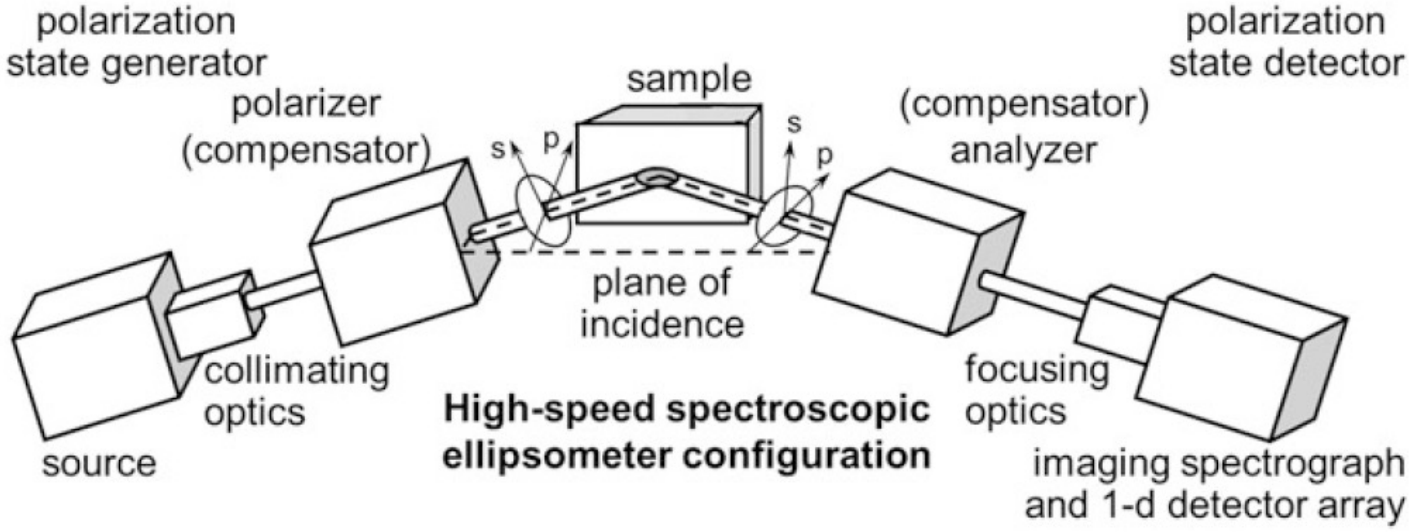
Incidence angle:

- Measurements typically performed at oblique angles near the Brewster angle (50° to 75°), where the largest changes in polarization occur (and phase changes)
- Standard measurements of thickness and refractive index only require a single angle of incidence
- If sample complexity increases → need for multiple angles of incidence

Analyzer:

Simplest method determine the shape of a polarization ellipse

→ Measure light irradiance at different rotation angles of analyzer



Detector:

- Monochromatic light: PMT or Si photodiode
- Multiple wavelength or broadband light:

→ Monochromator + PMT or photodiode, or

→ Spectrograph and a linear detector array

Ellipsometry vs. T/R measurements :

- In conventional transmittance/reflectance (T/R) measurements, absolute light intensities are characterized
- Measured light intensities are influenced by the imperfections of the instrument, calibration and samples (i.e., light scattering)

Example of $CuInSe_2$

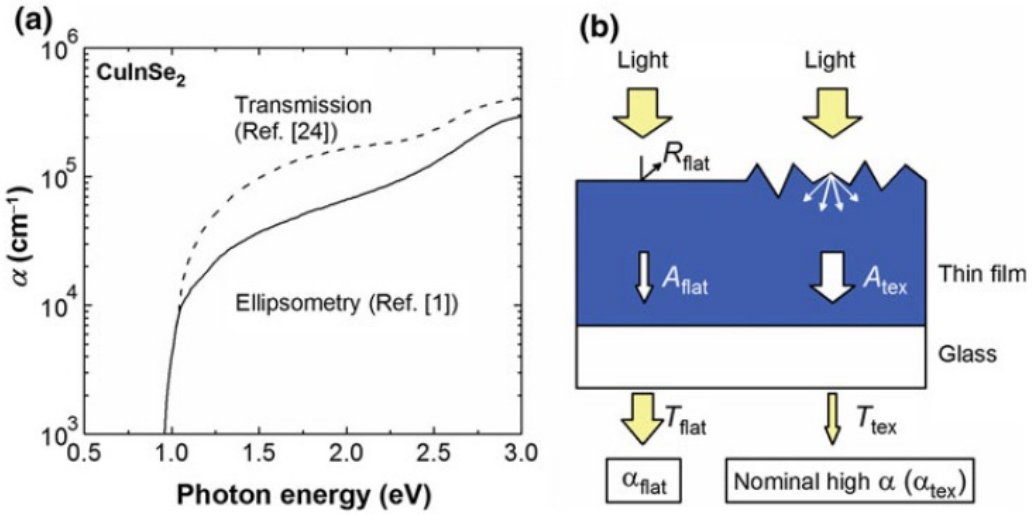


Fig. 6.8 **a** α spectra of CISe determined from SE [1] and transmission [24] measurements and **b** optical responses in flat and textured structures. In (**a**), the α spectrum of [1] corresponds to that shown in Fig. 6.7b. In (**b**), R, A and T represent the reflectance, absorptance and transmittance of the optical system and the subscripts of "flat" and "tex" show the flat and textured structures. The resulting α values (α_{flat} and α_{tex}) are also indicated

- In T/R analysis k(or α) is often deduced assuming a constant *n* in a light absorbing region, which is not a valid assumption for most materials (*n* depends on wl)

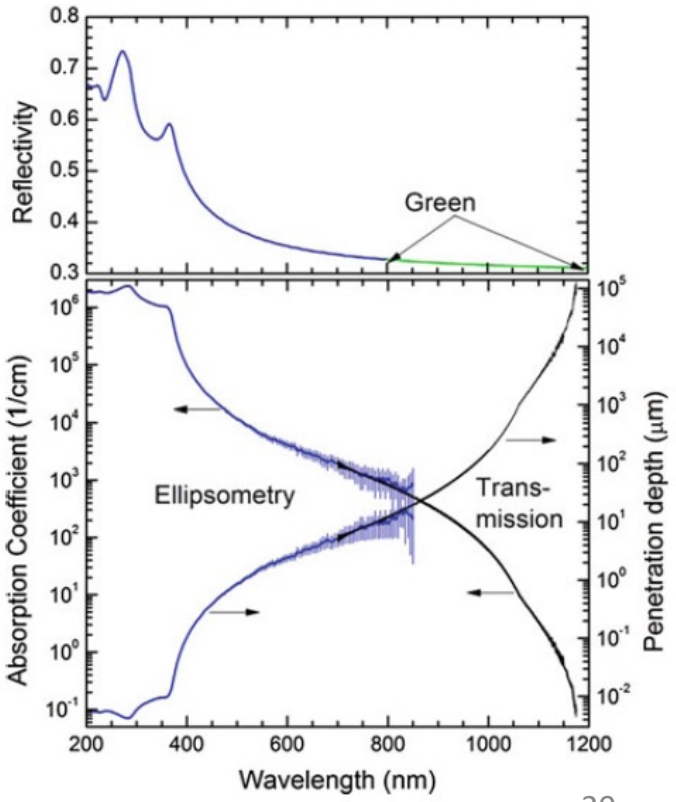
→ T/R techniques are generally more prone to measurement errors

Ellipsometry vs. T/R measurements :

- ψ, Δ characterized in ellipsometry can be measured more accurately (most reliable technique for the determination of n,k)
- When the optical properties in weak absorbing regions ($\propto$ < 500 cm^{-1}) are characterized, a transmission measurement still needs to be used as a complementary technique, as reflection-type ellipsometry has limited sensitivity for light absorption

- Ellipsometry is a specular measurement → scattering may cause problems and depolarize the beam (especially if structure size > 0.1 λ)

Fig. 8.3 The reflectivity (R, top) and optical absorption coefficient (α, bottom) for silicon. Ellipsometry measurements are shown from 200 to 850 nm for R and α, as well as the error limits for α. The compilation data from Green [22] is shown for R from 800 to 1200. Independent transmission data is shown for the absorption coefficient from 700 to 1200 nm. The equivalent penetration depth (in μm) is also shown in the bottom panel



Example of silicon

Data analysis

$$\rho \equiv \tan\psi \exp(i\Delta)$$

When sample structures are simple, isotropic, homogeneous and infinitely thick films: (example: substrate only)

- Amplitude ratio ψ = refractive index n (how "fast" the light waves travel in a material)

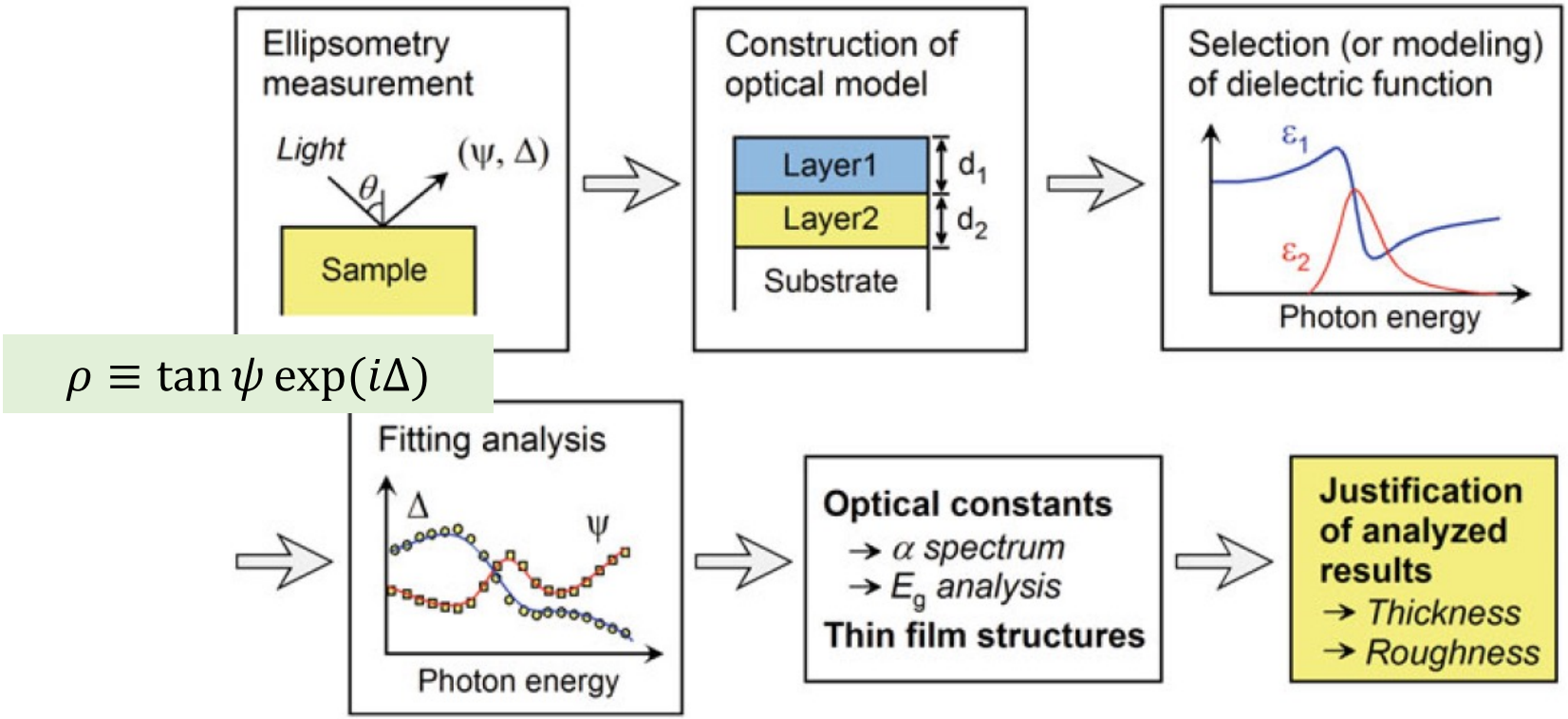
This is related to Fresnel coefficients that define how much light is reflected/refracted

- Phase difference Δ = light absorption described by k or the absorption coefficient ($\propto$), describes attenuation

In all other cases a layer model must be established!

Note: If sample is birefringent, one has to estimate cross-polarization coefficients (r_{ps}, r_{sp})

Data analysis



$$\rho \equiv \tan\psi \exp(i\Delta)$$

Modelling:

- Ψ and Δ values are calculated using Fresnel's equations
- Calculated spectra are fitted to measured spectra
- Use an iterative procedure: vary unknown **optical constants** and/or **thickness**
- From the parameters that provide the best fitting, the optical constants and thin film structure/thickness are determined
- Multiple-angle incidence is generally used for more complex multilayers, to ensure that the used model is unique

Effect of roughness

- Ellipsometry has a very high sensitivity for layer thicknesses (~0.1 Å)
- But high thickness sensitivity can become a disadvantage if samples have complex structures and the precise optical modeling of the sample structures is difficult
- Possible solution: Use the effective medium approximation (EMA)

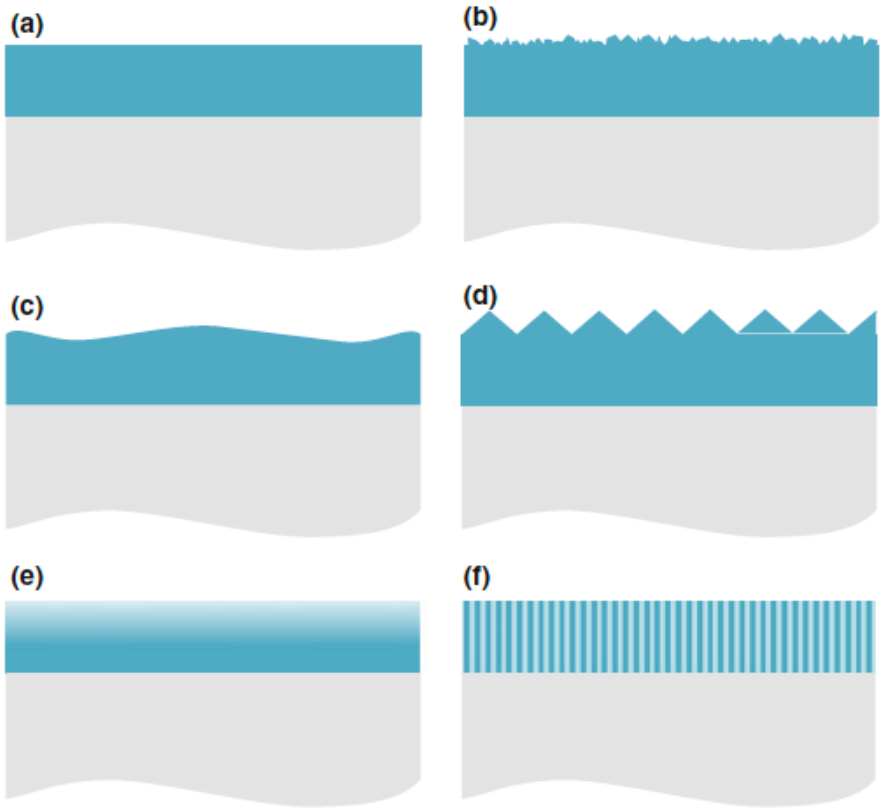
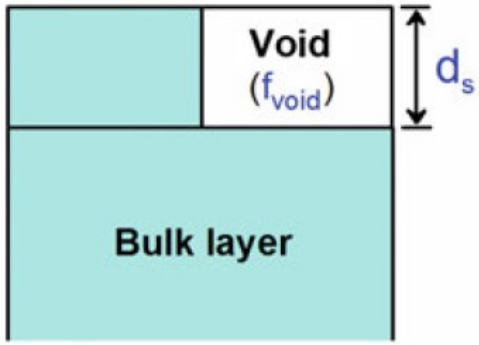
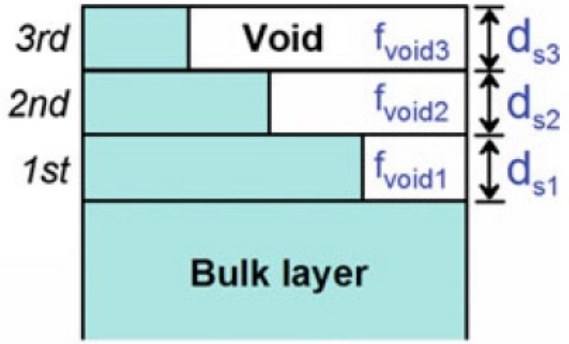


Fig. 3.29 a Ideal model consists of planar, homogenous layer with perfect interfaces. Non-ideal models may incorporate **b** rough surface, **c** non-uniform film thickness, **d** textured surface, **e** graded film index, or **f** anisotropic films



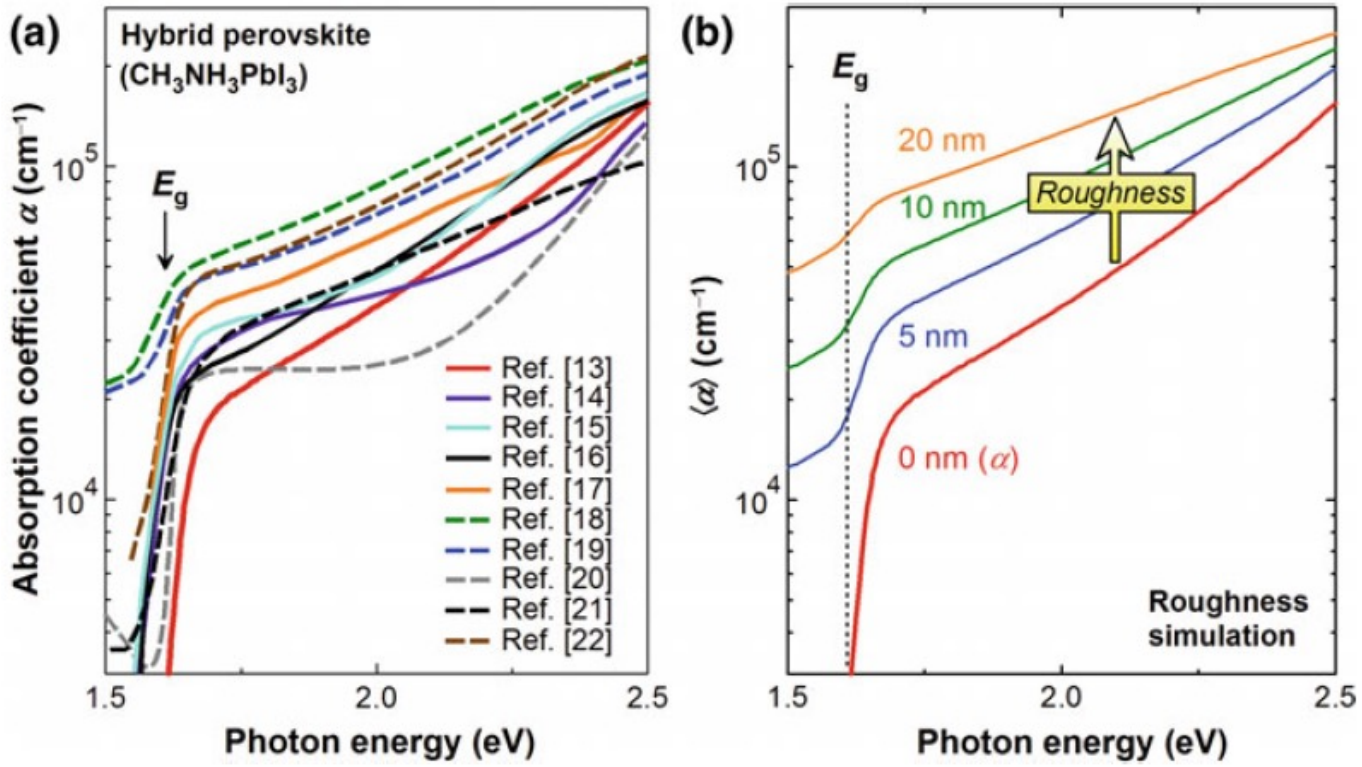
Single EMA model



EMA multilayer model

Effect of roughness

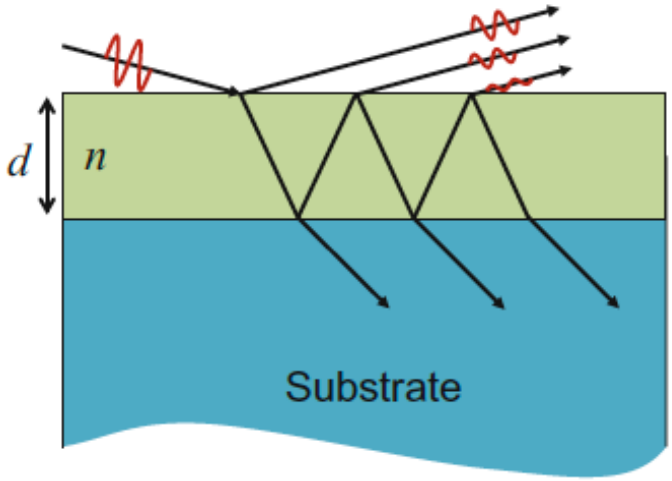
Example of perovskites



→ 20 nm surface roughness is enough to loose the possibility to determine E_g!

Thickness determination

- When film thickness increases → increasing separation between light reflected from the surface and the light that travels through the film
- Causes a phase delay that is related to both the physical thickness and the index of refraction
- Information about the thickness is based on the position (vs. wl) and number of interference oscillations
- But if sample is highly absorptive…There is a limit to the thickness!



- n,k must be known or determined along with the thickness to get the correct results optical measurement
- For transparent materials: k is zero or close to zero, so only two unknowns left

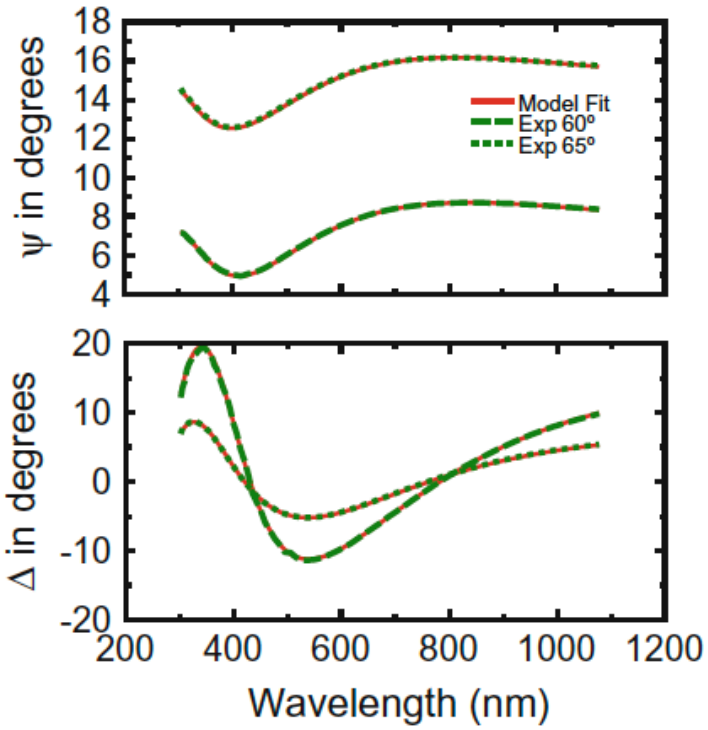
Thickness determination

- For transparent materials:

Example of thin SiO_2 film on glass substrate

Thickness can be determined to 171.85 nm with 2.7 nm of roughness!

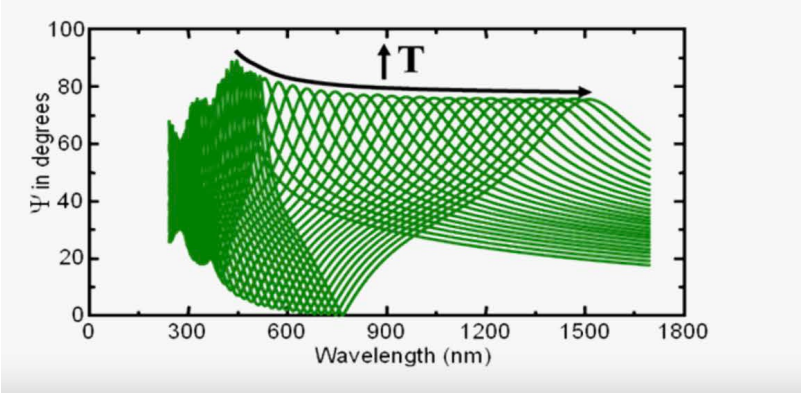
Oxide layer is transparent over the entire measured spectral range



- For materials transparent at some wavelengths and absorbing at others: try to determine thickness from the "transparent part"

- For absorbing materials: other strategies needed

Example: films of different thicknesses
→ as the thickness (T) increases, the interference oscillations shift toward longer wavelengths



https://www.jawoollam.com/resources/ellipsometry-faq#toggle-id-5