ICSE 8 BARCELONA 2019

Ellipsometric Data Analysis:

2. Anisotropic materials

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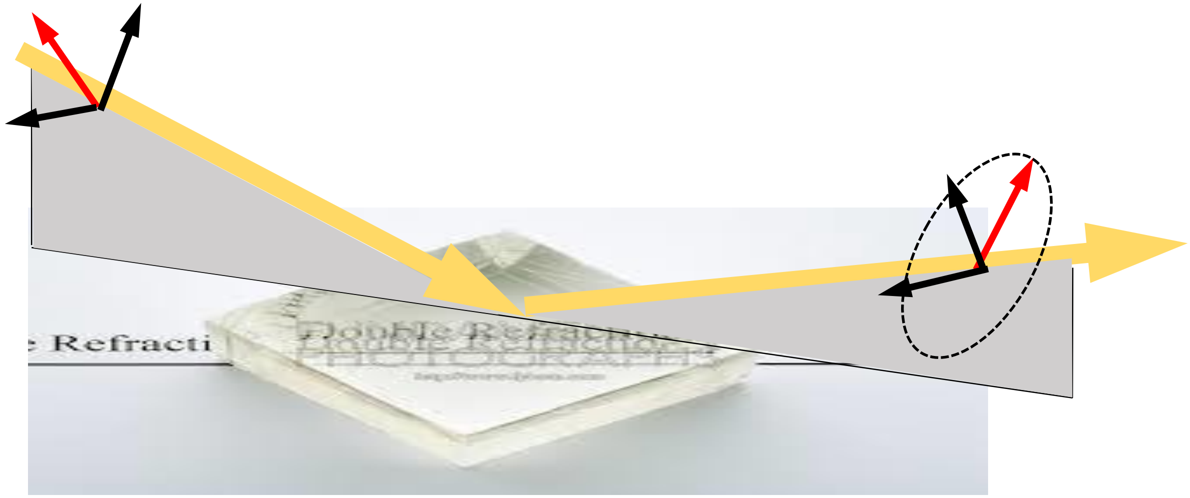
Part 2. Organization

This is a tutorial about the particularities of ellipsometry and polarimetry with **anisotropic materials**.

- *What information can we get from anisotropic materials?*
- *How anisotropic materials can be recognized by spectroscopic ellipsometry?*
- *What is the difference between Generalized Ellipsometry and Mueller Matrix Ellipsometry?*
- *Special instruments are needed?*
- *How calculations for anisotropic materials can be done?*



A reminder: ellipsometry in isotropic samples

Nondepolarizing ellipsometry data is fully characterized by two parameters:

$$\mathbf{J}_{sample} = \begin{bmatrix} \rho & 0 \\ 0 & 1 \end{bmatrix}$$

$$\rho = (\rho_{real} + i\rho_{imag}) = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta} = \frac{C + iS}{1 + N}$$

$$\mathbf{M}_{sample} = \begin{bmatrix} 1 & -N & 0 & 0 \\ -N & 1 & 0 & 0 \\ 0 & 0 & C & S \\ 0 & 0 & -S & C \end{bmatrix}$$

$$N = \cos(2\psi)$$
$$S = \sin(2\psi)\sin(\Delta)$$
$$C = \sin(2\psi)\cos(\Delta)$$
$$N^2 + S^2 + C^2 = 1$$

<u>Some ideas from Part 1</u>

- Ellipsometry measures intensities that depend on **Mueller matrix elements**
- Physical parameters of interest are not directly measured
- Comparing model results with experimental data can be tricky for isotropic materials: even more for anisotropic materials! Because there are more input parameters.

Ellipsometry in anisotropic samples

Nondepolarizing data is usually given by six parameters defined from the Jones matrix (and not directly measured by ellipsometers, E-fields oscillate!)

$$\mathbf{E}_{out} = \mathbf{J}\mathbf{E}_{in}$$

$$\mathbf{J} = \begin{bmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{bmatrix} \xrightarrow{\text{norm.}} \begin{bmatrix} \rho & \rho_{ps} \\ \rho_{sp} & 1 \end{bmatrix}$$

$$\rho = \frac{r_{pp}}{r_{ss}} = \tan(\psi)e^{i\Delta}$$

$$\rho_{ps} = \frac{r_{ps}}{r_{ss}} = \tan(\psi_{ps})e^{i\Delta_{ps}}$$

$$\rho_{sp} = \frac{r_{sp}}{r_{ss}} = \tan(\psi_{sp})e^{i\Delta_{sp}}$$

Parameters associated to **cross-polarization** (s- and p-polarizations are not eigenmodes of reflection)

$$\mathbf{M}_{nd} = \mathbf{T}(\mathbf{J} \otimes \mathbf{J}^*)\mathbf{T}^{-1}$$

$$\mathbf{T} = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & i & -i & 0 \end{bmatrix}$$

$$\mathbf{S}_{out} = \mathbf{M}_{nd}\mathbf{S}_{in}$$

$$\mathbf{M}_{nd} = \begin{bmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{bmatrix}$$

- A Jones matrix depends on **8 parameters** and a nondepolarizing Mueller matrix on **7 parameters** (the absolute phase is lost).
- After normalization both depend on **6 parameters**

Ellipsometry in anisotropic samples. Mueller matrices

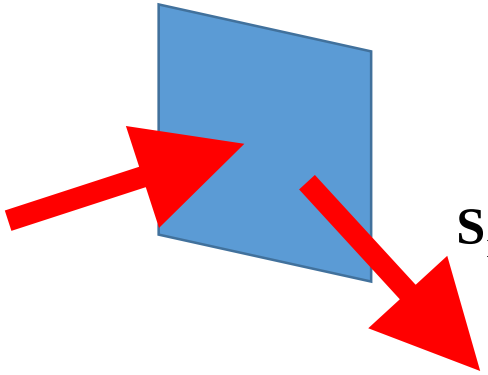
Ellipsometers measure **Mueller matrix** elements

$$\mathbf{M} = \begin{bmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{bmatrix}$$

History

- Paul Soleillet* (1902-1992)
- Francis Perrin (1901-1992)
- Hans Mueller (1900-1965)

$$\mathbf{S}_0 = \begin{bmatrix} I_0 \\ Q_0 \\ U_0 \\ V_0 \end{bmatrix}$$

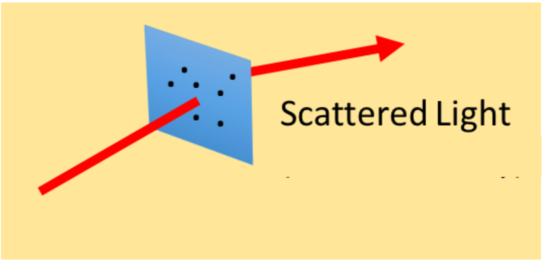


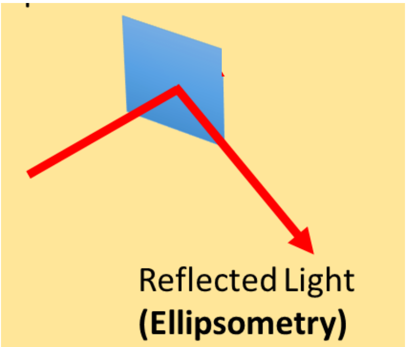
$$\mathbf{S}_1 = \begin{bmatrix} I_1 \\ Q_1 \\ U_1 \\ V_1 \end{bmatrix}$$

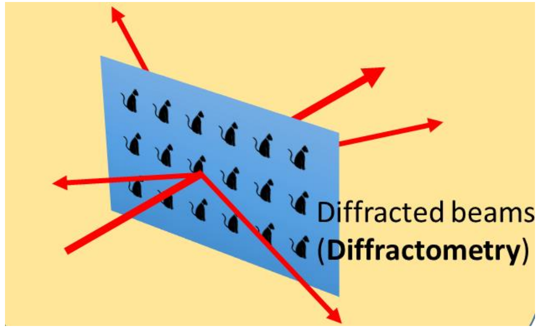
$$\mathbf{S}_1 = \mathbf{M}\mathbf{S}_0$$

(* This year is the 90th anniversary!: *P. Soleillet, Annales de physique 12, 23 (1929)*)

- In absense of depolarization MM elements provide *redundant information* (not all are needed).
- MM elements are observables: ellipsometers measure them either completely or partially.
- Any linear interaction of a medium with a beam of light can be described by a Mueller matrix



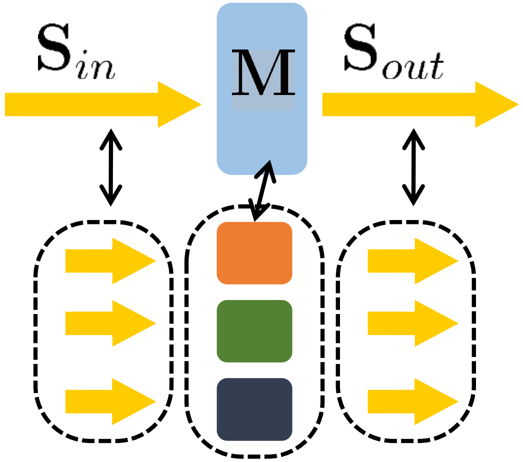




Ellipsometry in anisotropic samples. Depolarization

Depolarizing data is fully characterized by 16 parameters (15 after normalization)

Depolarization is the reduction of the degree of polarization of light. Typically occurs when emerging light is composed of several incoherent contributions.



- Sum of incoherent contributions
- The sample exhibits spatial, temporal or frequency heterogeneity within the measurement capabilities of the instrument.

- Quantification of the depolarization: **Depolarization index (DI)**

$$DI = \frac{\sqrt{\sum_{ij} m_{ij}^2 - m_{00}^2}}{\sqrt{3} m_{00}}$$

$$0 \leq DI \leq 1$$

The DI of a nondepolarizing Mueller matrix is 1

J. J. Gil, E. Bernabeu, Opt. Acta 32 (1985) 259

Generalized Ellipsometry vs Mueller matrix ellipsometry(I)

Generalized ellipsometry

- Suitable to have the complete response of a anisotropic **nondepolarizing** sample
- Partial Mueller matrix ellipsometry
- At least 9 elements (8 if normalized) need to be measured

Seven missing elements, e.g:

$$\begin{bmatrix} m_{00} & m_{01} & \bullet & m_{03} \\ \bullet & \bullet & \bullet & \bullet \\ m_{20} & m_{21} & \bullet & m_{23} \\ m_{30} & m_{31} & \bullet & m_{33} \end{bmatrix}$$

(e.g. 2-MGE)

Four missing elements, e.g.:

$$\begin{bmatrix} m_{00} & m_{01} & m_{02} & \bullet \\ m_{10} & m_{11} & m_{12} & \bullet \\ m_{20} & m_{21} & m_{22} & \bullet \\ m_{30} & m_{31} & m_{32} & \bullet \end{bmatrix}$$

(e.g. RPCE)

$$\mathbf{J} = \begin{bmatrix} \rho & \rho_{ps} \\ \rho_{sp} & 1 \end{bmatrix}$$

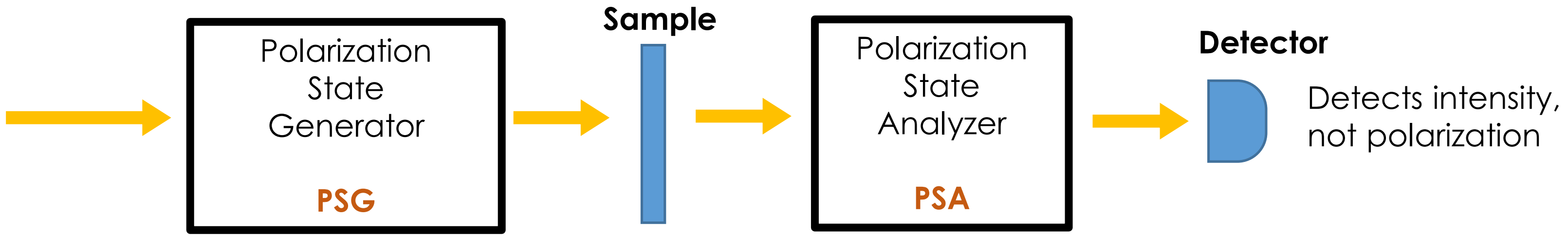
Mueller matrix ellipsometry

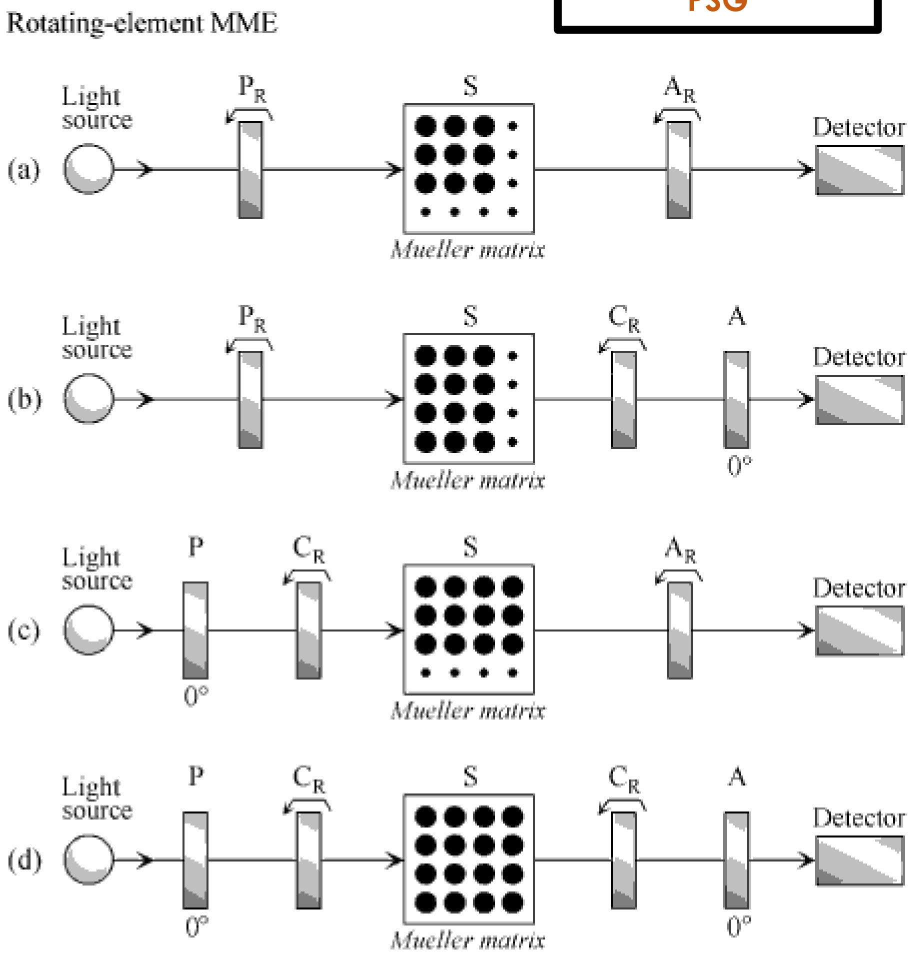
- Suitable for any sample
- The complete Mueller matrix is measured
- Instrumentation-wise requires complete PSG and complete PSA

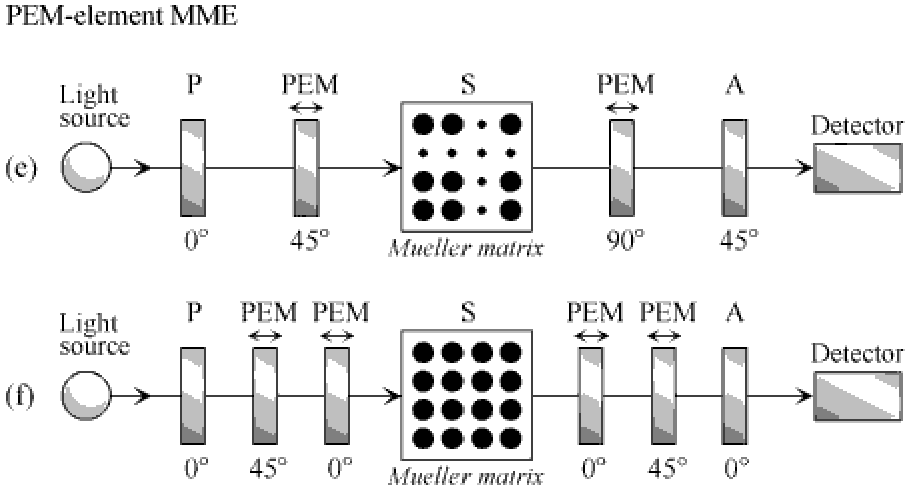
$$\begin{bmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{bmatrix}$$

R. Ossikovski and O. Arteaga, J. Opt. Soc. Am. A 36, 403-415 (2019)
O. Arteaga and R. Ossikovski, J. Opt. Soc. Am. A 36, 416-427 (2019)

Generalized Ellipsometry vs Mueller matrix ellipsometry (II)



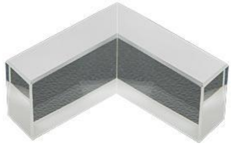
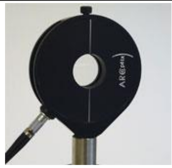
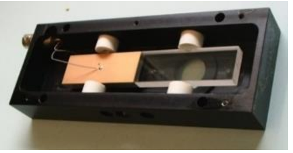




P. S. Hauge, Surf. Sci. 96(1-3), 108–140 (1980)

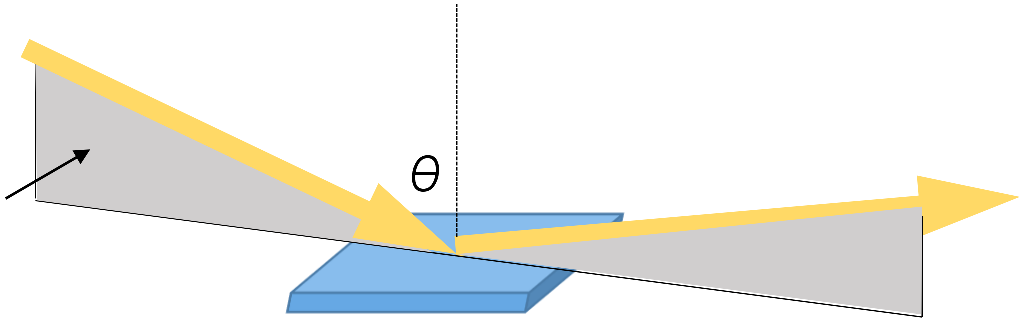
Remark about instrumentation: compensators

Polarizers ~ almost ideal optical response in a wide spectral range.
Compensators ~ more problematic. We need at least 1 (often 2 or 4!)

Rotating Retarders   P. S. Hauge, J. Opt. Soc. Am. **68**, 1519-1528 (1978)	• Fixed Retardation • Changing azimuth	• Waveplates are not acromatic • Fresnel rohms are hard to rotate • Mechanical rotation
Liquid crystal cells  E. Garcia-Caurel et al. Thin Solid Films 455 120-123 (2004).	• Variable Retardation (nematic LC) • Changing azimuth (ferroelectric LC)	• Not transparent in the UV • Temperature dependence • No frequency domain analysis
Crystal variable retarders e. g. Berek, Babinet Soleil  R.A. Synowicki, et al. Thin Solid Fillms 455, 624-627 (2004)	• Variable Retardation • Fixed azimuth	• Two retarders for complete PSG or PSA • No frequency domain analysis
Piezo-optic modulators (photoelastic mod.)  O. Arteaga et al. Appl. Optics 51.28 6805-6817 (2012).	• Variable Retardation • Fixed azimuth	• Two PEMs for complete PSG or PSA • Too fast for imaging
Electro-optic modulators (Pockels cells)  R. C. Thompson et al. Appl. Opt. 19, 1323–1332 (1980).	• Variable Retardation • Fixed azimuth	• Two cells for each PSG or PSA • Small acceptance angle • Too fast for imaging

The angle of incidence

Ellipsometry measurements are conditioned by the existence of a plane of incidence



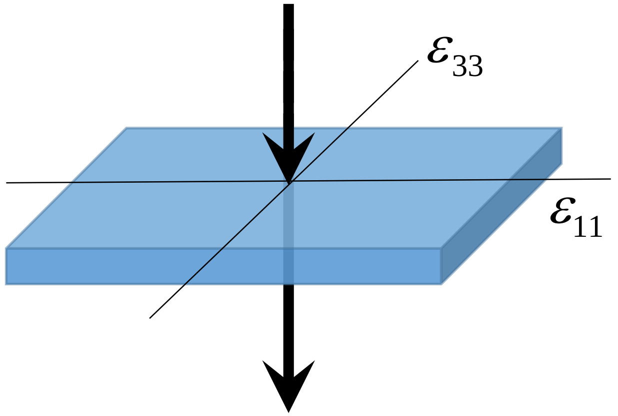
When the **angle of incidence is zero** there is no preferential plane of incidence and

In isotropic nondepolarizing samples	**In anisotropic samples**
$\mathbf{M}_{trans} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$ $\mathbf{M}_{backrefl} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$	$\mathbf{M}_{trans} \neq \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$ $\mathbf{M}_{backrefl} \neq \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$
No physical information can be obtained	**Information about the anisotropy can be obtained**

Normal incidence

Normal incidence ellipsometry (polarimetry) measurements are sensitive to the anisotropy of the dielectric tensor in the plane of the sample, but not to the actual values of the components.

E.g. consider a uniaxial crystal with dielectric tensor



$$\begin{bmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{33} & 0 \\ 0 & 0 & \varepsilon_{11} \end{bmatrix}$$

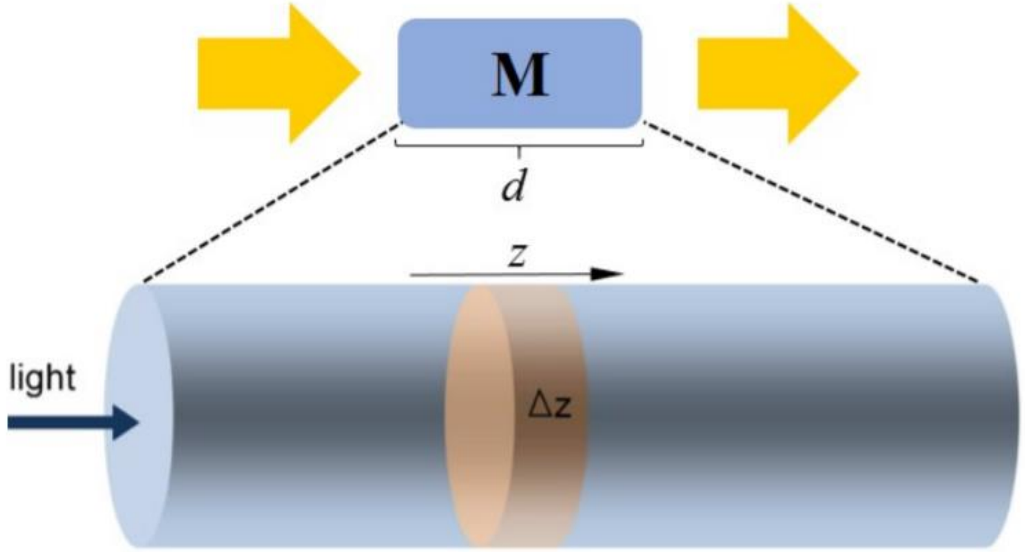
Normal incidence ellipsometry transmission or reflection measurements will be:

- Very sensitive to $\sqrt{\varepsilon_{11}} - \sqrt{\varepsilon_{33}}$
- Basically unsensitive to $\sqrt{\varepsilon_{11}}$ and $\sqrt{\varepsilon_{33}}$ individually

There is no contrast for the change of refractive index along the direction of propagation of light!

Normal incidence transmission (I)

Differential analysis offers a direct physical interpretation for the normal incidence transmission Mueller matrix of an homogenous medium



We study bulk propagation

$$\frac{d\mathbf{M}(z)}{dz} = \mathbf{mM}(z)$$

Paul Soleillet pioneered the differential calculus in 1929!! *(P. Soleillet, Annales de physique 12, 23 (1929))*

History: O. Arteaga, JOSA A 34(3), 410-414, 2017

Calculus: R. M. A. Azzam, JOSA A 68, 1756-1767 (1978) and R. Ossikovski, Opt. Lett. 36, 2330-2332 (2011)

Normal incidence transmission (II)

Solving the differential equation:

$$\left.\begin{array}{r}\dfrac{d\mathbf{M}(z)}{dz}=\mathbf{mM}(z)\\ \mathbf{L}=\mathbf{m}d\end{array}\right] \rightarrow \begin{array}{l}\mathbf{M}=\exp\mathbf{L}\\ \mathbf{L}=\ln\mathbf{M}\end{array}$$

When there is no depolarization:

$$\mathbf{L}=\begin{bmatrix} A & -LD & -LD' & CD \\ -LD & A & CB & LB' \\ -LD' & -CB & A & -LB \\ CD & -LB' & LB & A \end{bmatrix}$$

For normal incidence the effect of the interfaces is vanishing small, and we measure **bulk propagation**

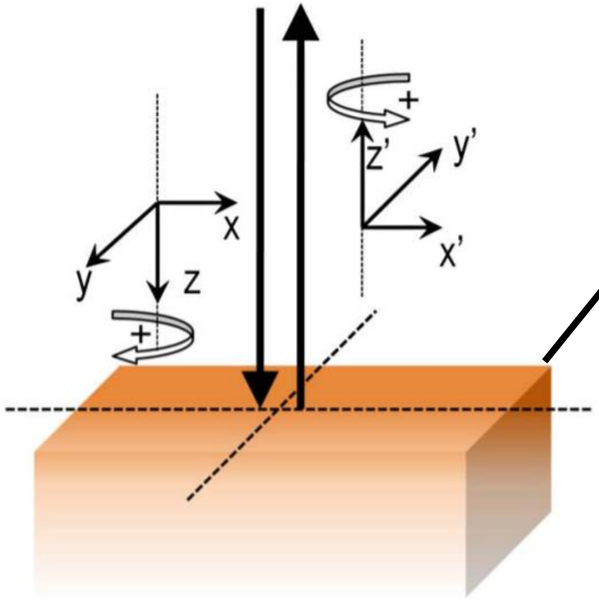
Physical interpretation of differential Mueller matrix elements (holding in transmission)

$$LB=\tfrac{2\pi}{\lambda}\left(n_x-n_y\right)d$$
$$LB'=\tfrac{2\pi}{\lambda}\left(n_{45}-n_{135}\right)d$$
$$CB=\tfrac{2\pi}{\lambda}\left(n_L-n_R\right)d$$

$$LD=\tfrac{2\pi}{\lambda}\left(k_x-k_y\right)d$$
$$LD'=\tfrac{2\pi}{\lambda}\left(k_{45}-k_{135}\right)d$$
$$CD=\tfrac{2\pi}{\lambda}\left(k_L-k_R\right)d$$

CD: Circular dichorism
CB:Circular birefringence
LD: Horizontal linear dichroism
LB: Horizontal linear birefringence
LD': 45° linear dichroism
LB': 45° linear birefringence

Normal incidence reflection



$$\begin{bmatrix} 1 & m_{01} & m_{02} & m_{03} \\ m_{01} & m_{11} & m_{12} & m_{13} \\ -m_{20} & -m_{12} & m_{22} & m_{23} \\ m_{03} & m_{13} & -m_{23} & m_{33} \end{bmatrix}$$

9 parameters (when normalized)

The system has fewer degrees of freedom because the incident radiation travels in one direction and the reflected radiation in the reverse direction (there is always **reciprocal symmetry**)

Sensitive to ***differences*** of (complex) refractive indices in the plane of the sample. E.g. we measure:

- Differential phase retardations
- Differential reflectivity

There is no contrast for the change of refractive index along the direction of propagation of light!

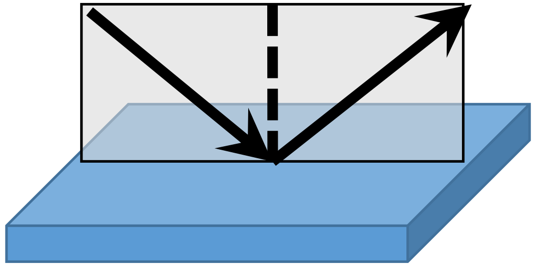
A technique born as Reflection Anisotropy Spectroscopy (RAS)
D. E. Aspnes, A.A. Studna Phys. Rev. Lett. 54 1924 (1985)

A more recent implementation: G. E. Jellison, J. D. Hunn, C. M. Rouleau, Appl. Opt. 45, 5479-5488 (2006)

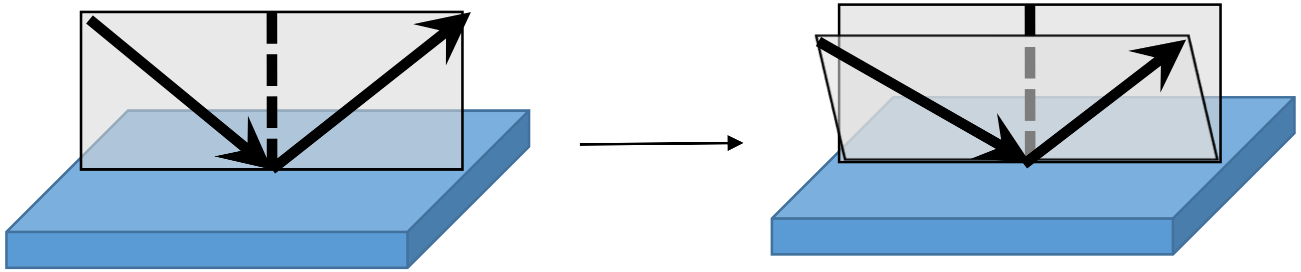
Matrix symmetries and anisotropy (I)

Symmeries in the Mueller or Jones matrix can be often correlated with **material symmetries**

- We consider ellipsometry mesurements in reflection: a well defined plane of incidence.



- **Caution!** Symmetric (isotropic) materials can lead to a substantially nonsymmetric Mueller matrix if the sample is **poorly aligned.**

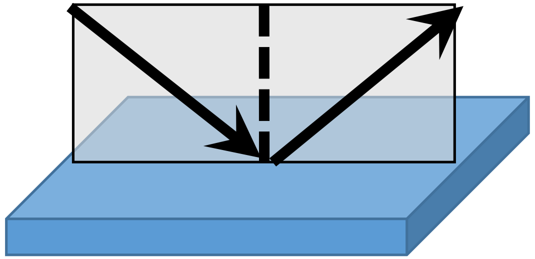


Sample misaligned with respect to the plane of incidence

Isotropic samples can be used for instrument aligment.

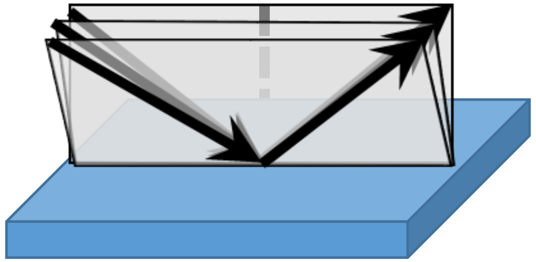
Matrix symmetries and anisotropy (II). Example: isotropic sample

If the plane of incidence of the ellipsometer contains the sample normal



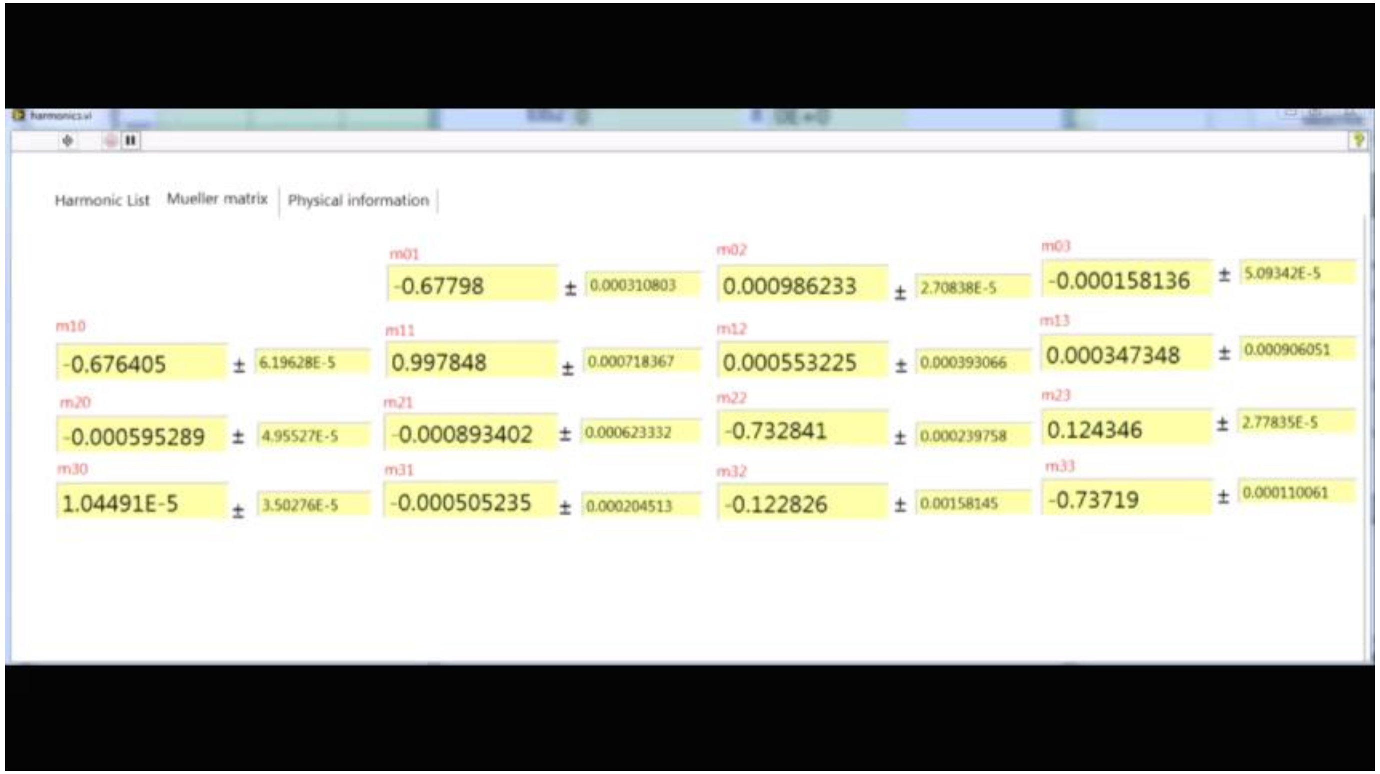
$$\begin{bmatrix} 1 & m_{01} & 0 & 0 \\ m_{01} & 1 & 0 & 0 \\ 0 & 0 & m_{22} & m_{23} \\ 0 & 0 & -m_{23} & m_{22} \end{bmatrix}$$

If the plane of incidence of the ellipsometer does **not** contain the sample normal



$$\begin{bmatrix} 1 & m_{01} & m_{02} & 0 \\ m_{01} & m_{11} & m_{12} & m_{13} \\ m_{02} & m_{12} & m_{22} & m_{23} \\ 0 & m_{13} & -m_{23} & m_{22} \end{bmatrix}$$

Mueller matrix ellipsometry on Si



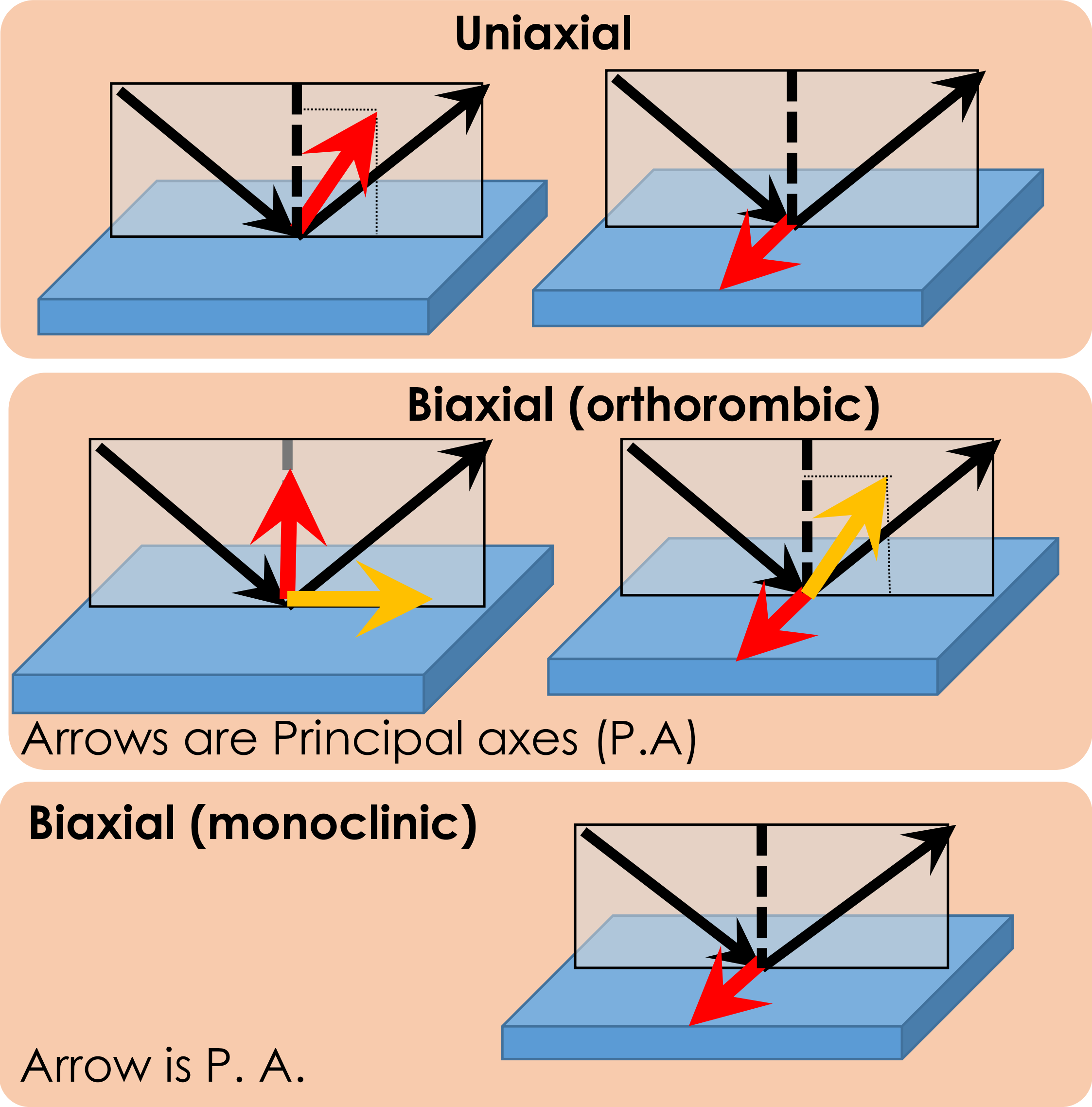
Matrix symmetries and anisotropy(III)

In the **isotropic** case and some anisotropy situations

$$\mathbf{M} = \begin{bmatrix} 1 & m_{01} & 0 & 0 \\ m_{01} & 1 & 0 & 0 \\ 0 & 0 & m_{22} & m_{23}\,* \\ 0 & 0 & -m_{23}\,* & m_{22} \end{bmatrix} \qquad \mathbf{J} = \begin{bmatrix} r_p & 0 \\ 0 & r_s \end{bmatrix}$$

This symmetry appears whenever the sample coincides with its own mirror image with respect to the incidence plane (i.e. the sample is mirror-symmetric with respect to this plane)

* The elements with an asterisk vanish when **J** is real



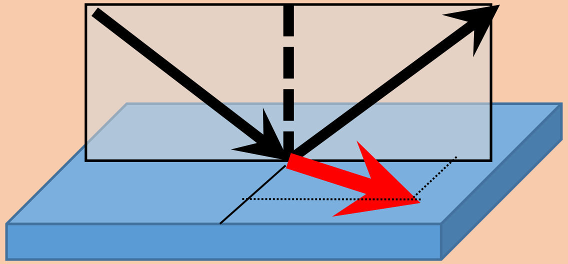
Matrix symmetries and anisotropy(IV)

$$\mathbf{M} = \begin{bmatrix} 1 & m_{01} & m_{02} & m_{03}\,* \\ m_{01} & m_{11} & m_{12} & m_{13}\,* \\ -m_{02} & -m_{12} & m_{22} & m_{23}\,* \\ m_{03}\,* & m_{13}\,* & -m_{23}\,* & m_{33} \end{bmatrix} \qquad \mathbf{J} = \begin{bmatrix} r_{pp} & r_{ps} \\ -r_{ps} & r_{ss} \end{bmatrix}$$

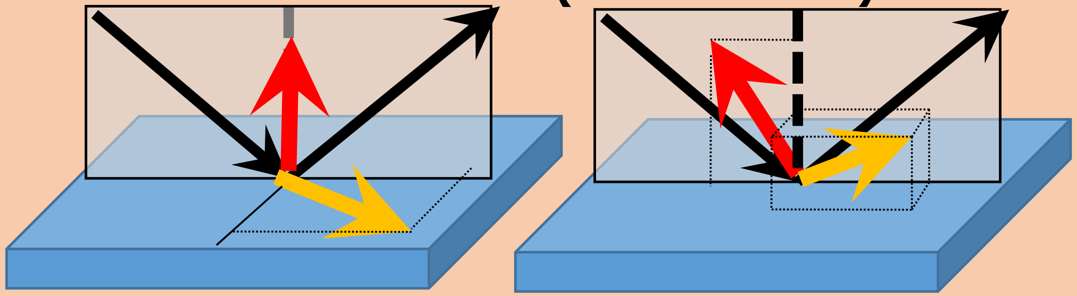
A 180°-rotation of the sample about its normal brings the same measurement
(incident and scattered beams can be interchanged)

* The elements with an asterisk vanish when **J** is real

Uniaxial

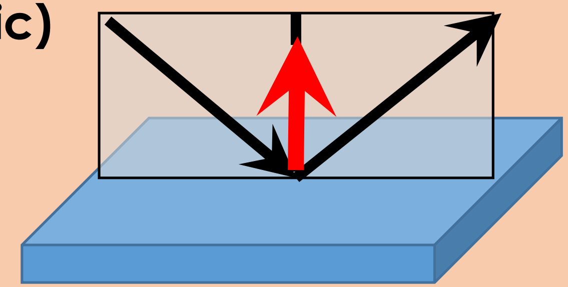


Biaxial (orthorombic)



Arrows are Principal axes (P.A)

Biaxial (monoclinic)



Arrow is P. A.

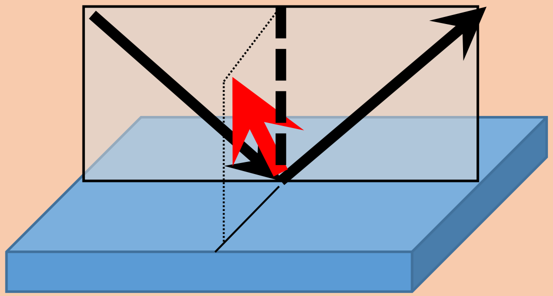
Matrix symmetries and anisotropy (V)

$$\mathbf{M}=\begin{bmatrix} 1 & m_{01} & m_{02} & m_{03}\,* \\ m_{01} & m_{11} & m_{12} & m_{13}\,* \\ m_{02} & m_{12} & m_{22} & m_{23}\,* \\ -m_{03}\,* & -m_{13}\,* & -m_{23}\,* & m_{33} \end{bmatrix} \qquad \mathbf{J}=\begin{bmatrix} r_{pp} & r_{ps} \\ r_{ps} & r_{ss} \end{bmatrix}$$

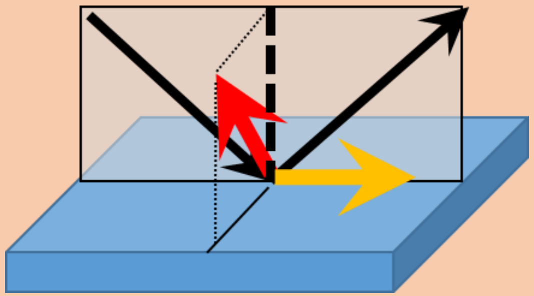
The sample is mirror-symmetric with respect to the plane perpendicular to the incidence plane and containing the sample normal

* The elements with an asterisk vanish when **J** is real

Uniaxial

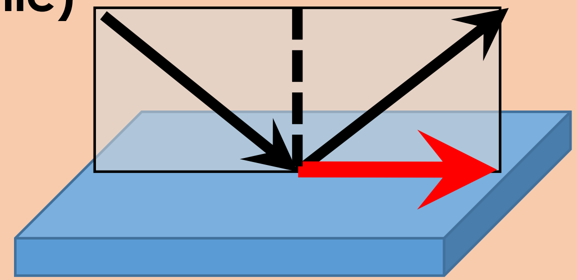


Biaxial (orthorombic)



Arrows are Principal axes (P.A)

Biaxial (monoclinic)



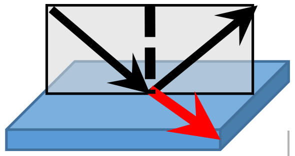
Arrow is P. A.

A general idea about anisotropy and ellipsometry

Samples with zero or small cross-polarization elements can still be anisotropic.

$$\mathbf{M}=\begin{bmatrix} m_{00} & m_{01} & m_{02} & m_{03} \\ m_{10} & m_{11} & m_{12} & m_{13} \\ m_{20} & m_{21} & m_{22} & m_{23} \\ m_{30} & m_{31} & m_{32} & m_{33} \end{bmatrix} \quad \mathbf{J}=\begin{bmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{bmatrix}$$

- In the semi-infinite case (reflection from a **single anisotropic interface**), cross polarization elements tend to be **small**.



E.g. Reflection on a calcite substrate

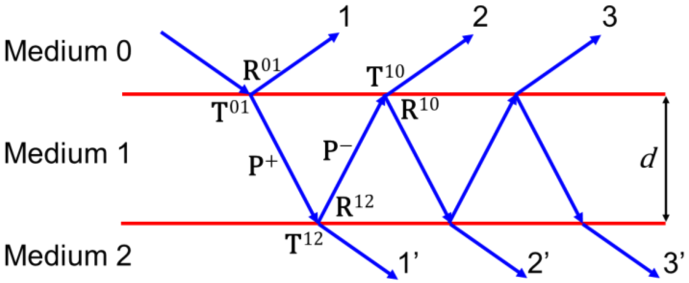
AOI 65º

$\varepsilon_o = 2.749$

$\varepsilon_e = 2.208$

1	-0.8864	-0.08172	0
-0.8864	0.9877	0.1331	0
0.08172	-0.1331	0.4434	0
0	0	0	0.4557

- Anisotropic layers:



Bulk propagation contributes to the measurement → Crosspolarization elements can be **large**

Calculations and data analysis for anisotropic materials

THEORY

CONSTITUTIVE TENSORS

↓

Light propagation in anisotropic media:
Matrix Wave equation
(Berreman formulation based on 4x4 matrices)

↓

MATRIX MULTIPLICATION of complex 4x4 matrices (forward and backward propagating waves) →

EXPERIMENT

MUELLER MATRIX
(partial or complete)

↓

Complex reflection Coefficients

Compare/Fit calculated and measured data

Abelés matrices 2x2 → Berreman matrices 4x4

s- and p- polarizations are eigenmodes and can be *treated separately*

s- and p- polarized light are not eigenmodes

Calculations for anisotropic materials: constitutive equations

$$\vec{D} = \boldsymbol{\varepsilon}\vec{E} - i\boldsymbol{\alpha}\vec{H}$$

$$\vec{B} = \boldsymbol{\mu}\vec{H} + i\boldsymbol{\alpha}^T\vec{E}$$

Electric Permittivity $\boldsymbol{\varepsilon}$

Magnetic permeability $\boldsymbol{\mu}$

Optical activity - Gyration $\boldsymbol{\alpha}$

- Frequency dependent; complex valued if material is absorbing light.
- # of parameters depends on symmetry of the crystal.
- Become diagonal in a special coordinate system of the crystal,

E.g.

$$\boldsymbol{\varepsilon} = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{13} & \varepsilon_{23} & \varepsilon_{33} \end{bmatrix} \longrightarrow \mathbf{A}\boldsymbol{\varepsilon}\mathbf{A}^{-1} = \begin{bmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{bmatrix}$$

A is a orthogonal transformation matrix

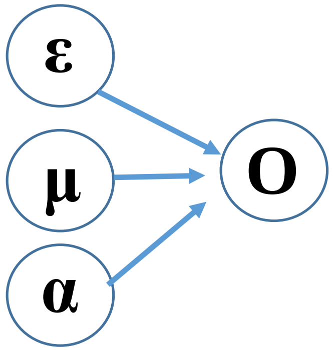
$$\mathrm{A}^T = \mathrm{A}^{-1}$$

$$\mathbf{A}(\alpha,\beta,\gamma) = \begin{bmatrix} C_\alpha C_\gamma - C_\beta S_\alpha S_\gamma & -C_\alpha S_\gamma - C_\beta C_\gamma S_\alpha & S_\alpha S_\beta \\ C_\gamma S_\alpha + C_\alpha C_\beta S_\gamma & C_\alpha C_\beta C_\gamma - S_\alpha S_\gamma & -C_\alpha S_\beta \\ S_\beta S_\gamma & C_\gamma S_\beta & C_\beta \end{bmatrix}$$

Calculations for anisotropic materials: matrix wave equation

Combining constitutive equations into a 6x6 matrix equation,

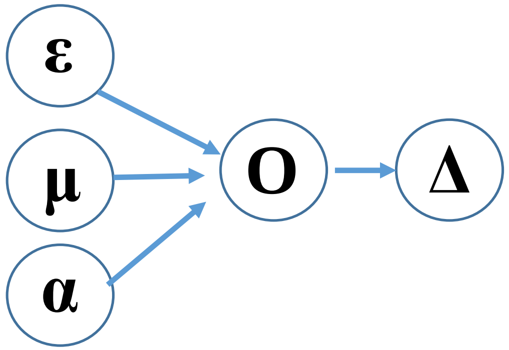
$$\begin{bmatrix}\vec{D}\\ \vec{B}\end{bmatrix} = \begin{bmatrix}\boldsymbol{\varepsilon} & -i\boldsymbol{\alpha}\\ \boldsymbol{\alpha}^{\mathrm{T}} & \boldsymbol{\mu}\end{bmatrix}\begin{bmatrix}\vec{E}\\ \vec{H}\end{bmatrix} = \mathbf{O}\begin{bmatrix}\vec{E}\\ \vec{H}\end{bmatrix}$$

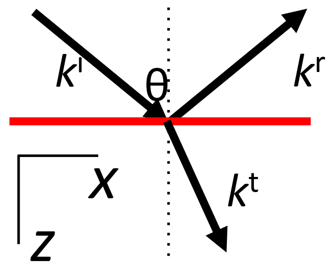


Derivation of a matrix wave equation:

$$\frac{\partial}{\partial z}\begin{bmatrix}E_x\\ H_y\\ E_y\\ -H_x\end{bmatrix} = -i\omega\begin{bmatrix}\Delta_{11} & \Delta_{12} & \Delta_{12} & \Delta_{14}\\ \Delta_{21} & \Delta_{22} & \Delta_{23} & \Delta_{24}\\ \Delta_{31} & \Delta_{32} & \Delta_{33} & \Delta_{34}\\ \Delta_{41} & \Delta_{42} & \Delta_{43} & \Delta_{44}\end{bmatrix}\begin{bmatrix}E_x\\ H_y\\ E_y\\ -H_x\end{bmatrix} \rightarrow \frac{\partial}{\partial z}\boldsymbol{\psi} = -i\omega\boldsymbol{\Delta}\boldsymbol{\psi}$$

4x4 Berreman matrix





[D. W. Berreman, J. Opt. Soc. Am A, 502-510 (1972)]

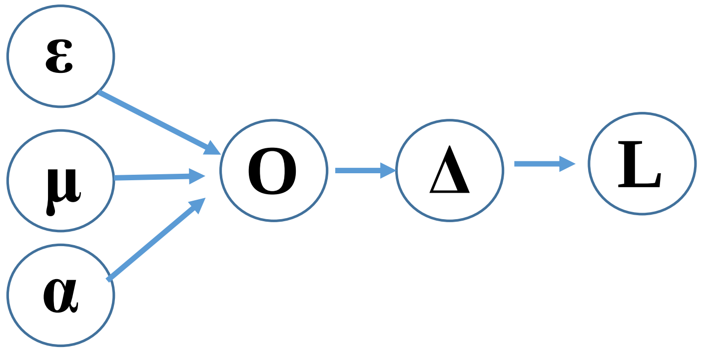
The details of the calculations are not shown in this tutorial!

Calculations for anisotropic materials: wave equation solution

Solving the partial differential equation for a <u>homogeneous</u> layer of thickness *d*:

$$\boldsymbol{\psi}(z+d) = \underbrace{\exp(-i\omega\boldsymbol{\Delta} d)}\boldsymbol{\psi}(z) = \mathbf{L}(d)\boldsymbol{\psi}(z)$$

This matrix exponential can only handled analytically in relatively simple cases → In general: Matrix diagonalization



The *s* and *p* fields at each (multi)layer side are related by:

$$\begin{pmatrix} E_p^+(0) \\ E_p^-(0) \\ E_s^+(0) \\ E_s^-(0) \end{pmatrix} = \mathbf{M} \begin{pmatrix} E_p^+(d) \\ E_p^-(d) \\ E_s^+(d) \\ E_s^-(d) \end{pmatrix}$$

(Here **M** is NOT a Mueller matrix)

- A single interface: $\mathbf{M} = \boldsymbol{\Psi}_0^{-1}\boldsymbol{\Psi}_e$ (note there is no bulk contribution)
- A single slab: $\mathbf{M} = \boldsymbol{\Psi}_0^{-1}\mathbf{L}(-d)\boldsymbol{\Psi}_e$
- A multilayer: $\mathbf{M} = \boldsymbol{\Psi}_0^{-1}\mathbf{L}_1(-d_1)\mathbf{L}_2(-d_2)\ldots\mathbf{L}_N(-d_N)\boldsymbol{\Psi}_e$

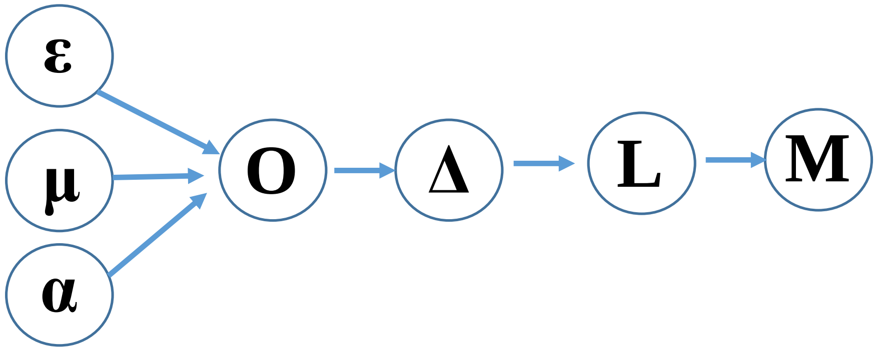
Ambient matrix medium (usually isotropic)

$$\boldsymbol{\Psi}_0 = \begin{bmatrix} \cos\theta_0 & -\cos\theta_0 & 0 & 0 \\ n_0 & n_0 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & n_0\cos\theta_0 & -n_0\cos\theta_0 \end{bmatrix}$$

Substrate (exit) matrix medium (isotropic/anisotropic)

↓

$\boldsymbol{\Psi}_e$



Calculations for anisotropic materials: result

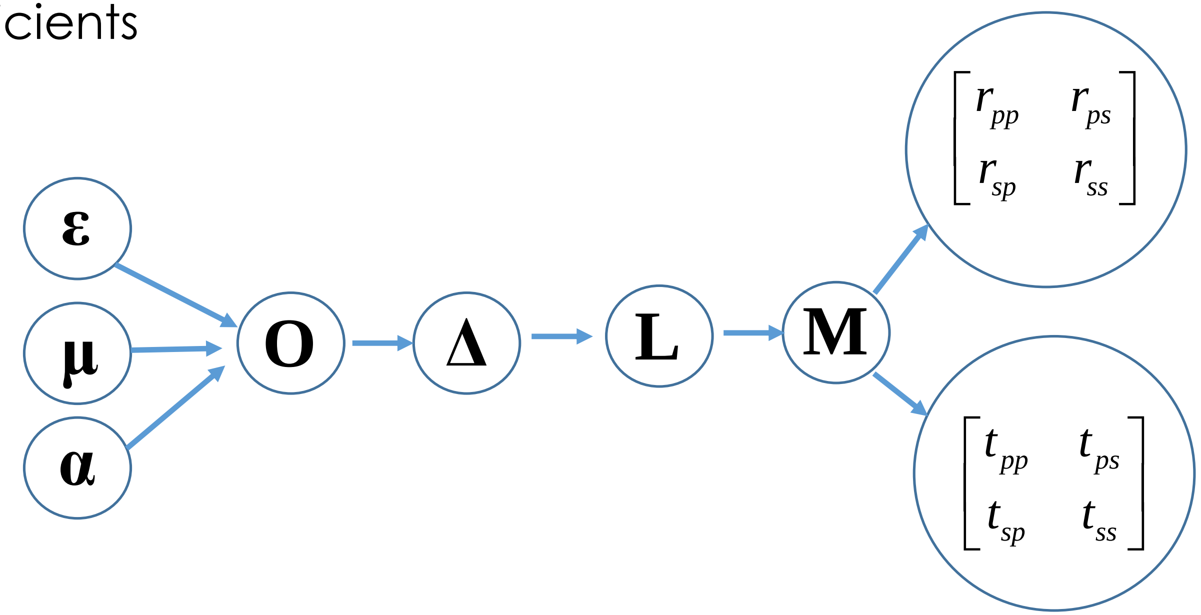
Last step: calculating reflection and transmission coefficients

$$r_{pp} = \frac{M_{12}M_{20} - M_{10}M_{22}}{M_{02}M_{20} - M_{00}M_{22}} \qquad t_{pp} = \frac{M_{22}}{M_{00}M_{22} - M_{02}M_{20}}$$

$$r_{ss} = \frac{M_{30}M_{02} - M_{32}M_{00}}{M_{02}M_{20} - M_{00}M_{22}} \qquad t_{ss} = \frac{M_{00}}{M_{00}M_{22} - M_{02}M_{20}}$$

$$r_{ps} = \frac{M_{32}M_{20} - M_{30}M_{22}}{M_{02}M_{20} - M_{00}M_{22}} \qquad t_{ps} = \frac{-M_{20}}{M_{00}M_{22} - M_{02}M_{20}}$$

$$r_{sp} = \frac{M_{10}M_{02} - M_{12}M_{00}}{M_{02}M_{20} - M_{00}M_{22}} \qquad t_{sp} = \frac{-M_{02}}{M_{00}M_{22} - M_{02}M_{20}}$$



The scheme is adapted from:

R M A Azzam and N M Bashara
Ellipsometry and Polarized Light
North Holland (1977).

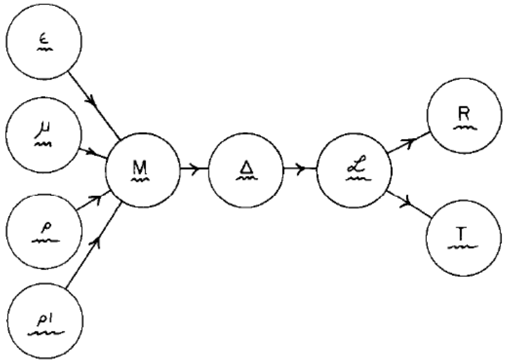


Fig. 4.41. Schematic flow chart of the steps required for the calculation of the reflection and transmission matrices ***R*** and ***T*** from the dielectric ***ε***, magnetic permeability ***μ*** and optical activity (rotation) ***ρ***, ***ρ'*** tensors.

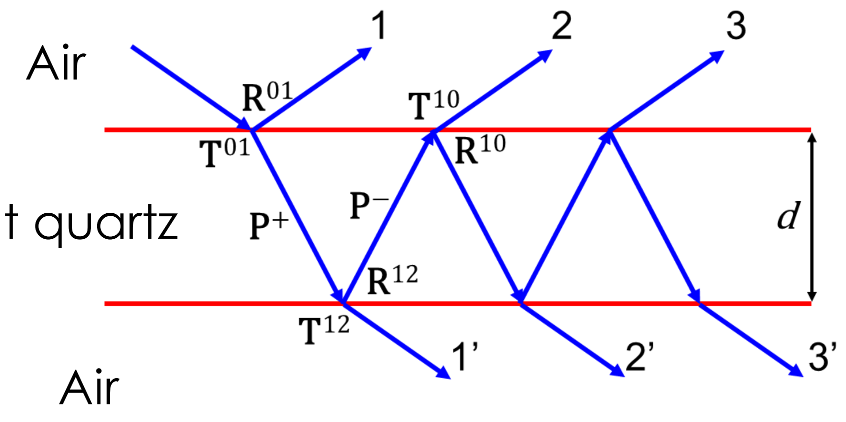
Examples. Quartz crystal

Quartz is uniaxial and it also has optical activity

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{11} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix} \qquad \boldsymbol{\alpha} = \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix} \qquad \boldsymbol{\mu} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

To determine *both* $\boldsymbol{\varepsilon}$ and $\boldsymbol{\alpha}$ it is convenient to **do both reflection and transmission measurements**.

(reflection measurements have poor sensitivity to $\boldsymbol{\alpha}$ elements)



d=1mm

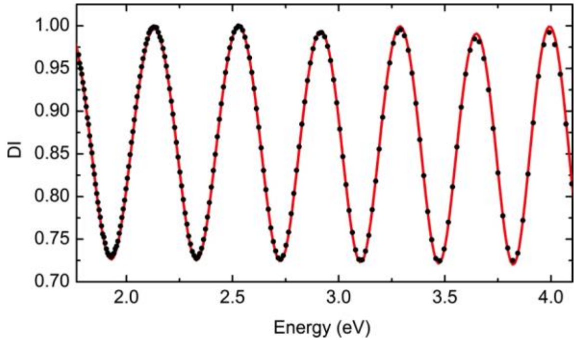
Incoherent sum of waves

↓

Depolarization

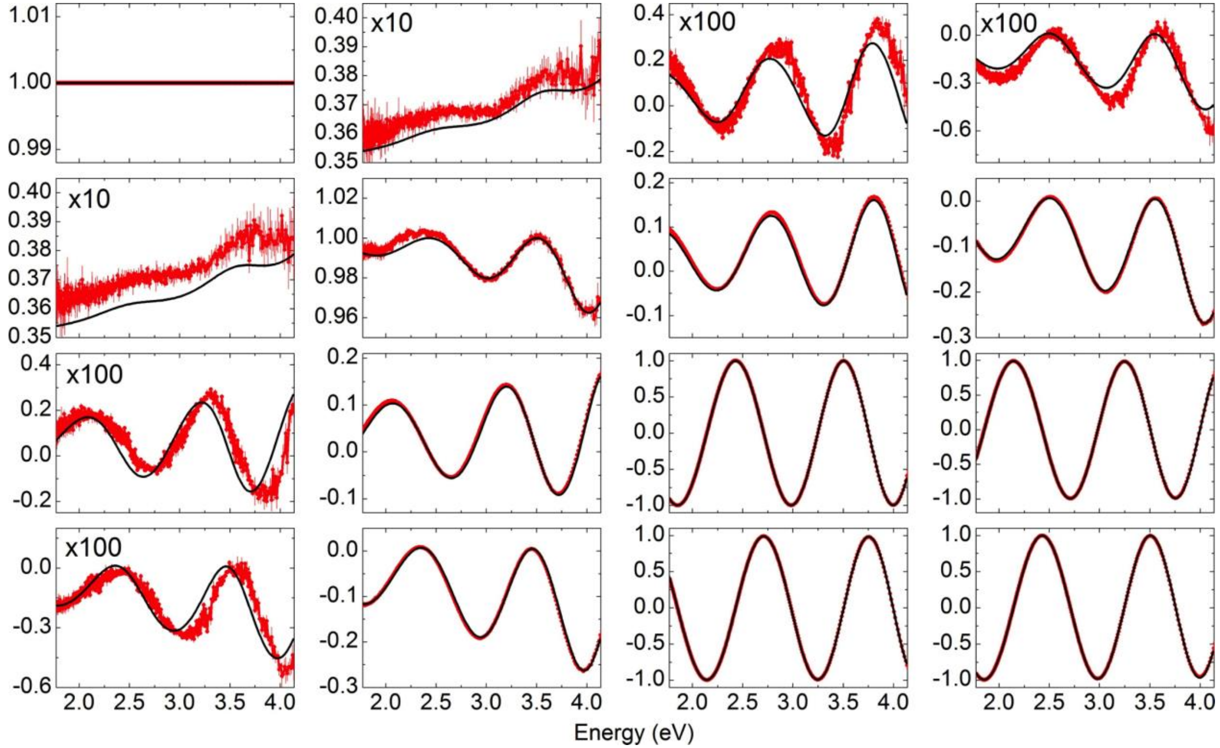
↓

Complete Mueller matrix measurements needed

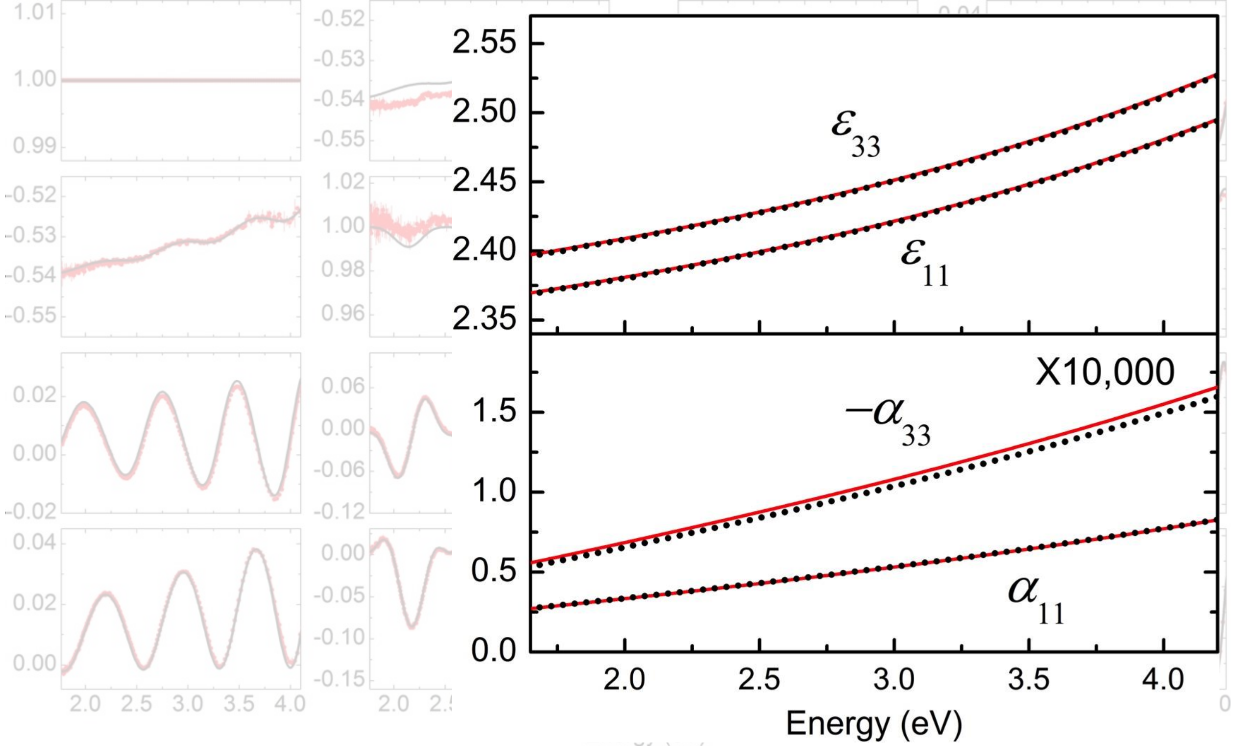


Examples. Quartz crystal

1 mm [001] quartz; Transmission. AOI = 30°



1 mm [001] quartz; Reflection. AOI = 36°



INPUT

2 Mueller matrix measurements in transmission (AOI 0° and 30°)
4 Mueller matrix measurements in reflection (AOI 36° to 56°)

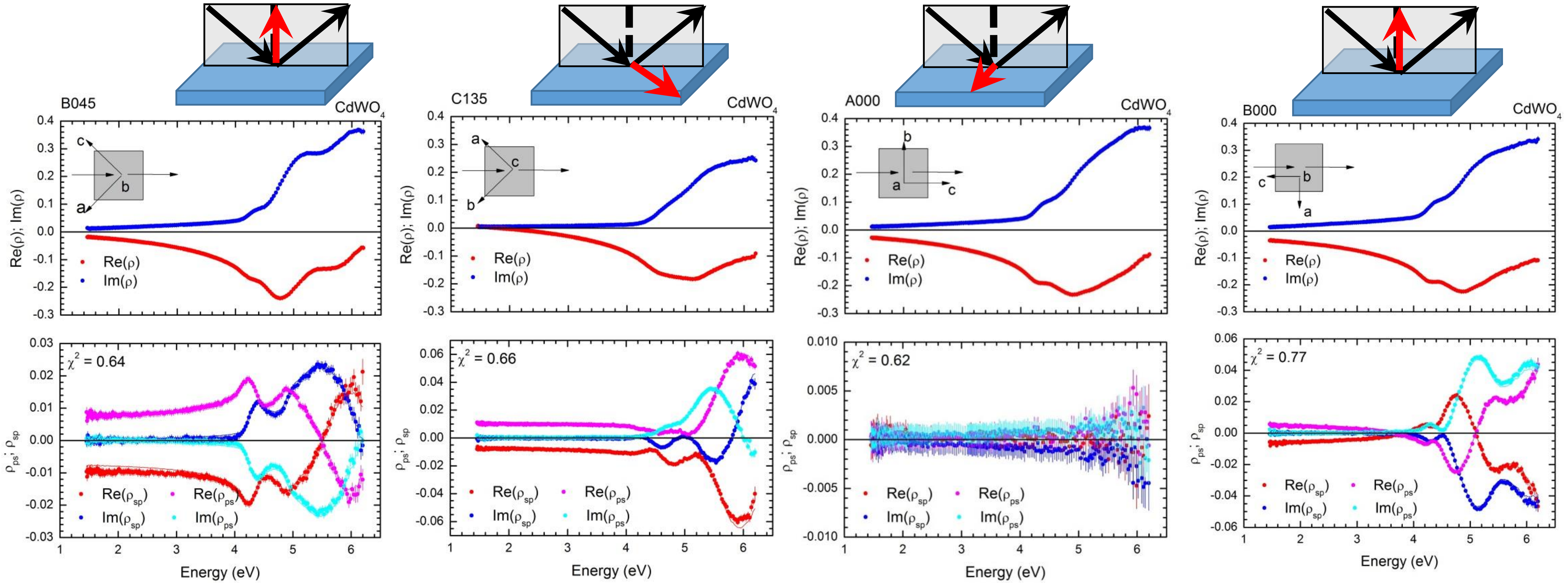
MAIN OUTPUTS

2 real parameters (dielectric) + 2 real parameters (gyration), thickness

S. Nichols, O. Arteaga, A. Martin, B. Kahr. *JOSA A*, 32, **2015**, 2049.

Examples. Monoclinic $CdWO_4$

Monoclinic $CdWO_4$



$$\begin{bmatrix} \rho & \rho_{ps} \\ -\rho_{ps} & 1 \end{bmatrix} \quad \begin{bmatrix} \rho & \rho_{ps} \\ \rho_{sp} & 1 \end{bmatrix} \quad \begin{bmatrix} \rho & 0 \\ 0 & 1 \end{bmatrix} \quad \begin{bmatrix} \rho & \rho_{ps} \\ -\rho_{ps} & 1 \end{bmatrix}$$

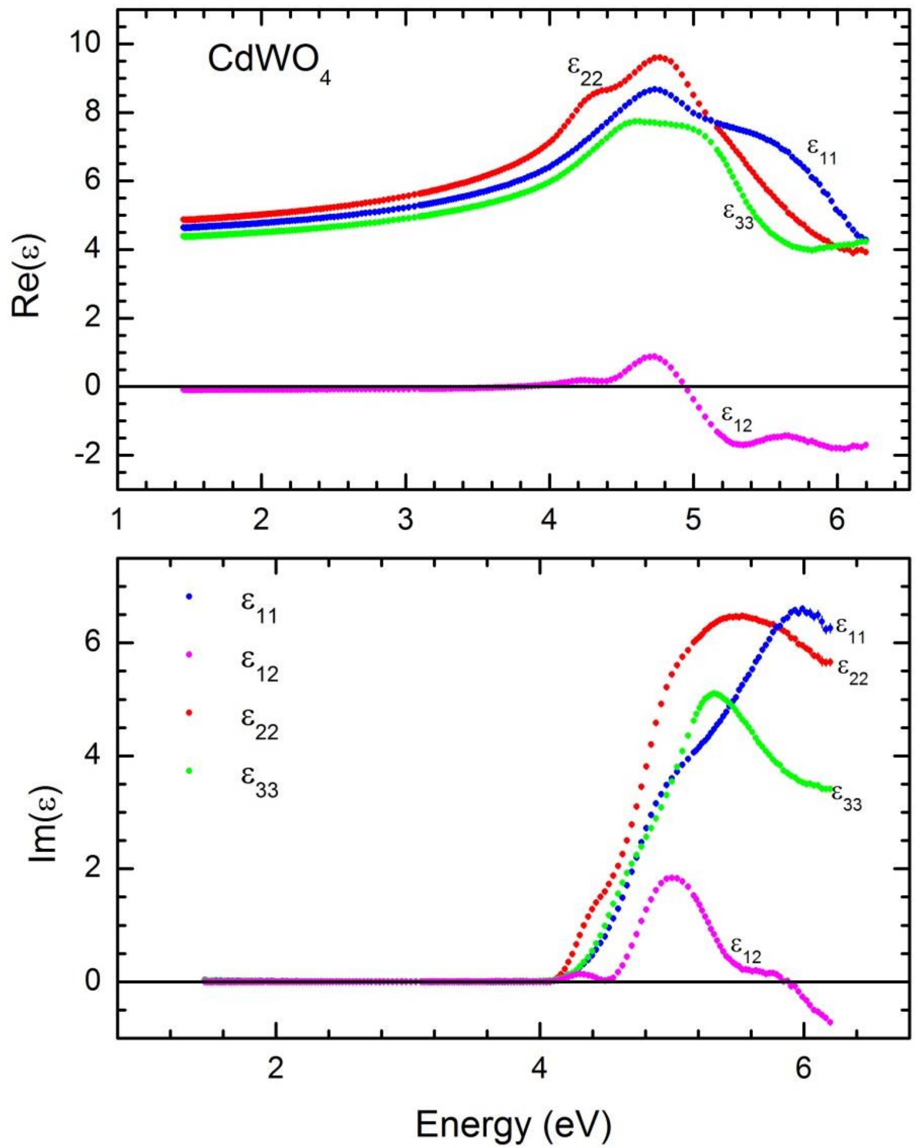
Jellison, McGuire, Boatner, Budai, Specht, and Singh, *Phys. Rev. B* **84**, 195439 (2011).

Examples. Monoclinic $CdWO_4$

- Crystal structure: C_{2h} (2/m)=> monoclinic
  - β=91.5°
- Overdetermined sytem
  - Complete generalized ellipsometry measurements (ρ, ρ_{sp}, ρ_{ps}) 6 parameters
  - Measure 3 orthogonal faces, 4 measurements on each face, each rotated by 45° (12 GE measurements).
  - Fit to 4 complex number **for each wavelength**

$$\boldsymbol{\varepsilon} = \begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & 0 \\ \varepsilon_{12} & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{bmatrix}$$

Data analysis for anisotropic crystals is often made by **collecting as much data as possible** (e.g. multiple faces, multiple azimuths, multiple AOI) and doing a fit for each wavelength (i. e. without considering a dispersion relation).



Some extra references of ellipsometry on anisotropic crystals

This is not an exhaustive list!

Rutile TiO2 (uniaxial)

- M. Schubert, B. Rheinlander, J. A. Woollam, B. Johs, and C. M. Herzinger, J. Opt Soc. Am. A 13, 875 (1996)
- G. E. Jellison, F. A. Modine, and L. A. Boatner, Opt. Lett. 22, 1808 (1997)
- T. Tiwald and M. Schubert, Proc. SPIE 4103, 19 (2000).
- G. E. Jellison, L. A. Boatner, J. d. Budai, B.-S. Jeong and D. P. Norton, J. Appl. Phys. 93, 9537 (2003).

ZnO (uniaxial)

- G. E. Jellison, L. A. Boatner, Phys. Rev. B **58**, 3586 (1998).

KTP (uniaxial and optically active)

- C. Sturm, V. Zviagin and M. Grundmann, Opt. Letter 44 (2019).

Ga_2O_3 (monoclinic)

- C. Sturm, J. Furthmüller, F. Beschstedt, R. Schimidt-Grund, M. Grundmann, APL materials 3, 106106 (2015).
- T. Onuma, S. Saito, K. Sasaki, T. Masui, T. Yamaguchi, T. Honda, A. Kuramta, and M. Higashiwaki, Jpn. J. Appl. Phys., 55 1202B2, (2016)
- M. Schubert et al., Phys. Rev. B 93, 125209, (2016). [IR]

PTCDA (monoclinic)

- M.I. Alonso, M. Garriga, J. O. Ossó, F. Schreiber, R. Scholz, Thin solid film 571, 420-425.

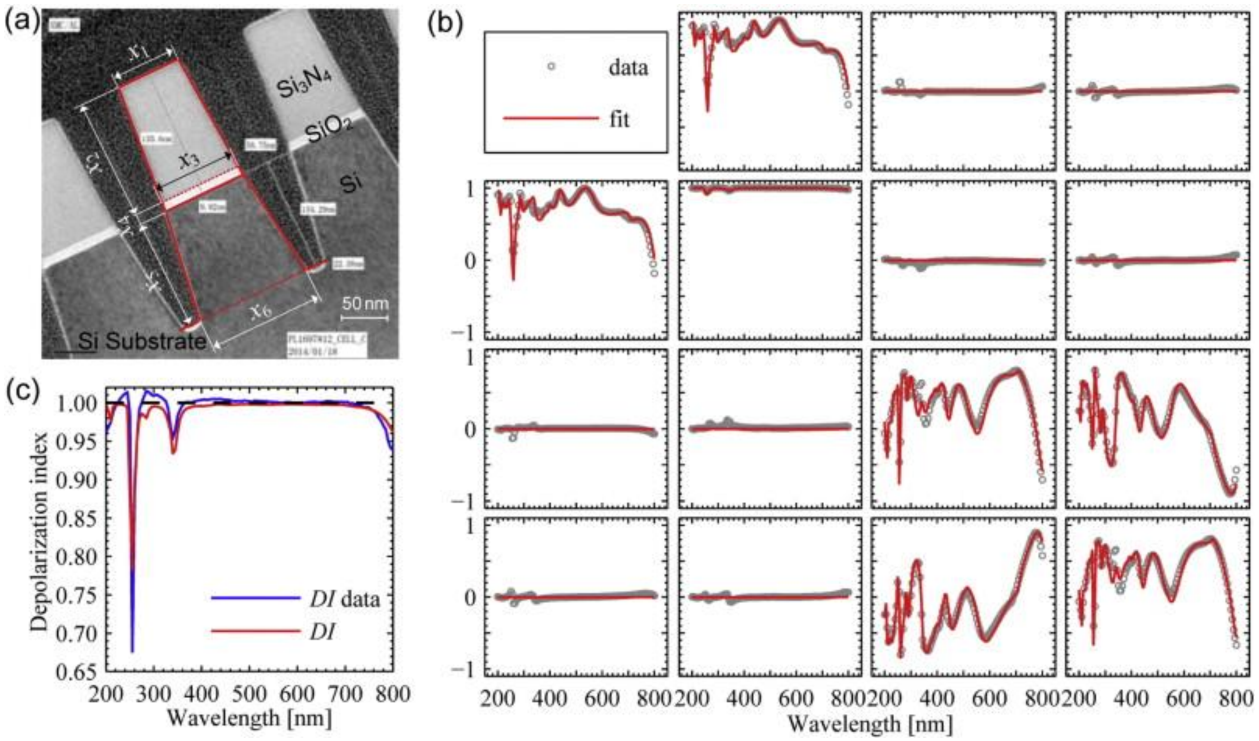
$AgGaS_2$ (uniaxial and optically active)

- O. Arteaga, Opt. Lett. 40, 4277-4280 (2015).

But not only crystals!

Anisotropy is not exclusive of crystals. Many samples that exhibit **structural (form) anisotropy** can be studied by ellipsometry

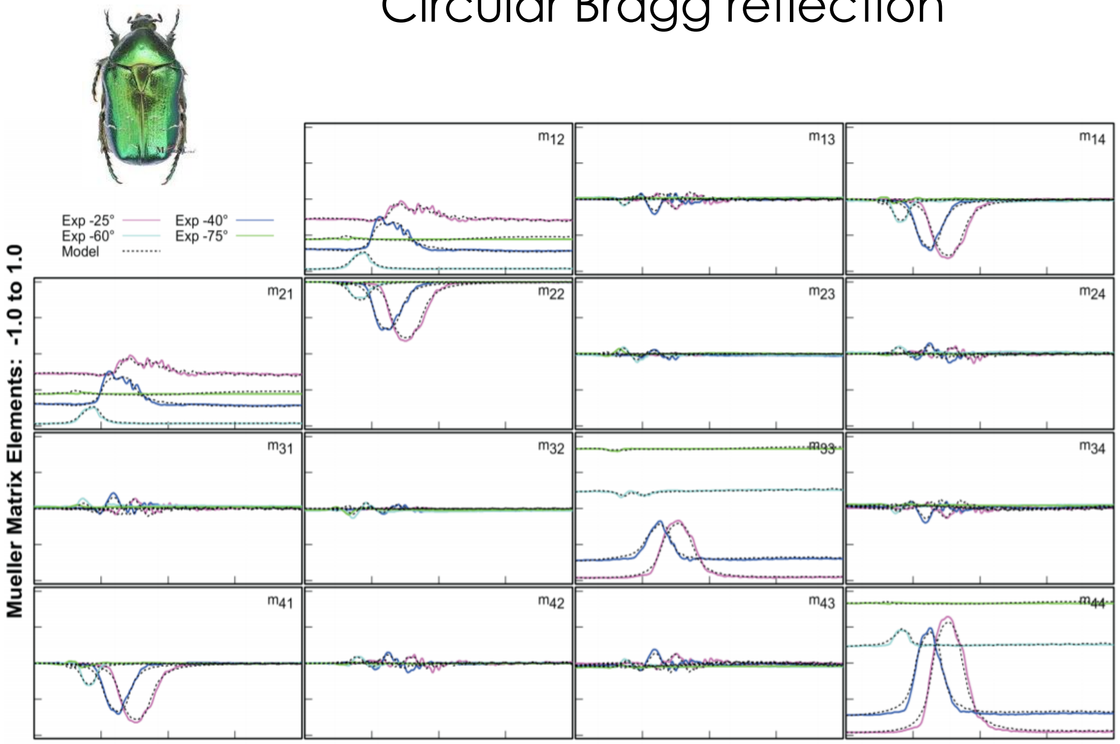
Mueller matrix scatterometry



S. Liu, X. Chen, and C. Zhang, Thin Solid Films 584, 176-185 (2015)

See the next tutorial!

Circular Bragg reflection



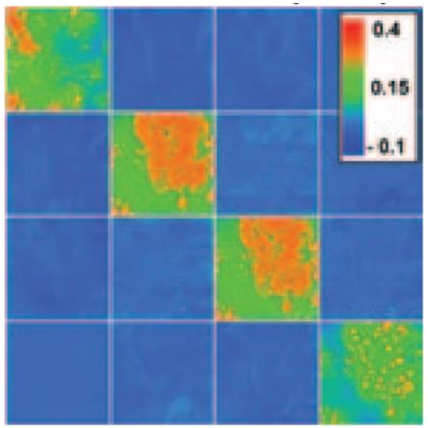
H. Arwin, T. Berlind, B. Johs and K. Järrendahl, Optics Exp. 21, 22645-22656 (2013)

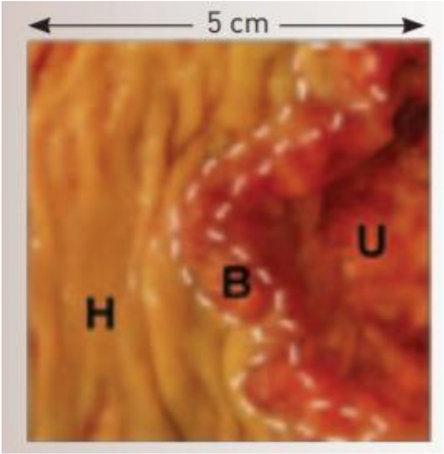
More aplications

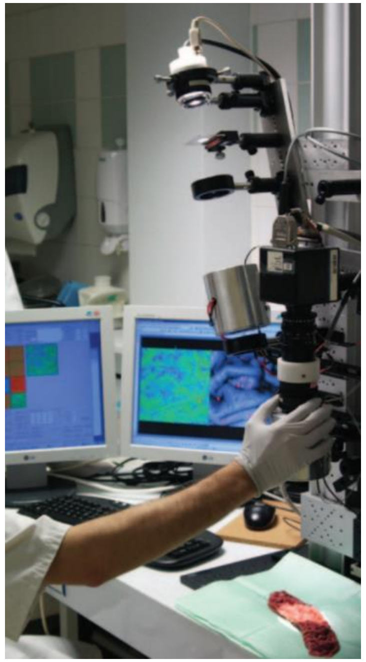
The study of anisotropic samples is at the core of many other applications of ellipsometry/polarimetry.

Biomedical applications: tissue analysis

- Typically measured at normal incidence backscattering
- Phenomenological analysis of Retardation, diattenuadion and depolarization of parts of the tissue. (Healthy vs pathologic tissues)
- **Imaging** is essential!





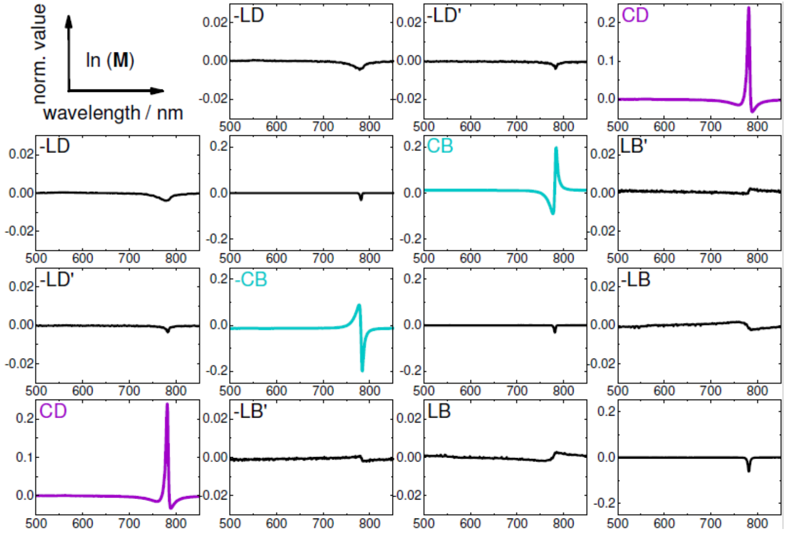


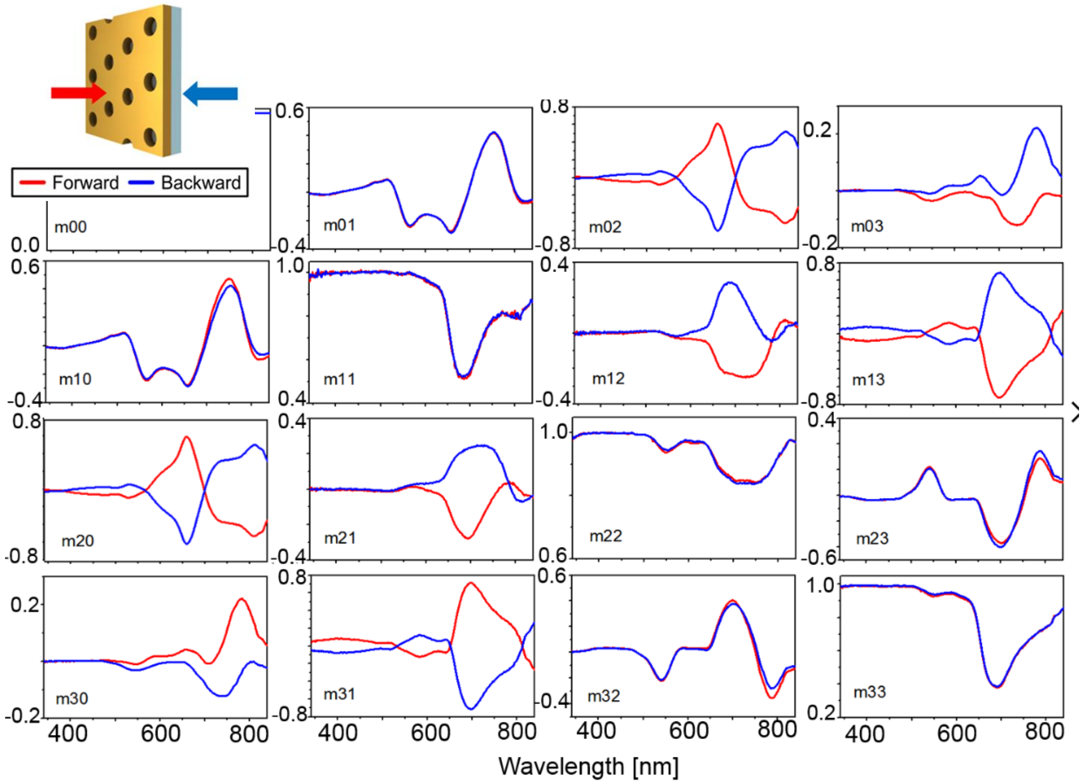
T. Novikova, A. Pierangelo, A. De Martino, A. Benali, P. Validire, Opt. and Phot. News 23, 26-33 (2012)

Chiroptical studies

- Typically measured at normal incidence transmission.
- Phenomenological detection of circular dichroism and circular birefringence together with linear dichroism/birefringence.
- **Sensitivity** is often very important

$$\begin{bmatrix} A & -LD & -LD' & CD \\ -LD & A & CB & LB' \\ -LD' & -CB & A & -LB \\ CD & -LB' & LB & A \end{bmatrix}$$





M. Schulz et al. M. *Nat. Commun.* **2018**, 9, 2413,

O. Arteaga et al., *Opt. Express*, **22**, 13719, (2014)

Some questions

I have an anisotropic sample, can I study it with standard ellipsometry?

Most likely yes, although Mueller matrix ellipsometry is argueably better suited. The measured ρ will be correct. Reorientations are going to be necessary. Will fail if there is some significant depolarization

I have an isotropic sample, is there any advantage in using Mueller matrix ellipsometry/generalized ellipsometry?

Standard ellipsometry offers the required data. However, checking the matrix symmetries can help to reach a perfect alignment of the sample.

I measure a weak cross-polarization, does it is mean the sample is weakly anisotropic?

Not necessarily. Expect small cross-polarization elements in semi-infinite systems (i.e. single interface systems). Large cross-polarization often come from bulk contributions. In transmission bulk contributions dominate.

My sample is depolarizing, can it be still studied?

Depolarization is not something intrinsic of a sample but a combination of: sample + instrument (light source and detector). Try to adjust your instrument (e.g. increase the coherence length) or add incoherence to your model.

The measured Mueller matrix does not have any apparent symmetry, does it mean that the system is depolarizing?

NO. Symmetries are satisfied by both depolarizing and nondepolarizing systems. A nondepolarizing Mueller matrix can also be completely asymmetric if the sample shows no symmetries with respect to the plane of incidence.

The end

Thank you!