PHS6317
NANO-ENGINEERING OF THIN FILMS

Bill Baloukas, Eng., Ph.D.
Research Professional with the FCSEL
bill.baloukas@polymtl.ca
www.polymtl.ca/larfis

Based on the notes first prepared in 2008 by Stéphane Larouche
Research Professor
Center for Metamaterials and Integrated Plasmonics
Electrical and Computer Engineering Department
Pratt School of Engineering, Duke University

Winter 2024

Bienvenue - Welcome

POLYTECHNIQUE
MONTRÉAL

PHS 6317 Nanoengineering of thin films

Course schedule – Winter 2024

12 January	Introduction – Scientific and technological challenges
19	Fabrication methods – Vacuum physics and vapor-phase techniques
26*	Fabrication methods – Plasma processes and process optimization
2 February	Fabrication methods - Plasma-surface interactions and diagnostics
9**	Fabrication methods – Thermal/Plasma spray technologies
16*	Optics of thin films 1, optical characterization, *Miniquiz 1 (5%)*
23*	Optics of thin films 2, design of optical filters
1*** March	*Presentations – Emerging fabrication techniques (30%)*
	March 4-8 - Winter/Spring break
15**	Tribomechanical properties of films and coatings
22**	Electrochemical properties – corrosion and tribo-corrosion*(filter-20%)*
5 April	Passive functional films and coatings, *Miniquiz 2 (5%)*
12	Active functional films and coatings
16	Life cycle analysis and environmental impact
19***	*Presentations – Emerging applications of nanostructured films (40%)*

Deadlines:

Project #1 – Fabrication technique:

Choice of the subject: **26 January**

Abstract and references: **9 February**

Report and presentation: **1st March**

Projet #2 – Design of an optical filter:

Choice of the subject: **23 February**

Report: **22 March**

Projet #3 – Application of nanostructured thin films:

Choice of the subject: **16 February**

Abstract and references: **15 March**

Report and presentation: **19 April**

Evaluation

1. **Project 1:** Bibliographic research on an emerging fabrication technique of thin films - Report and presentation 30%

2. **Project 2:** Design of an optical filter - Report 20%

3. **Project 3:** Bibliographic research on a specific application of the nano- engineering of thin films - Report and presentation 40%

4. **Miniquiz** 1 and 2 (@ 5%) 10%

Project 2: Design of an optical filter (20%)

Specific requirements:

Deliverables: Report, maximum 8 pages (letter size paper, 2 cm margins, Times New Roman 12 pts).

Structure and contents:

- Introduction – describe the choice of the specific filter and its application
- Optical specifications of the filter: spectral characteristics in T and R, color coordinates, tolerances, etc.
- Methodology of the design: architecture, materials, optimization, etc.
- Discussion of the performance and sensitivity to the fabrication process
- Conclusions

Deadlines

Choice of filter: **February 23**
Report: ……… **March 22**

PHS 6317 Nanoengineering of thin films

Course schedule – Winter 2022

14 January	Introduction – Scientific and technological challenges
21	Fabrication methods – Vacuum physics and vapor-phase techniques
28*	Fabrication methods – Thermal/Plasma spray technologies
4 February	Fabrication methods – Plasma processes
11*	Fabrication methods - Plasma-surfaces interactions and diagnostics
18***	Optics of thin films 1, optical characterization, *Miniquiz1 (5%)*
25**	Optics of thin films 2, design of optical filters

February 28 - March 4 - Winter/Spring break

11* March	*Presentations – Emerging fabrication techniques (30%)*
18***	Tribomechanical properties of films and coatings
25**	Electrochemical properties – corrosion and tribo-corrosion*(filter-20%)*
1 April	Passive functional films and coatings, *Miniquiz 2 (5%)*
8	Active functional films and coatings
15	Life cycle analysis and environmental impact
19***	*Presentations – Emerging applications of nanostructured films (40%)*

Deadlines:

Project #1 – Fabrication technique:

Choice of the subject: **28 January**

Abstract and references: **11 February**

Report and presentation: **11 March**

Projet #2 – Design of an optical filter:

Choice of the subject: **25 February**

Report: **25 March**

Projet #3 – Application of nanostructred thin films:

Choice of the subject: **18 February**

Abstract and references: **18 March**

Report and presentation: **19 April**

Project 2: Design of an optical filter (20%)

Specific requirements:

Deliverables: Report, maximum 10 pages (letter size paper, 2 cm margins, Times new roman 12 pts)

Structure and contents:

- Introduction – describe the choice of the specific filter
- Optical specifications of the filter: spectral characteristics in *T* and *R*, tolerances, etc.
- Methodology of the design (architecture, materials, optimization,…)
- Discussion of the performance and sensitivity to the fabrication process
- Conclusions

Deadlines:
Choice of the filter: .. **25 February**
Report: ……………. **25 March**

ÉCOLE
POLYTECHNIQUE
MONTRÉAL

Outline

Optical metrology

1. Spectrophotometry
2. Data analysis methodology for spectrophotometric data
    a. The envelope method
3. Spectroscopic ellipsometry
4. Data analysis methodology of ellipsometric data
5. *OpenFilters* design software

Spectrophotometry

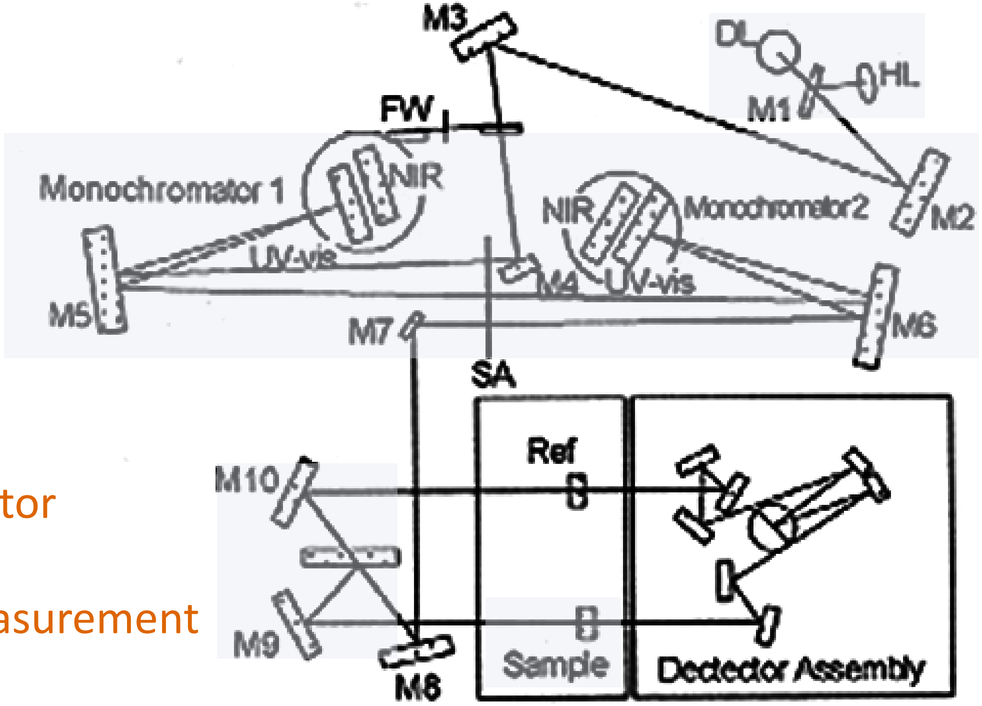
- When designing an optical filter, we are interested in determining :
  - the optical properties of the substrate (n, k);
  - the optical properties of each material that is used (n, k) and their deposition rate, typically through the deposition of a film with thickness X in a given time.
- We also want to know :
  - if the deposited layers are homogeneous;
  - if the layers diffuse light;
  - if they possess a surface or interface roughness.
- Finally, once the filter is fabricated, we want to check its performance.

All these steps can be performed by using spectrophotometry.

ÉCOLE
POLYTECHNIQUE
MONTRÉAL

Spectrophotometer

- A spectrophotometer is a system which allows one to measure the transmission and reflection of a sample.
- The measurements may be specular, diffusive or total.



Lamp sources

Monochromators

Beam selector

-

Reference and measurement

Sample

From: Perkin-Elmer Lambda 19 User Guide.

Substrate characterization

How can we obtain the substrate’s refractive index using its transmission spectrum?

One can demonstrate that the transmission in the low absorption region is given by:

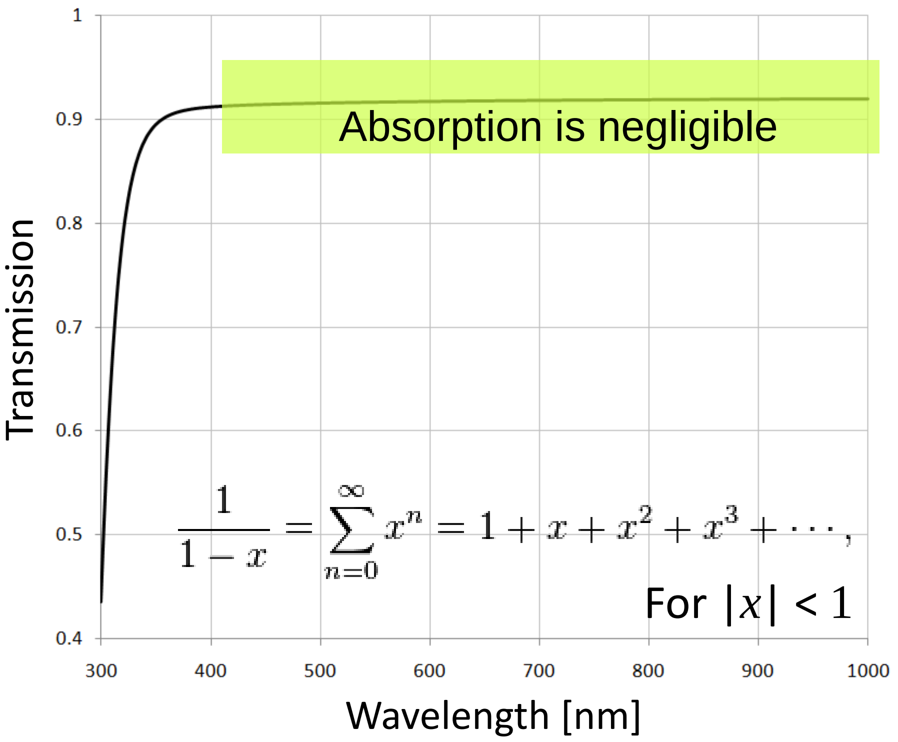
$$T = \frac{(1-R)^2}{(1-R^2)}$$

with R, the reflection coefficient in intensity at an interface:

$$R = \left(\frac{n-1}{n+1}\right)^2$$

We can then demonstrate:

$$n = \left(\frac{1+\left(\frac{1-T}{1+T}\right)^{1/2}}{1-\left(\frac{1-T}{1+T}\right)^{1/2}}\right)$$

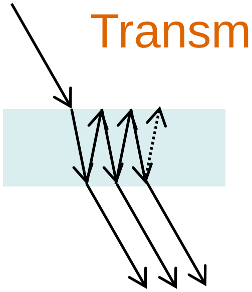


Absorption is negligible

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \cdots,$$

For $|x| < 1$

Transmission of a B270 substrate



$$T = (1-R)^2(1+R^2+R^4+\ldots+R^{2i})$$

where i is an integer

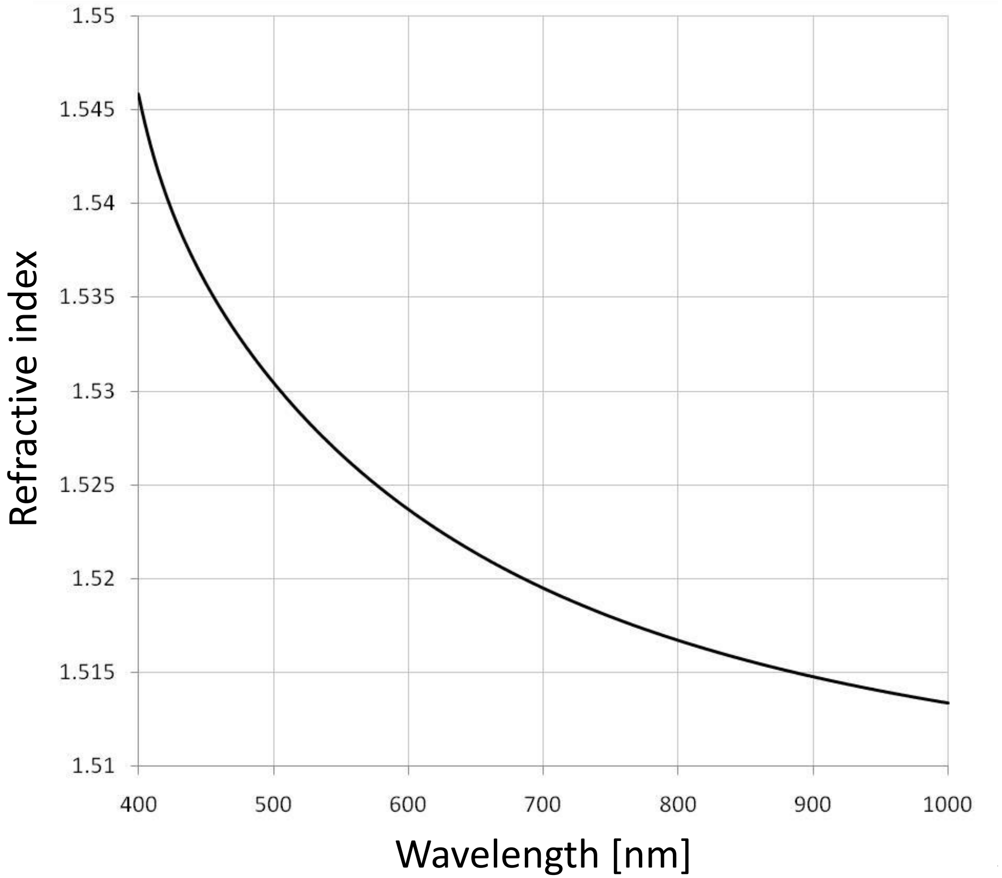
PHS6317 – Nanoengineering of thin films

Chapter 8B

Substrate characterization (2)

ÉCOLE POLYTECHNIQUE MONTRÉAL

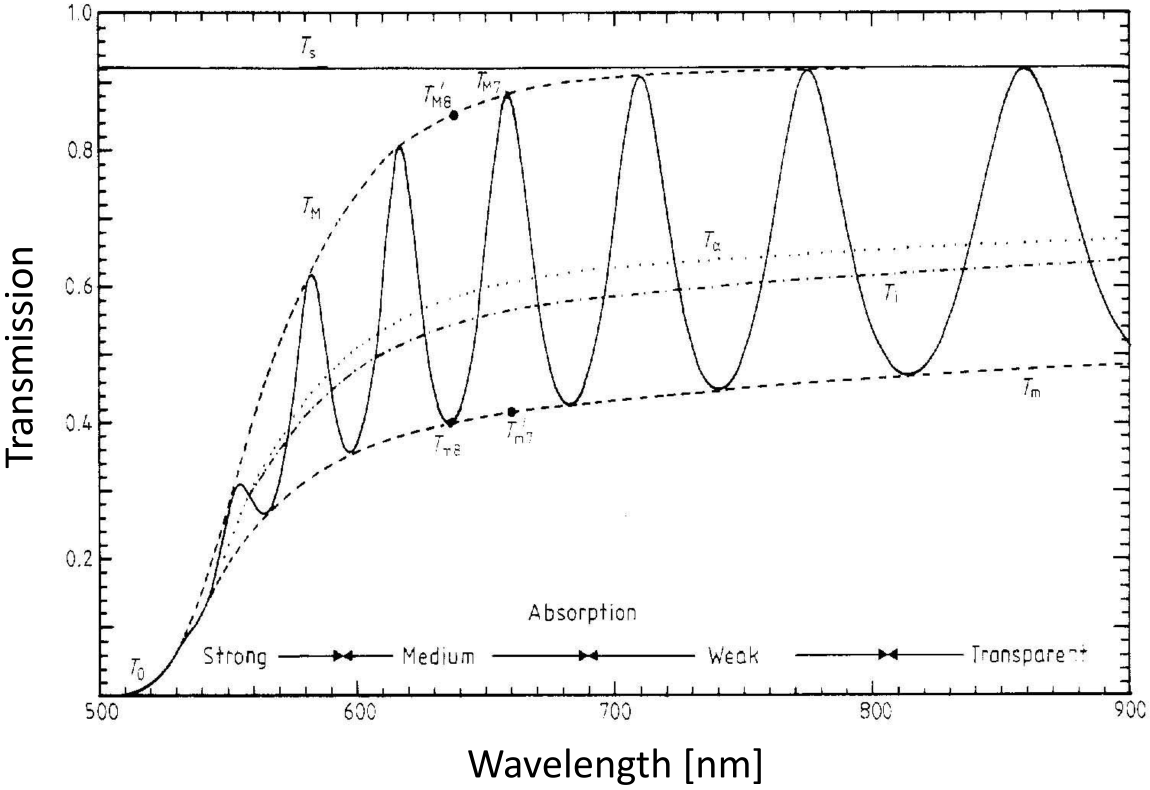
Using the previously defined equation and the transmission spectrum of a B270 glass substrate, we obtain the following refractive index dispersion curve.



Refractive index of a B270 glass substrate.

The envelope method

When studying the transmission or reflection spectra of a thin film on a substrate, one can observe a series of minima and maxima. The traced lines which join all these points together are termed envelopes.



R. Swanepoel, « Determination of the thickness and optical constants of amorphous silicon », *J. Phys. E.*, vol. 16, 1983, p. 1214–1223.

The envelope method (2)

- Let us demonstrate the envelope method in the simplest case: a non-absorbing thin film on a semi-infinite substrate.
- We have seen during the previous course that:

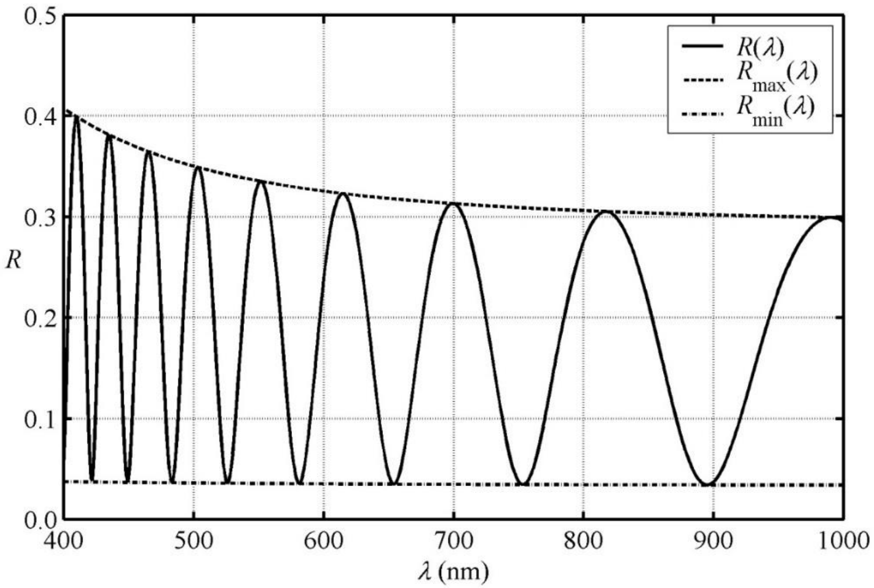
$$r = \frac{r_{2\to1} + r_{1\to0}e^{i2\phi}}{1 + r_{2\to1}r_{1\to0}e^{i2\phi}}$$

where

$$r_{2\to1} = \frac{n_2 - n_1}{n_2 + n_1},$$

$$r_{1\to0} = \frac{n_1 - n_0}{n_1 + n_0} \quad \text{and}$$

$$\phi = 2\pi\frac{N_1 d}{\lambda}.$$



Reflection of a thin film on a glass substrate.

The envelope method (3)

- The minimum envelope $R_{\text{min}}(\lambda)$ corresponds to half-wave points, i.e. the coating is « absent », and therefore, we obtain the reflection spectrum of the substrate.
- The maximum envelope corresponds to quarter-wave points. At these points, exp($i2\phi$) = -1, and consequently

$$r_{\max} = \frac{r_{2\to1} - r_{1\to0}}{1 - r_{2\to1} r_{1\to0}}$$

- By inserting the expressions for the various interface reflections, we obtain:

$$r_{\max} = \frac{\dfrac{n_2 - n_1}{n_2 + n_1} - \dfrac{n_1 - n_0}{n_1 + n_0}}{1 - \dfrac{n_2 - n_1}{n_2 + n_1}\dfrac{n_1 - n_0}{n_1 + n_0}} = \frac{\dfrac{(n_2 - n_1)(n_1 + n_0)}{(n_2 + n_1)(n_1 + n_0)} - \dfrac{(n_2 + n_1)(n_1 - n_0)}{(n_2 + n_1)(n_1 + n_0)}}{\dfrac{(n_2 + n_1)(n_1 + n_0)}{(n_2 + n_1)(n_1 + n_0)} - \dfrac{(n_2 - n_1)(n_1 - n_0)}{(n_2 + n_1)(n_1 + n_0)}}$$

$$= \frac{(n_2 - n_1)(n_1 + n_0) - (n_2 + n_1)(n_1 - n_0)}{(n_2 + n_1)(n_1 + n_0) - (n_2 - n_1)(n_1 - n_0)} = \frac{2n_2 n_0 - 2n_1^2}{2n_2 n_0 + 2n_1^2}$$

The envelope method (4)

- To obtain the reflection in intensity, we multiply *r* by its complex conjugate:

$$R_{\max} = r_{\max} r_{\max}^{*} = \left(\frac{2n_2 n_0 - 2n_1^2}{2n_2 n_0 + 2n_1^2} \right)^2 = \frac{4n_2^2 n_0^2 - 8n_2 n_1^2 n_0 + 4n_1^4}{4n_2^2 n_0^2 + 8n_2 n_1^2 n_0 + 4n_1^4}$$

which allows us to obtain:

$$R_{\max}\left(4n_2^2 n_0^2 + 8n_2 n_1^2 n_0 + 4n_1^4\right) = 4n_2^2 n_0^2 - 8n_2 n_1^2 n_0 + 4n_1^4$$
$$\rightarrow 4n_2^2 n_0^2 (R_{\max} - 1) + 8n_2 n_0 (R_{\max} + 1) n_1^2 + 4(R_{\max} - 1) n_1^4 = 0$$

which is a quadratic equation in $n_1{}^2$.

ÉCOLE POLYTECHNIQUE MONTRÉAL

The envelope method (5)

- The solution of this quadratic equation is:

$$n_1^2 = \frac{-8n_2n_0\left(R_{\max}+1\right)\pm\sqrt{64\left(R_{\max}+1\right)^2 n_2^2 n_0^2 - 64\left(R_{\max}-1\right)^2 n_2^2 n_0^2}}{8\left(R_{\max}-1\right)}$$

$$= \frac{-8n_2n_0\left(R_{\max}+1\right)\pm 8n_2n_0\sqrt{\left(R_{\max}+1\right)^2-\left(R_{\max}-1\right)^2}}{8\left(R_{\max}-1\right)}$$

$$= n_2n_0\frac{-\left(R_{\max}+1\right)\pm\sqrt{\left(R_{\max}+1\right)^2-\frac{\left(R_{\max}+1\right)^2\left(R_{\max}-1\right)^2}{\left(R_{\max}+1\right)^2}}}{\left(R_{\max}-1\right)}$$

$$= n_2n_0\frac{-\left(R_{\max}+1\right)\pm\left(R_{\max}+1\right)\sqrt{1-\frac{\left(R_{\max}-1\right)^2}{\left(R_{\max}+1\right)^2}}}{\left(R_{\max}-1\right)}$$

$$= n_2n_0\left(-\frac{\left(R_{\max}+1\right)}{\left(R_{\max}-1\right)}\pm\frac{\left(R_{\max}+1\right)}{\left(R_{\max}-1\right)}\sqrt{1-\frac{\left(R_{\max}-1\right)^2}{\left(R_{\max}+1\right)^2}}\right) = n_2n_0\left(-\frac{\left(R_{\max}+1\right)}{\left(R_{\max}-1\right)}\pm\sqrt{\frac{\left(R_{\max}+1\right)^2}{\left(R_{\max}-1\right)^2}-1}\right)$$

where the sign is chosen in order to obtain a physically acceptable solution.

The envelope method (6)

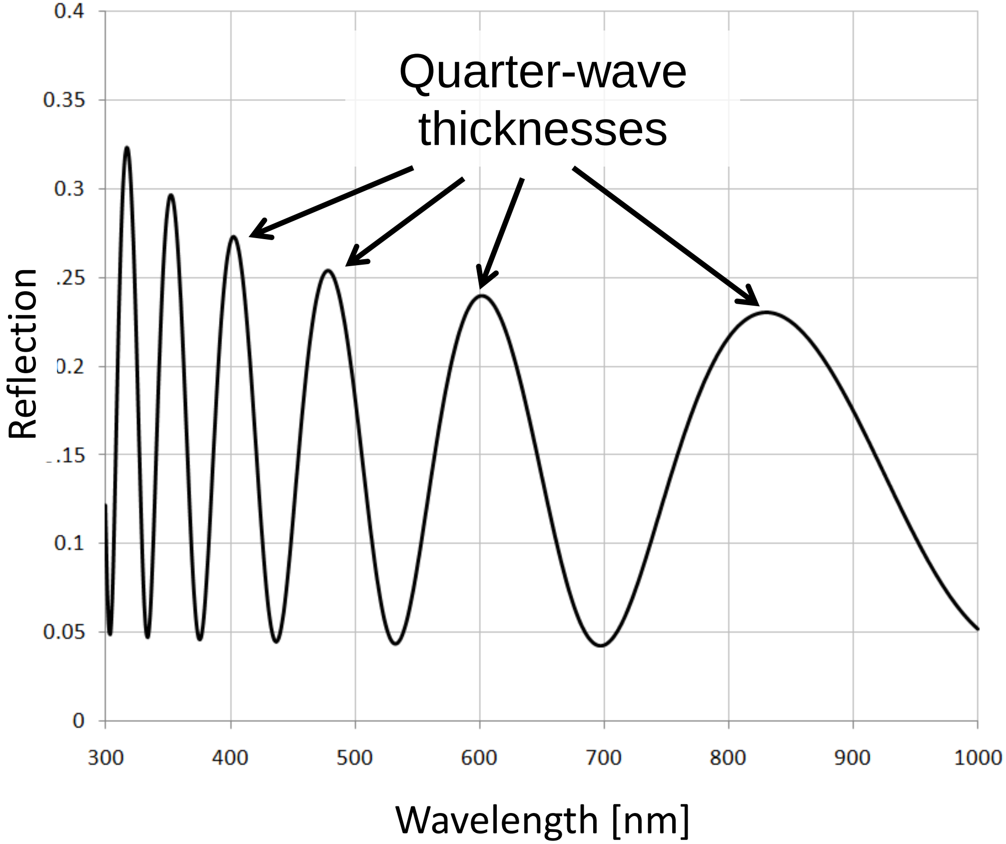
- To determine the thickness, one only needs to observe the spacing between the oscillations.
- It is possible to demonstrate that if λ_1 and λ_2 are the positions of two consecutive maxima or minima, the thickness of the coating is given by:

$$d = \frac{\lambda_1 \lambda_2}{2\left(\lambda_1 n_1(\lambda_2) - \lambda_2 n_1(\lambda_1)\right)}$$

where $n_1(\lambda_1)$ and $n_1(\lambda_2)$ are the refractive indices at λ_1 and λ_2.

The envelope method – an example

Here is an example of the reflection spectrum of a Ta_2O_5 thin film deposited by DIBS (dual ion beam sputtering) on a semi-infinite B270 substrate.

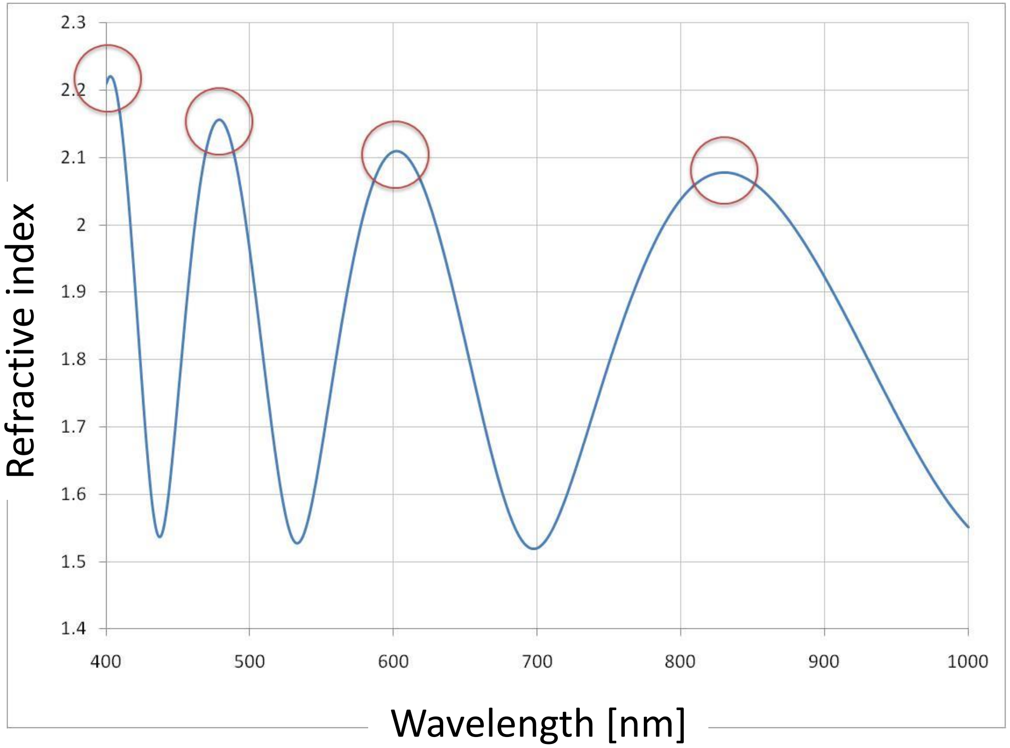


Reflection of a Ta_2O_5 thin film on a semi-infinite substrate of B270 glass.

The envelope method – an example (2)

Here is what we obtain if we calculate n using the reflection spectrum.
The maxima (red circles) correspond to the refractive index of the Ta_2O_5 thin film.

Calculating the thickness by using the indices at 602 nm and 830 nm, we obtain 499.6 nm.

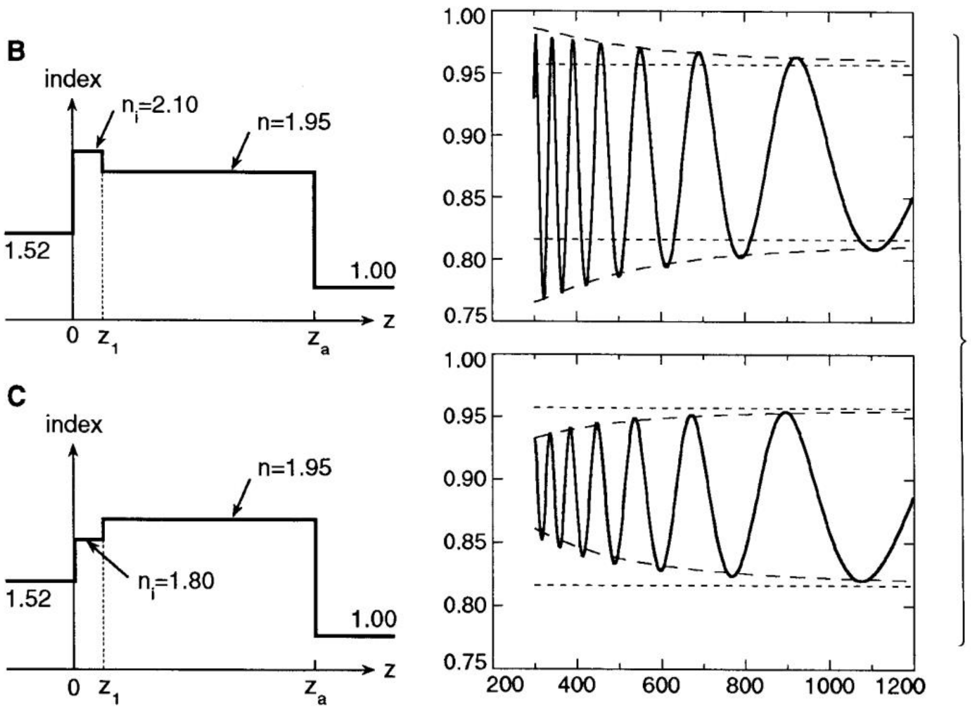


Refractive index calculation for a Ta_2O_5 thin film using the envelope method.

This methods works very well for most conditions; however, there are instances when it does not apply as well. For example, when the deposited film it too thin or when its refractive index is too close to the one of the substrate.

The envelope method – the impact of inhomogeneities

Transmittance



Envelopes of transmittance

$$\Gamma^{\max}(\lambda)=\frac{4n_a n_s}{(n_a+n_s)^2}\left\{1+\frac{\eta}{n}\frac{n_s-n_a}{n_s+n_a}\left[1-\cos\frac{4\pi n z_1}{\lambda}\right]\right\},$$

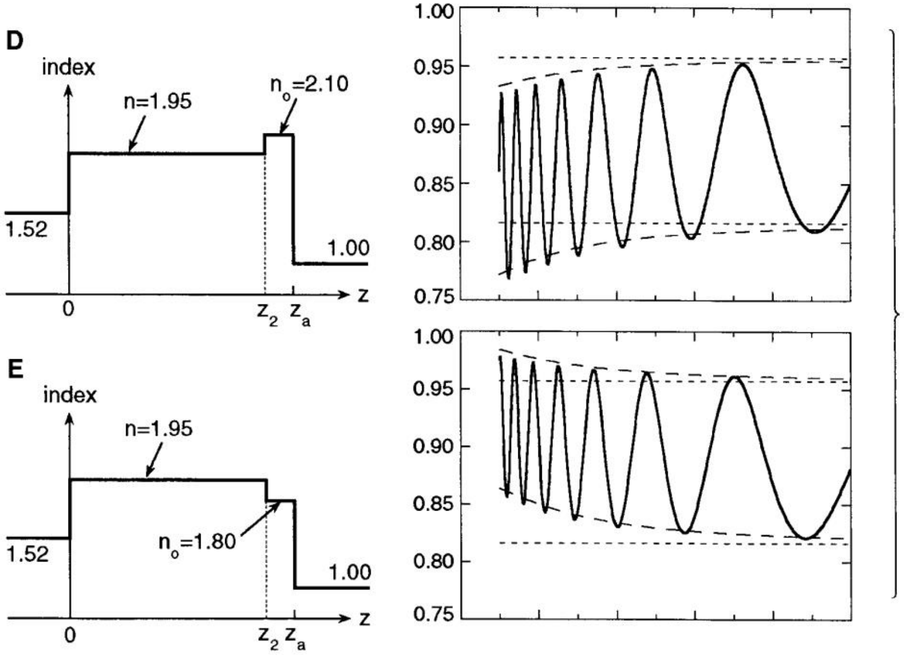
$$\Gamma^{\min}(\lambda)=\frac{4n_a n_s n^2}{(n_a n_s+n^2)^2}\left\{1-\frac{\eta}{n}\frac{n^2-n_a n_s}{n^2+n_a n_s}\left[1-\cos\frac{4\pi n z_1}{\lambda}\right]\right\},$$

where $n=n_o$ and $\eta=n_i-n$

A. V. Tikhonravov, M. K. Trubetskov, Brian T. Sullivan et J. A. Dobrowolski, « Influence of small inhomogeneities on the spectral characteristics of single thin films », *Appl. Opt.*, vol. 36, 1997, p. 7188-7199

The envelope method – the impact of inhomogeneities (2)

Transmittance **Envelopes of transmittance**



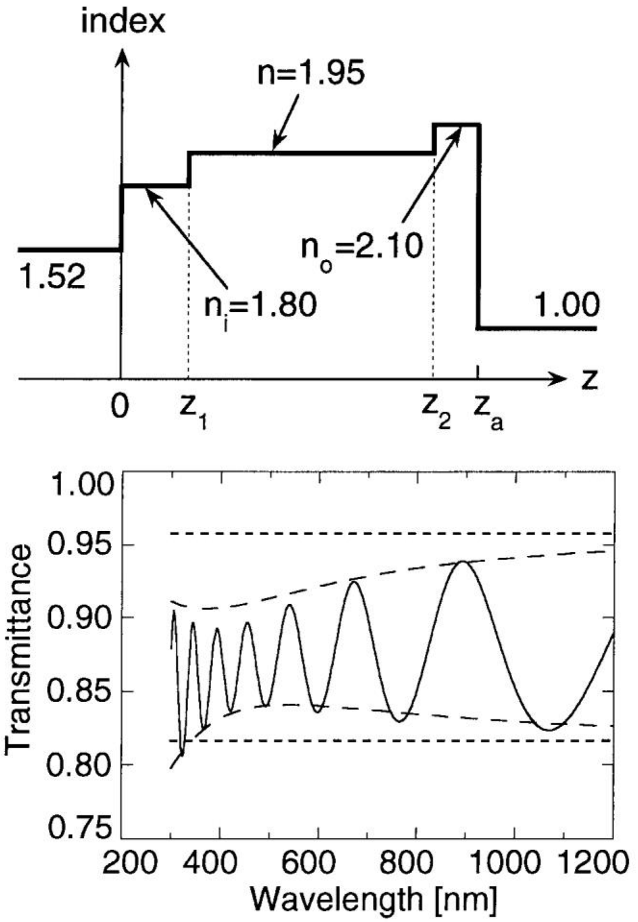
$$\Gamma^{\max}(\lambda)=\frac{4n_a n_s}{(n_a+n_s)^2}\left\{1+\frac{\eta}{n}\frac{n_s-n_a}{n_s+n_a}\left[\cos\frac{4\pi n(z_a-z_2)}{\lambda}-1\right]\right\},$$

$$\Gamma^{\min}(\lambda)=\frac{4n_a n_s n^2}{(n_a n_s+n^2)^2}\left\{1+\frac{\eta}{n}\frac{n^2-n_a n_s}{n^2+n_a n_s}\left[\cos\frac{4\pi n(z_a-z_2)}{\lambda}-1\right]\right\},$$

where $n=n_i$ and $\eta=n_o-n$

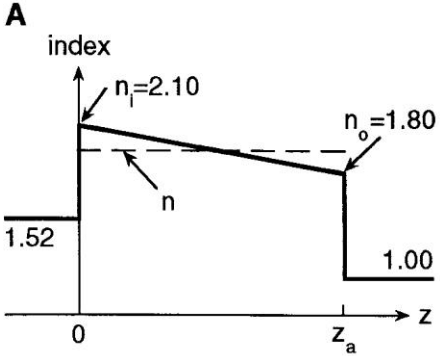
A. V. Tikhonravov, M. K. Trubetskov, Brian T. Sullivan et J. A. Dobrowolski, « Influence of small inhomogeneities on the spectral characteristics of single thin films », *Appl. Opt.*, vol. 36, 1997, p. 7188-7199

The envelope method – the impact of inhomogeneities (3)

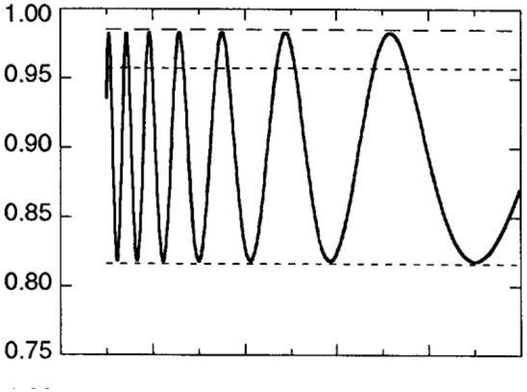


A. V. Tikhonravov, M. K. Trubetskov, Brian T. Sullivan et J. A. Dobrowolski, « Influence of small inhomogeneities on the spectral characteristics of single thin films », *Appl. Opt.*, vol. 36, 1997, p. 7188-7199

The envelope method – the impact of inhomogeneities (4)



Transmittance



Envelopes of transmittance

$$\Gamma^{\max}(\lambda)=\frac{4n_a n_s}{(n_a+n_s)^2}\left\{1+\frac{\eta}{n}\frac{n_s-n_a}{n_s+n_a}\right\},$$

$$\Gamma^{\min}(\lambda)=\frac{4n_a n_s n^2}{(n_a n_s+n^2)^2},$$

where $n=\frac{1}{2}(n_o+n_i)$ and $\eta=n_i-n_o$

A. V. Tikhonravov, M. K. Trubetskov, Brian T. Sullivan et J. A. Dobrowolski, « Influence of small inhomogeneities on the spectral characteristics of single thin films », *Appl. Opt.*, vol. 36, 1997, p. 7188-7199

ÉCOLE
POLYTECHNIQUE
MONTRÉAL

The envelope method – additional references

- J. C. Manifacier, J. Gasiot and J. P. Fillard, « A simple method for the determination of the optical constants *n*, *k* and the thickness of a weakly absorbing thin film », *J. Phys. E*, vol. 9, 1976, p. 1002–1004
- R. Swanepoel, « Determination of the thickness and optical constants of amorphous silicon », *J. Phys. E*, vol. 16, 1983, p. 1214–1223.
- Dirk Poelman and Philippe Frederic Smet, « Methods for the determination of the optical constants of thin films from single transmission measurements : a critical review », *J. Phys. D*, vol. 36, 2003, p. 1850–1857.
- A. V. Tikhonravov, M. K. Trubetskov, Brian T. Sullivan and J. A. Dobrowolski, « Influence of small inhomogeneities on the spectral characteristics of single thin films », *Appl. Opt.*, vol. 36, 1997, p. 7188-7199.
- Daniel Poitras, «Admittance diagrams of accidental and premeditated optical inhomogeneities in coatings », *Appl. Opt.*, vol. 41, 2002, p. 4671-4679.

Spectophotometry – Analysis methodology

- The envelope method allows one to gain insight into the structure of a thin film.
- In reality, we rarely evaluate the optical properties of a thin film « manually ». Indeed, this is typically done using software.
- The data analysis is performed very similarly as the refinement process during designing an optical filter. In fact, one must first specify an appropriate starting design, and the software then optimizes the model’s parameters to better represent the measured data.
- Contrary to a design process, all the solutions given by the software are not necessarily “real”. One must, therefore, have a good idea of the layers which are present before starting the analysis.

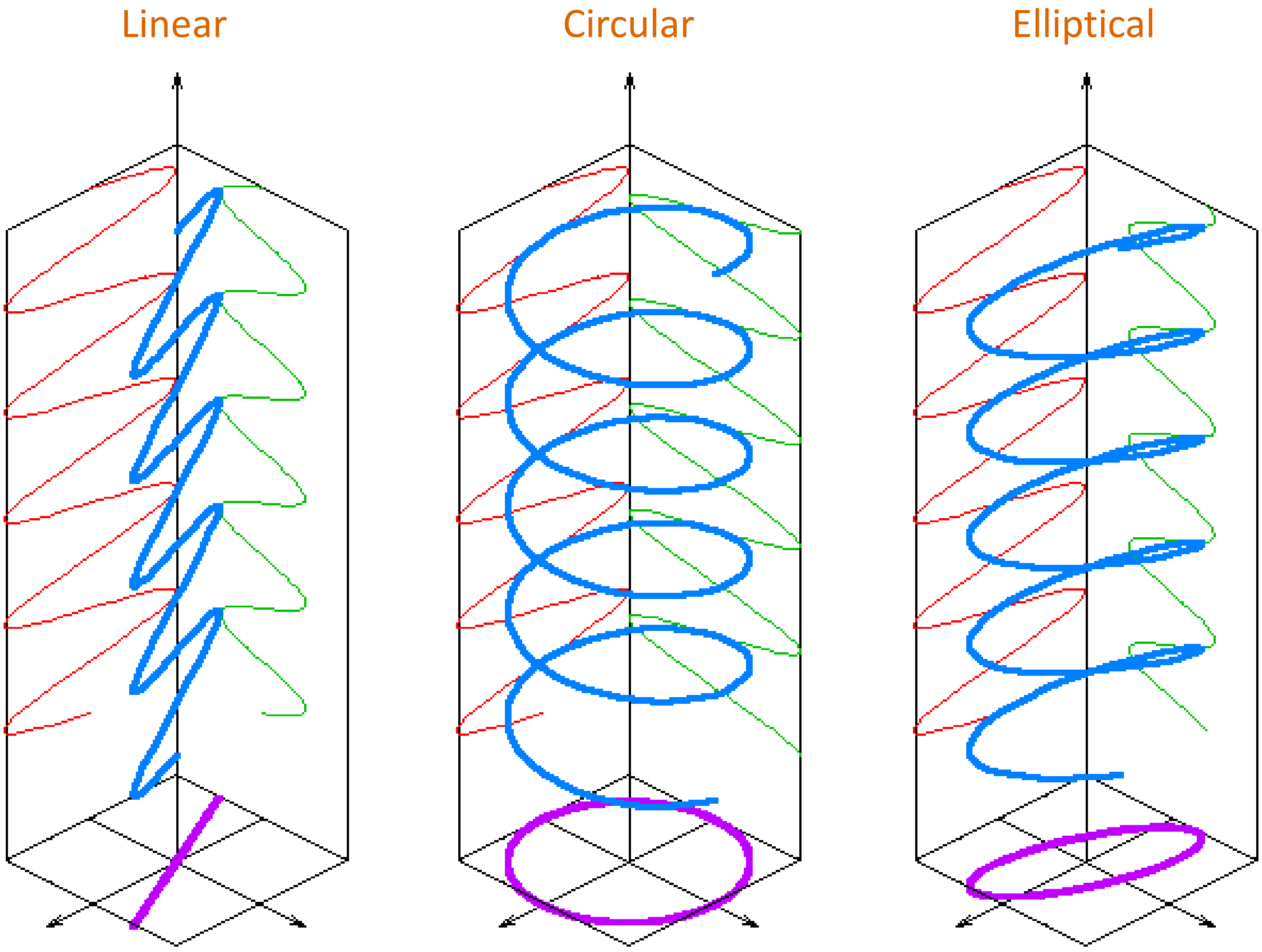
Spectophotometry – Analysis methodology (2)

- To determine the optical properties of a thin film, one should:
    1. Measure the transmission or reflection spectrum of the substrate.
    2. Measure the transmission or reflection spectrum of the thin film on the same substrate.
    3. Determine the approximate refractive index of the film using the envelope method.
    4. Evaluate the approximate thickness of the film using the spectrum.
    5. Adjust the thickness and refractive index using a data analysis software.
    6. Add absorption, non-homogeneity, interfaces, etc. to the model.

- Spectrophotometry allows the measurement of two data points per wavelength (T et R), which, therefore, allows for the determination of two parameters. If one supposes that the refractive index does not vary or that it varies according to a dispersion function, one can determine a larger number of parameters.

ÉCOLE POLYTECHNIQUE MONTRÉAL

Polarization of light



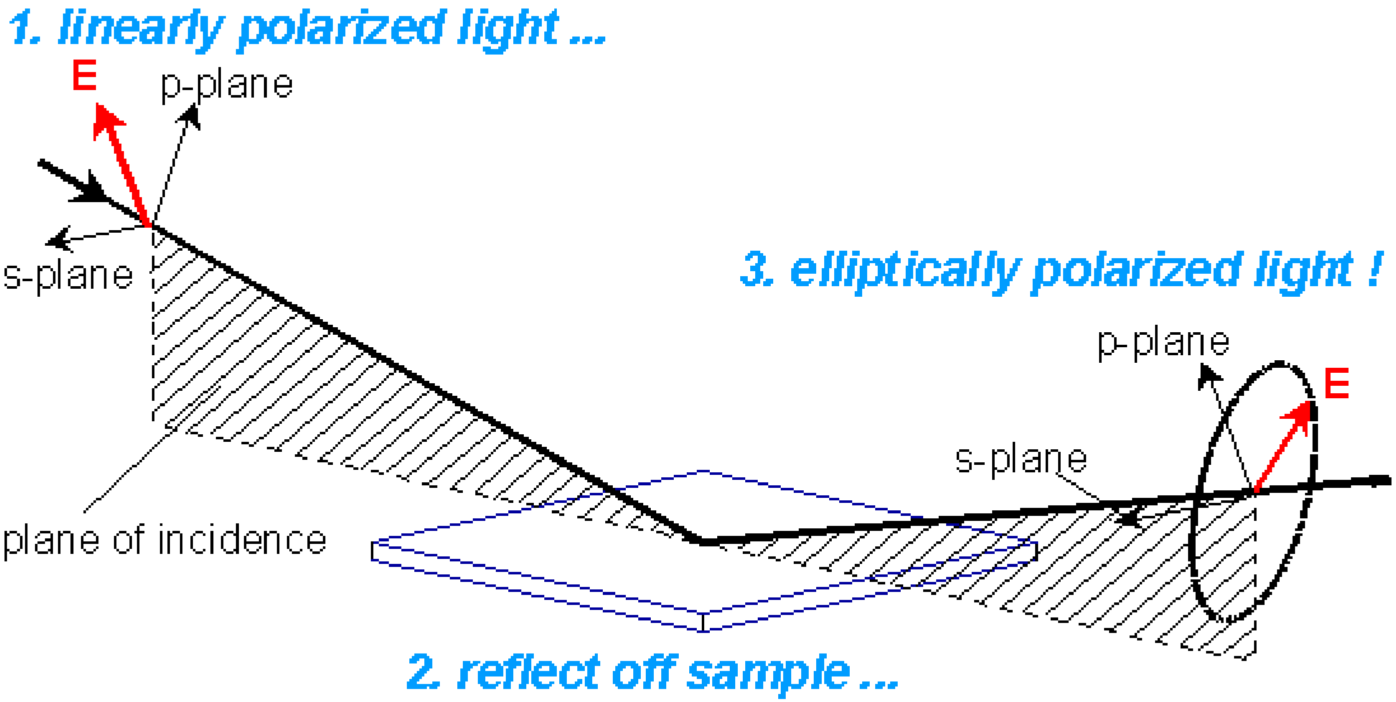
www.wikipedia.org

ÉCOLE POLYTECHNIQUE MONTRÉAL

PHS6317 – Nanoengineering of thin films

Chapter 8B

Why is it called ellipsometry?



J. A. Woollam Co., « Ellipsometry tutorial », www.jawoollam.com.

ÉCOLE POLYTECHNIQUE MONTRÉAL

Ψ and Δ: definitions

- We know that the reflection coefficients in amplitude, r_s and r_p, and in intensity differ depending on polarization. We can define:

$$\rho = \frac{-r_p}{r_s}$$

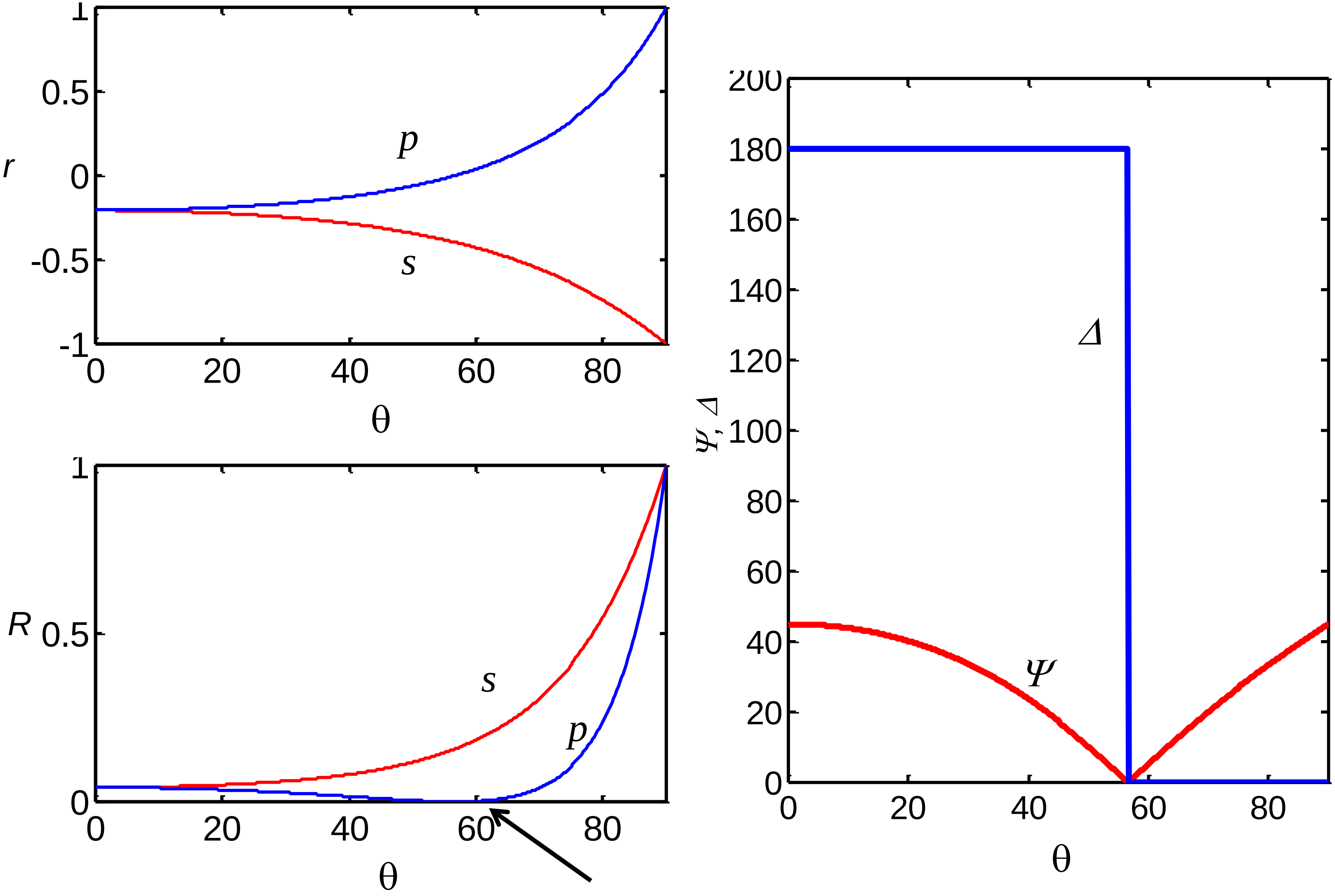
the ratio between two polarizations. We can express this ratio in polar coordinates to obtain:

$$\rho = \frac{-r_p}{r_s} = \tan \Psi \, e^{i\Delta}$$

where the two ellipsometric variables Ψ et Δ are defined. The variable Ψ corresponds to the amplitude ratio between the two polarizations, and Δ corresponds to the phase shift between the two.

- The – sign allows one to obtain $\Delta = 180°$ at normal incidence. It is simply an ellipsometric convention which many forget to mention. For more information on the different ellipsometric conventions consult Rolf H. Muller, « Definitions and conventions in ellipsometry », *Surf. Sci.*, vol. 16, 1969, p. 14–33.

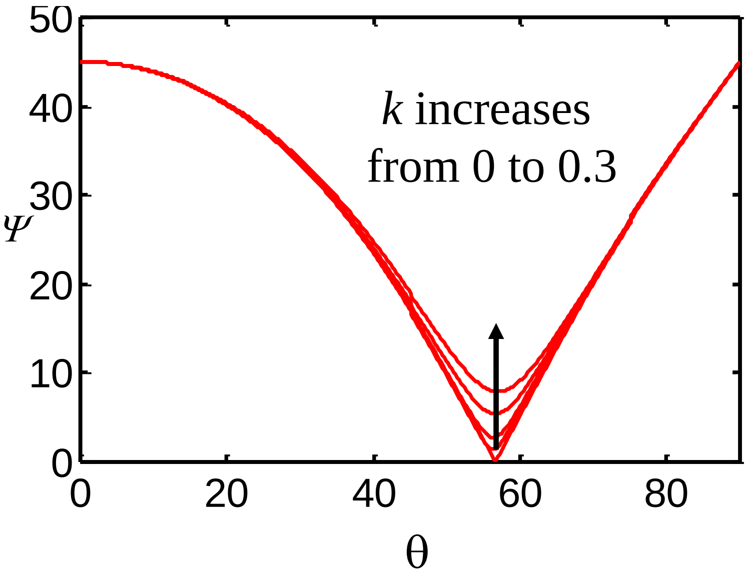
Ψ and Δ for a semi-infinite glass substrate (n = 1.52)

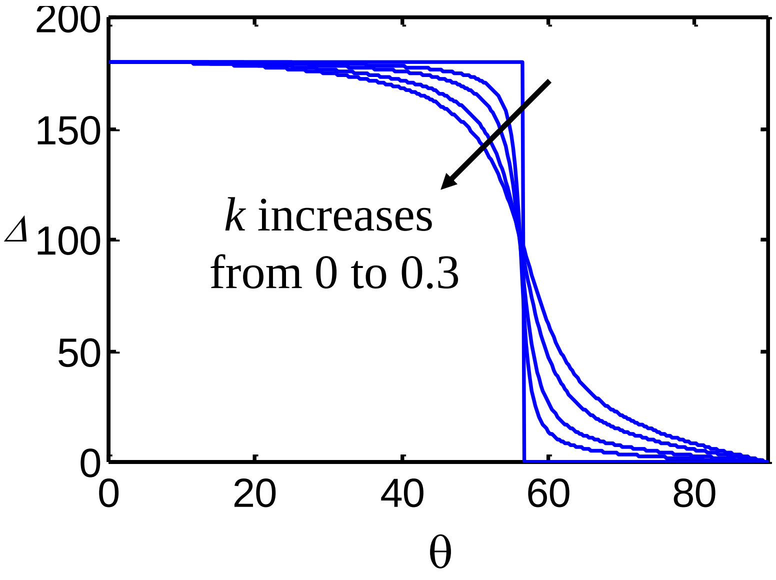


Brewster angle

The impact of absorption

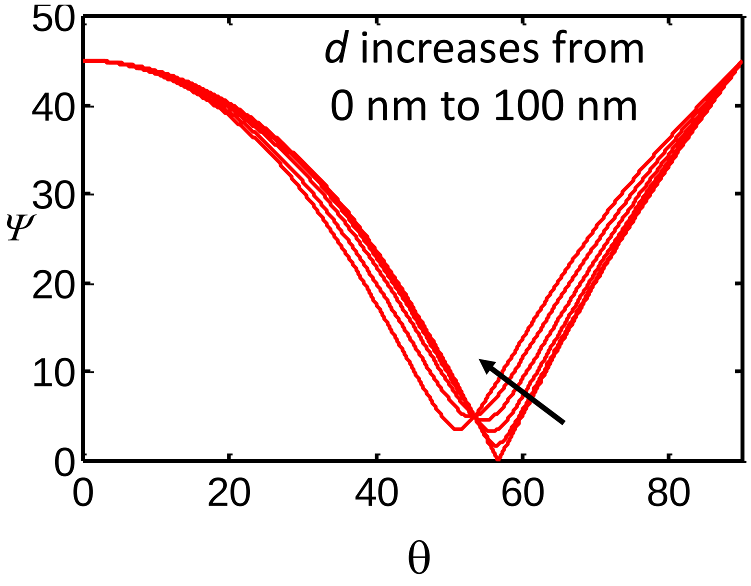
- When the substrate is absorbing, the *p*-polarized reflection no longer drops to zero and consequently neither does Ψ. In addition, r_s and r_p are no longer real, Δ can thus take on values different than 0° and 180°.
- The sensitivity of Ψ is the highest at the Brewster angle whereas Δ is most sensitive near the Brewster angle.

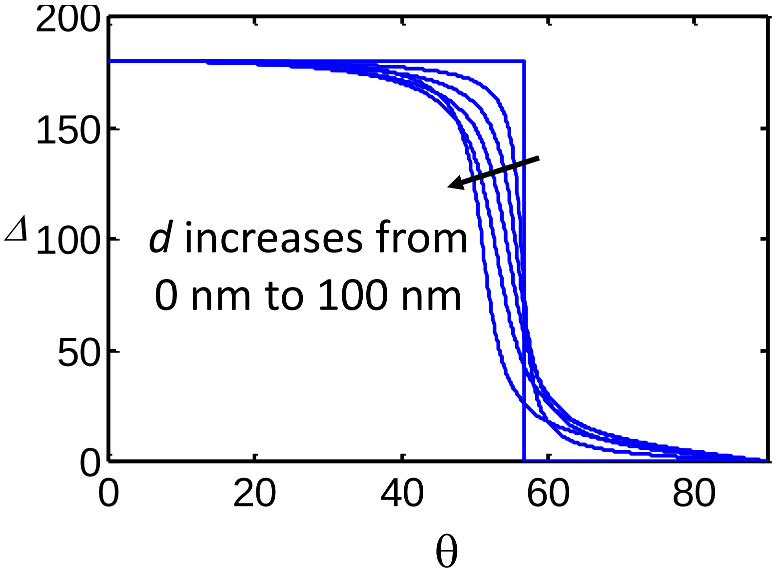




The addition of a MgF_2 thin film

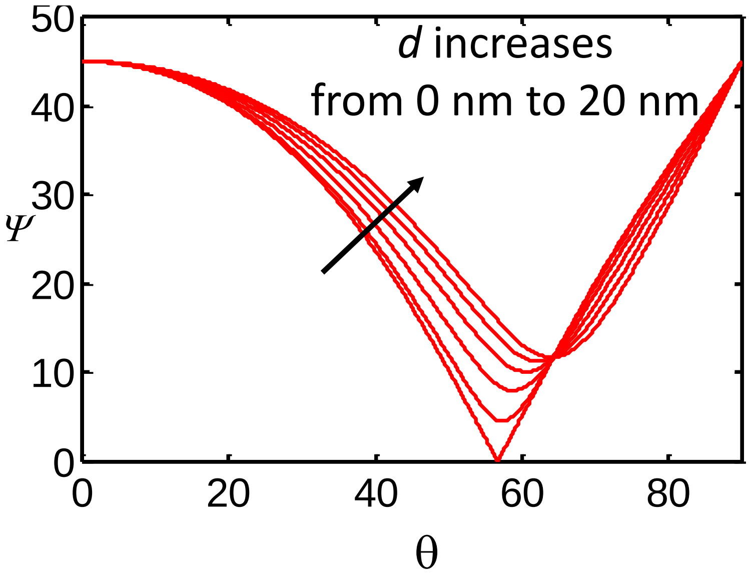
- The addition of a thin film of MgF_2 ($n = 1.38$) with a lower refractive index than the substrate displaces the minimum in Ψ towards lower angles.
- Since we are no longer in the case of a reflection from a single interface, we can no longer speak of a Brewster angle but of a pseudo-Brewster angle.

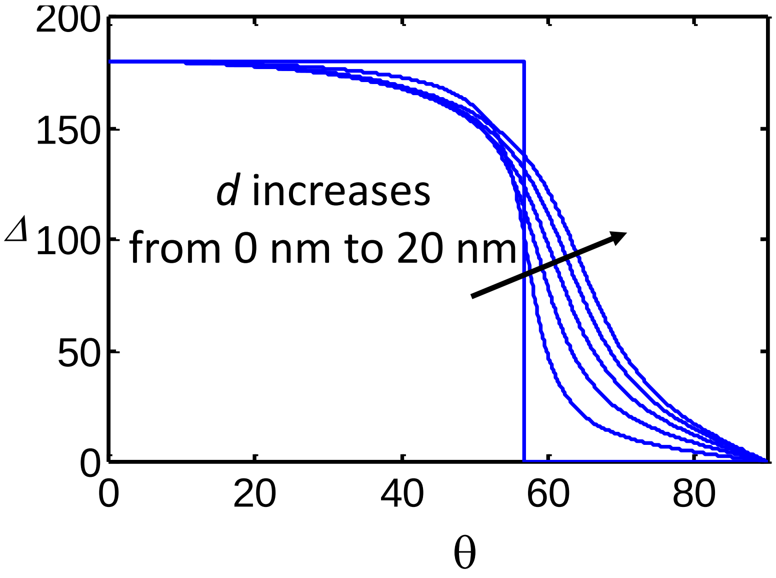




The addition of a TiO_2 thin film

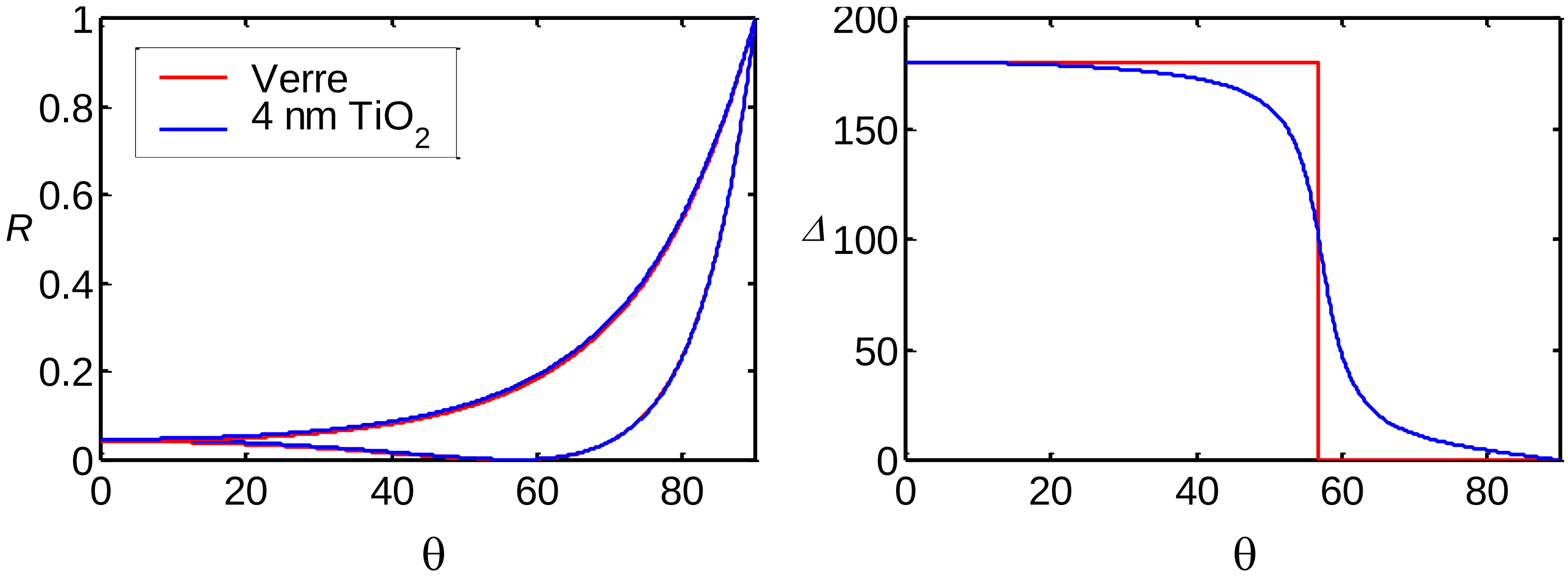
- The addition of a thin film of TiO_2 ($n = 2.35$) with a higher refractive index than the substrate displaces the minimum in Ψ towards higher angles (higher pseudo-Brewster angle).
- Since there is a larger optical contrast between the glass substrate and TiO_2, the addition of a very thin film generates significant changes in Ψ and Δ.





Comparing spectrophotometry with ellipsometry

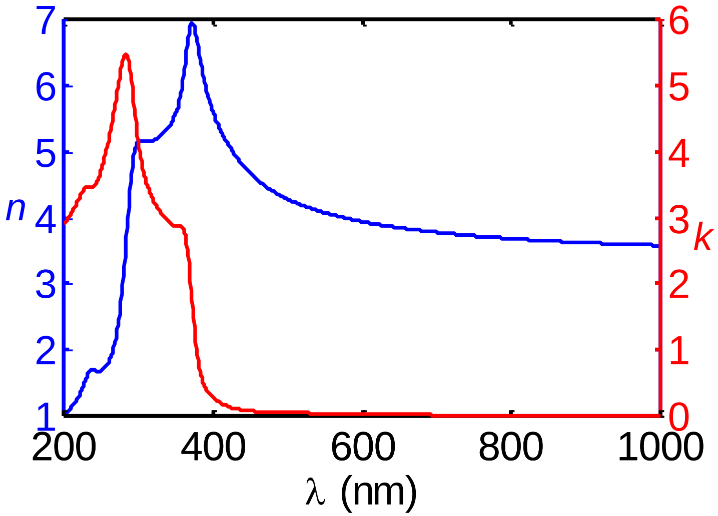
- While the reflection spectrum practically does not change following the addition of a 4-nm-thick TiO_2 film, the ellipsometric spectrum (in particular Δ) changes quite substantially.
- Ellipsometry is, therefore, advantageous for thin and ultra-thin films.

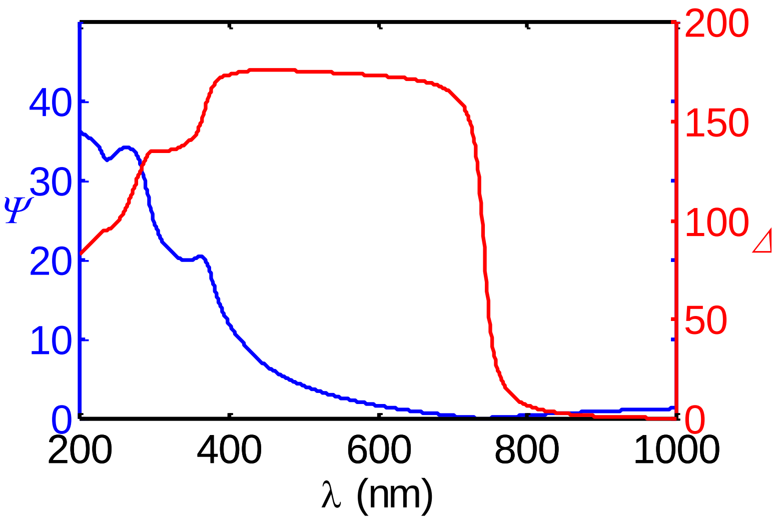


ÉCOLE POLYTECHNIQUE MONTRÉAL

Spectroscopic ellipsometry on Si

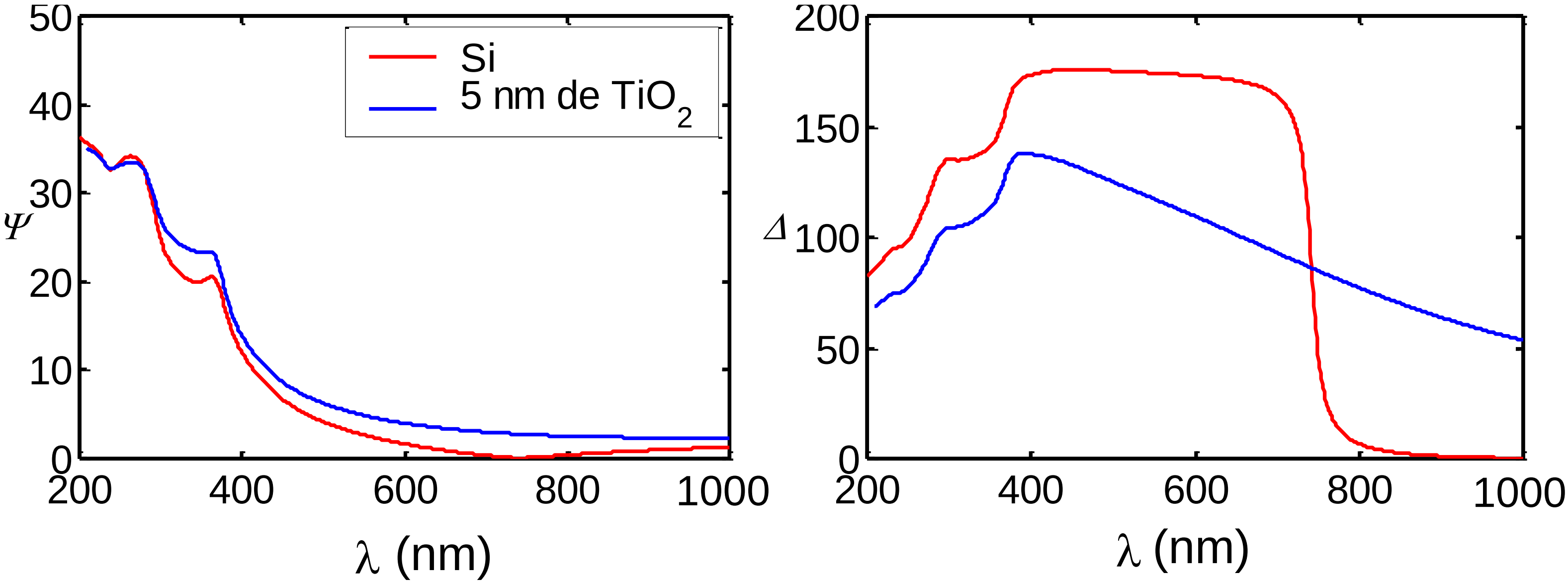
- The refractive index of a material changes with wavelength and so does the Brewster angle.
- If the absorption coefficient varies as well, the widening of the transition of Δ will also vary vs. wavelength.
- Taking a measurement close to the Brewster angle (75° in the present case) results in large Ψ and Δ differences as a function of wavelength; this allows precise assessment of n and k.
- Note that we are using two variables to determine two others, the system is, therefore, well defined.





Spectroscopic ellipsometry (5 nm of TiO_2 on Si)

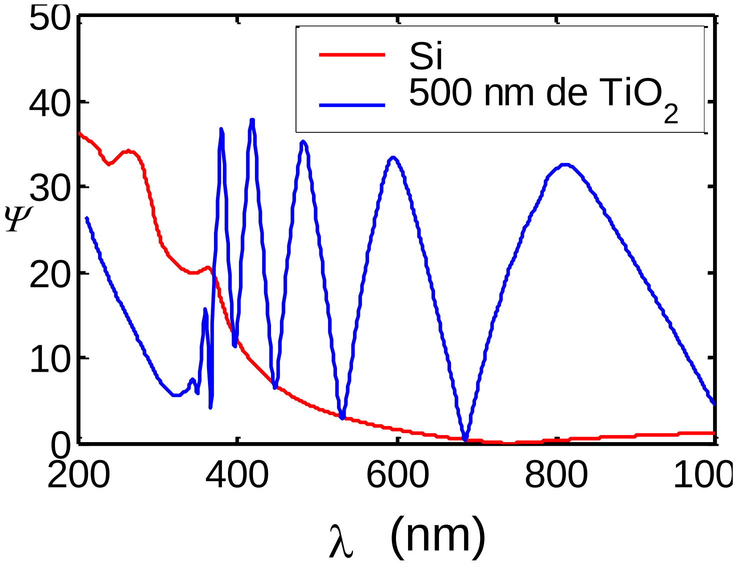
- Since we are close to the Brewster angle, we can observe quite large variations.



Spectroscopic ellipsometry (500 nm of TiO_2 on Si)

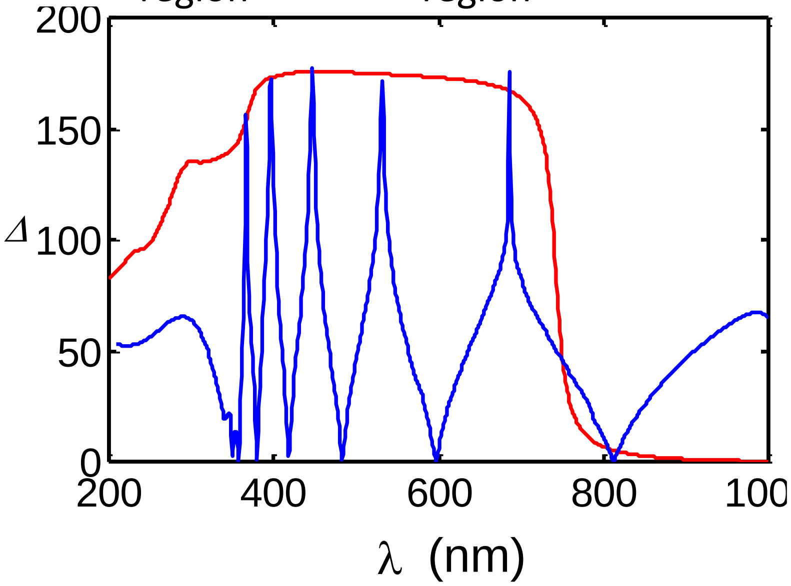
ÉCOLE POLYTECHNIQUE MONTRÉAL

- With the addition of a thick TiO_2 film, one can observe the appearance of interference fringes, just like in transmission and reflection spectra.
- In the transparent region, one can use a method similar to the envelope method to determine the refractive index and thickness of the film.
- In the absorbing region, we may consider the film as semi-infinite to determine its refractive index.



Absorbing region

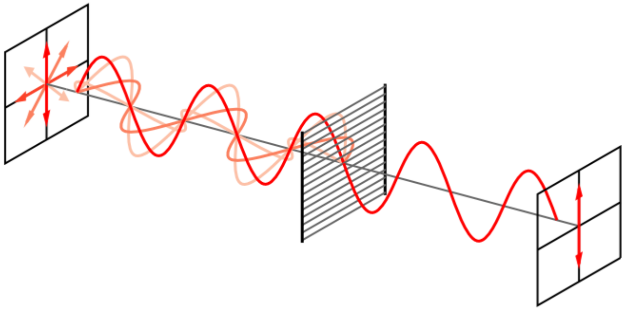
Transparent region



Polarizers and compensators

Polarizers

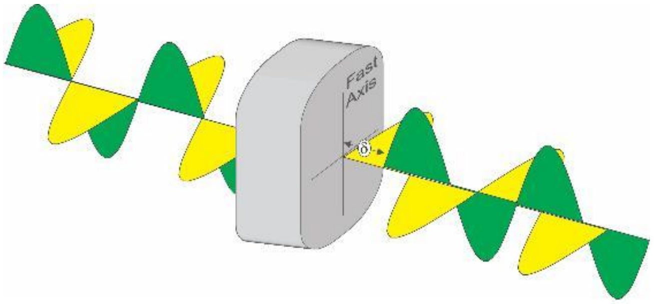
- They transmit light of a single polarization.
- It is impossible to differentiate a polarizer positioned at an angle θ from a polarizer at an angle $\theta + 180°$.
- The transmitted light is always linearly polarized.



www.wikipedia.org

Compensators

- They introduce a phase shift of 90° between both components of the incident light beam according to a slow and fast axis.
- They thus allow one to change the polarization state of the incident light. A light beam linearly polarized at an angle of 45° will be transformed into a circularly polarized beam.



J. A. Woollam Co., « Compensators », www.jawoollam.com.

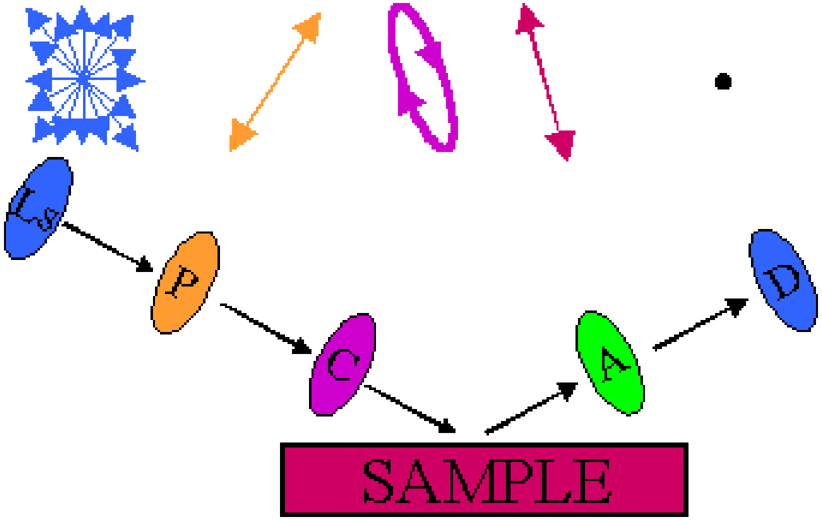
Null ellipsometer

Advantages

- Configuration with the most accurate and precise results.
- One can determine Ψ and Δ over their full range.

Disadvantages

- Measurements are long and hard to automate.



J. A. Woollam Co., « Ellipsometry tutorial », www.jawoollam.com.

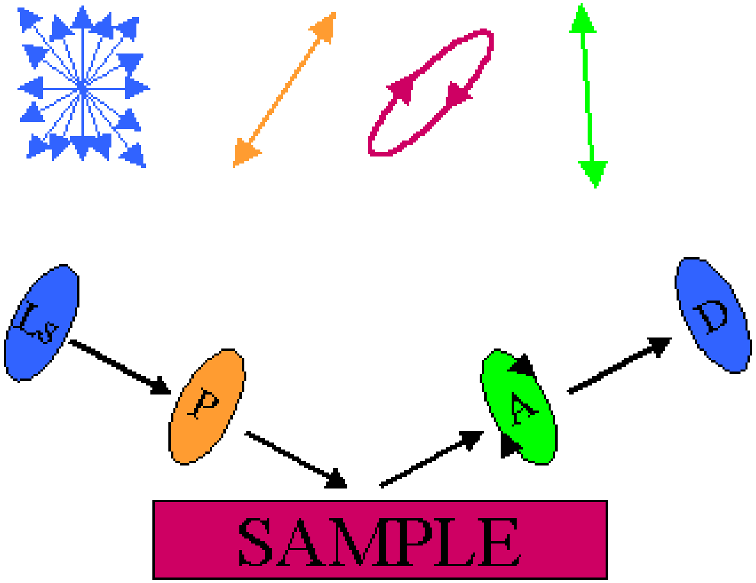
Rotating analyser ellipsometer, RAE

Advantages

- There are only two polarizers.
- It is easy to fabricate polarizers with very high extinction coefficients.
- It is easy to fabricate polarizers with a very low spectral dependence.

Disadvantages

- Impossible to distinguish Δ over its full range from 0° to 360°. Δ is limited between 0° and 180°.
- Very low sensitivity when Δ = 0° or Δ = 180°.
- The detector's sensitivity to changes in polarization can lead to errors.



J. A. Woollam Co., « Ellipsometry tutorial », www.jawoollam.com.

ÉCOLE POLYTECHNIQUE MONTRÉAL

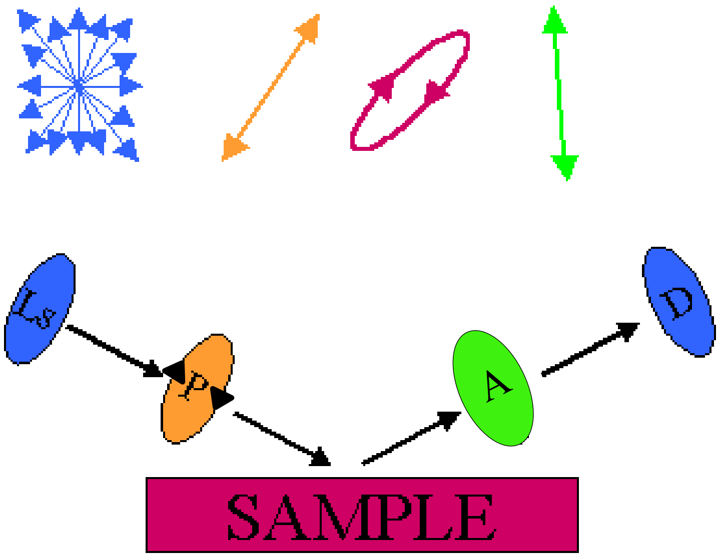
Rotating polarizer ellipsometer, RPE

Advantages

- There are only two polarizers.
- It is easy to fabricate polarizers with very high extinction coefficients.
- It is easy to fabricate polarizers with a very low spectral dependence.

Disadvantages

- Impossible to distinguish Δ over its full range from 0° to 360°. Δ is limited to between 0° and 180°.
- Very low sensitivity when $\Delta = 0°$ or $\Delta = 180°$.
- The light source's polarization can lead to errors.



J. A. Woollam Co., « Ellipsometry tutorial », www.jawoollam.com.

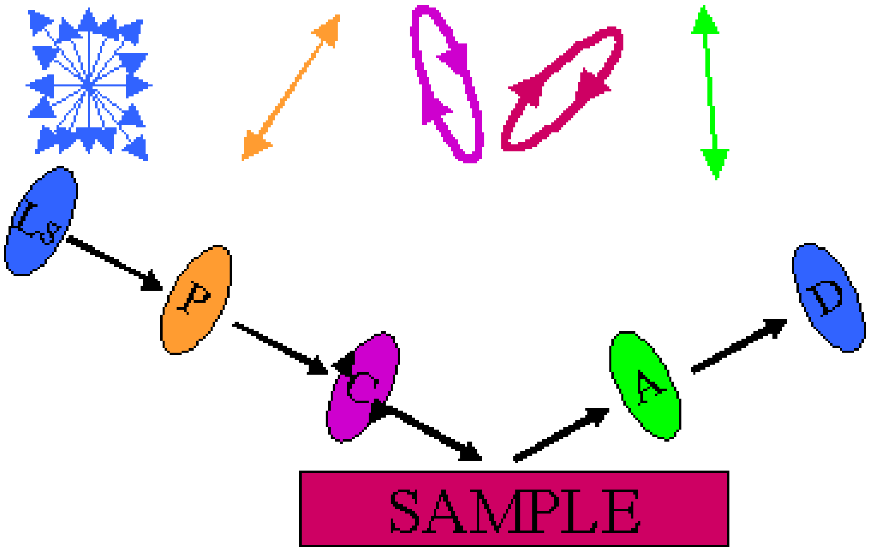
Rotating compensator ellipsometer, RCE

Advantages

- No region of low sensitivity.
- One can distinguish Δ from 0° to 360°.
- It is possible to perform generalized ellipsometry measurements.

Disadvantages

- It is difficult and costly to fabricated a compensator which performs ideally over a large wavelength spectrum.



J. A. Woollam Co., « Ellipsometry tutorial », www.jawoollam.com.

ÉCOLE
POLYTECHNIQUE
MONTRÉAL

Jones vector

- To study how an ellipsometer functions, we can express the electric field by:

$$\vec{E} = \begin{bmatrix} \tilde{E}_p \\ \tilde{E}_s \end{bmatrix} = \begin{bmatrix} E_p e^{i\phi_s} \\ E_s e^{i\phi_p} \end{bmatrix} \equiv \begin{bmatrix} E_p \\ E_s e^{i(\phi_p - \phi_s)} \end{bmatrix}$$

where E_p and E_s are the p and s components of the electric field; the final relation is possible since we are only interested in the relative phase difference between both polarizations.

- The linear polarizations p and s are therefore expressed by:

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix} \text{ and } \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

whereas left and right circularly polarized light are expressed by:

$$\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix} \text{ and } \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \end{bmatrix}.$$

Jones matrices

- The various optical elements which modify the electric field can be represented by a 2 x 2 matrix.
- Polarizing filters oriented in p or in s can be respectively represented by:

$$\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \text{ and } \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$$

whereas a polarizer oriented at ±45° will be represented by:

$$\frac{1}{2}\begin{bmatrix} 1 & \pm 1 \\ \pm 1 & 1 \end{bmatrix}.$$

- The reflection upon an isotropic sample is represented by:

$$\begin{bmatrix} r_p & 0 \\ 0 & r_s \end{bmatrix}.$$

- Finally, the rotation of an element by an angle θ is represented by:

$$\begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}.$$

Jones formalism for a RAE

- Using the Jones formalism, the electric field at the detector of a RAE is given by:

$$\begin{bmatrix} E_p \\ E_s \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \cos\theta_A & \sin\theta_A \\ -\sin\theta_A & \cos\theta_A \end{bmatrix} \begin{bmatrix} r_p & 0 \\ 0 & r_s \end{bmatrix} \begin{bmatrix} \cos\theta_P & -\sin\theta_P \\ \sin\theta_P & \cos\theta_P \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

H. Fujiwara, Spectroscopic Ellipsometry: Principles and Applications, 2007.

where θ_{P} and θ_{A} are the angles at which are positioned the polarizer and analyzer.

- The intensity which will be measured is therefore given by isolating the term θ_{A} since it is the analyzer which is rotating:

$$I = E_{\mathrm{p}}^2 + E_{\mathrm{s}}^2 \propto 1 + \frac{|\rho|^2 - \tan^2\theta_{\mathrm{P}}}{|\rho|^2 + \tan^2\theta_{\mathrm{P}}}\cos(2\theta_{\mathrm{A}}) + \frac{2\Re e(\rho)\tan\theta_{\mathrm{P}}}{|\rho|^2 + \tan^2\theta_{\mathrm{P}}}\sin(2\theta_{\mathrm{A}})$$

where $\rho = -r_{\mathrm{p}}/r_{\mathrm{s}} = \tan\Psi e^{i\Delta}$. This equation can also be expressed as:

$$I \propto 1 + \alpha\cos(2\theta_{\mathrm{A}}) + \beta\sin(2\theta_{\mathrm{A}})$$

where $$\alpha = \frac{|\rho|^2 - \tan^2\theta_{\mathrm{P}}}{|\rho|^2 + \tan^2\theta_{\mathrm{P}}} \quad \text{and} \quad \beta = \frac{2\Re e(\rho)\tan\theta_{\mathrm{P}}}{|\rho|^2 + \tan^2\theta_{\mathrm{P}}}.$$

Jones formalism for a RAE (2)

- Since the analyzer is rotating,

$$\theta_{\mathrm{A}}(t) = 2\pi f_{\mathrm{A}} t + \theta.$$

- Finally, using Fourier analysis, it is possible to demonstrate that:

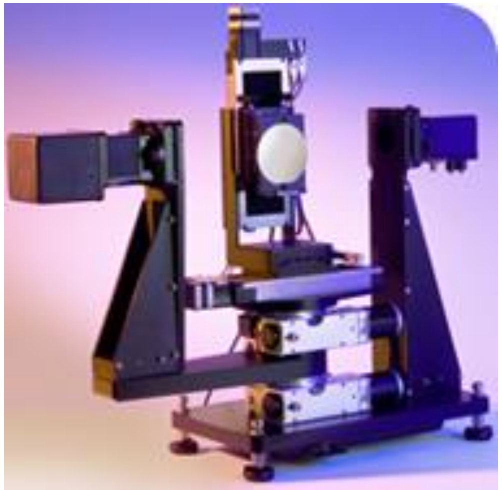
$$\tan\Psi = \sqrt{\frac{1+\alpha}{1-\alpha}}\left|\tan\theta_{\mathrm{P}}\right|$$

and

$$\cos\Delta = \frac{\beta}{\sqrt{1-\alpha^2}}\frac{\tan\theta_{\mathrm{P}}}{\left|\tan\theta_{\mathrm{P}}\right|}.$$

The RC2 by J.A. Woollam Co.

- One of the ellipsometers which the FCSEL possesses is a RC2-XI (Dual Rotating Compensators) from the company J.A. Woollam Co.
- It is a variable angle spectroscopic ellipsometer with two rotating compensators.
- It possesses a high accuracy over the whole range of Ψ and Δ. It offers the complete characterization of the Jones matrix (anisotropic samples) and the Mueller matrix (anisotropic and depolarizing samples).
- The measured wavelength range is from 210 nm to 2500 nm.
- The measurements are very fast due to the presence of a CCD detector.
- This allows for various types of measurements: rapid xy mapping, as a function of temperature using a heat cell, during electrochemical testing, etc.



www.jawoollam.com

$$\begin{bmatrix} r_{pp} & r_{sp} \\ r_{ps} & r_{ss} \end{bmatrix}$$

Jones matrix

$$\begin{bmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix}$$

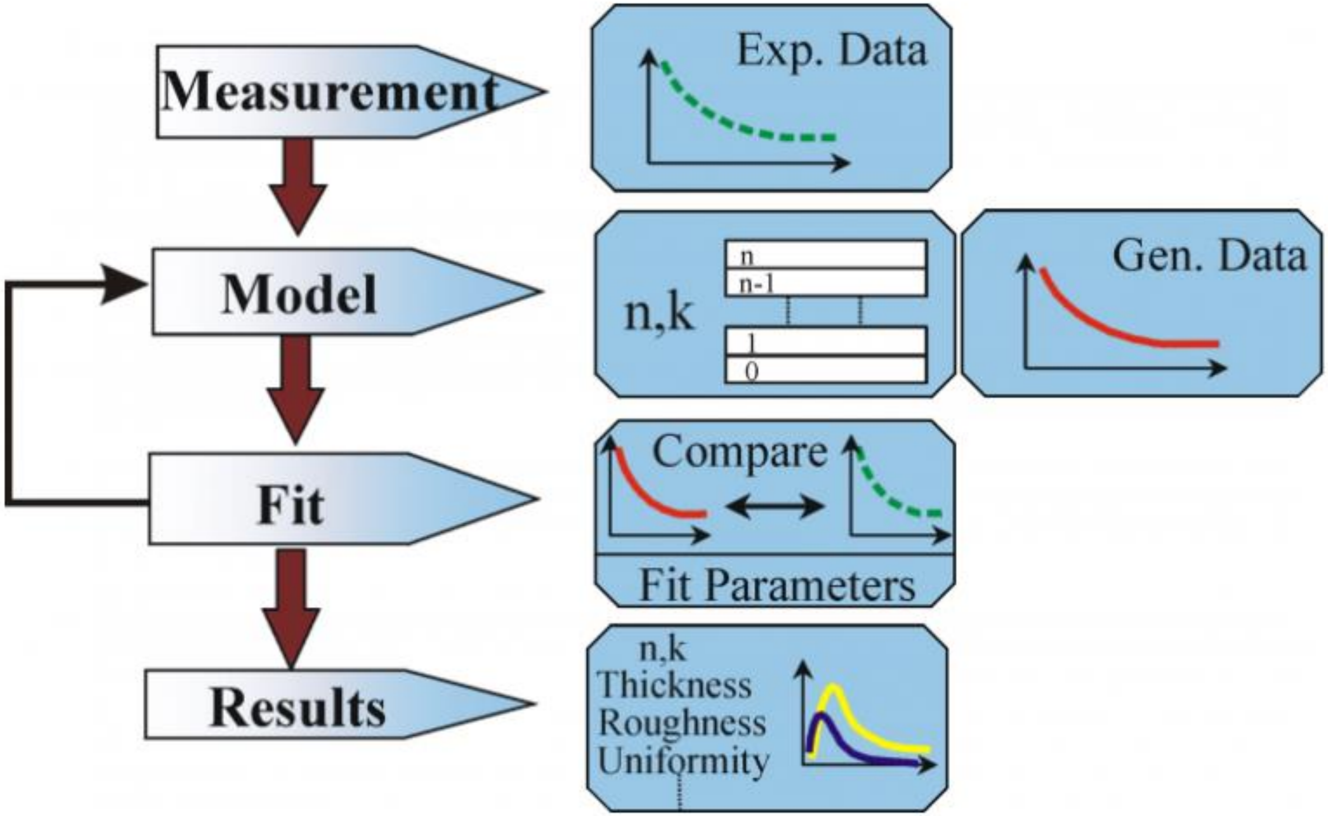
Mueller matrix

ÉCOLE POLYTECHNIQUE MONTRÉAL

PHS6317 – Nanoengineering of thin films

Chapter 8B

Analysis process



J. A. Woollam Co., « Ellipsometry tutorial », www.jawoollam.com.

Analysis process – The model

- The analysis of the ellipsometric data requires the development of an optical model. This model contains:
  - the substrate’s optical properties and thickness;
  - the total number of layers;
    - their individual thicknesses;
    - their optical properties;
  - the presence of surface roughness or of interfaces;
  - the presence of inhomogeneities;
  - the presence of non-uniformity;
  - the influence of the substrate’s backside reflection;
  - …
- If specific parameters are already known, they can be set; for the other parameters, it is preferable to supply reasonable starting values before optimizing the model.

Analysis process - MSE

- The optimization process of the model’s parameters will minimize the mean square error (MSE) between the model and experimental data:

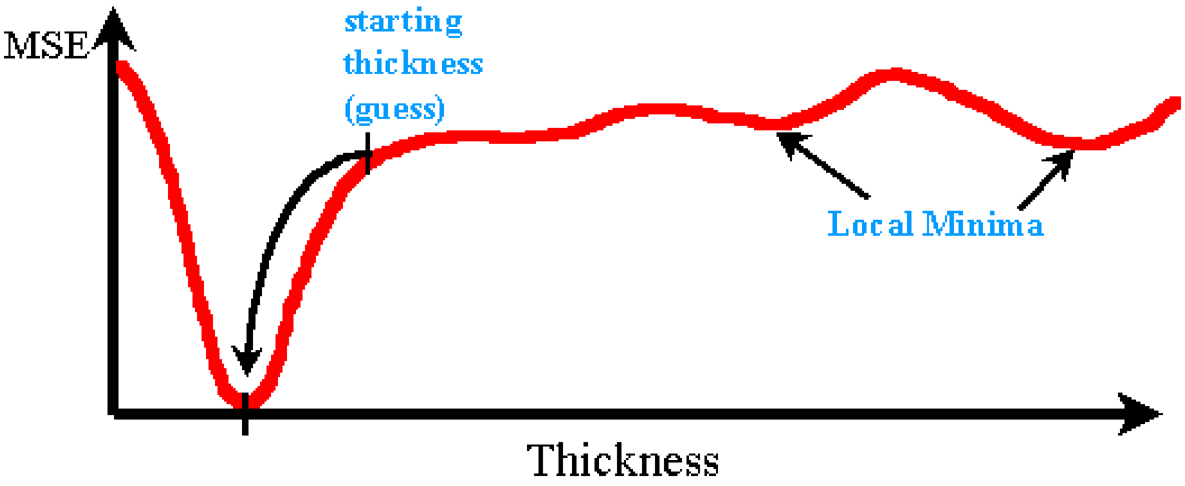
$$MSE = \frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\psi_i^{\mathrm{mod}}-\psi_i^{\mathrm{exp}}}{\sigma_{\psi,i}^{\mathrm{exp}}}\right)^2+\left(\frac{\Delta_i^{\mathrm{mod}}-\Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right]=\frac{1}{2N-M}\chi^2,$$

where $2N$ is the number of data points, M is the number of model parameters, the exponent *exp* identifies the experimental data, the exponent *mod* identifies the model and σ is the experimental uncertainty of each data point.

ÉCOLE POLYTECHNIQUE MONTRÉAL

Choice of the appropriate initial values

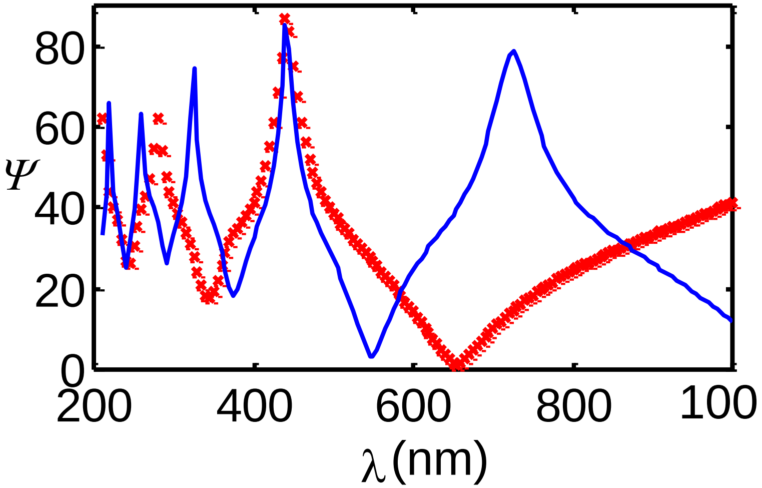
- The Levenberg-Marquart algorithm, used to optimize the model parameters, is a local optimization algorithm; it will, therefore, find the minimum MSE closest to the initial values (or one of the closest).
- To obtain accurate parameter values, it is important to pay attention to the initial parameter values.



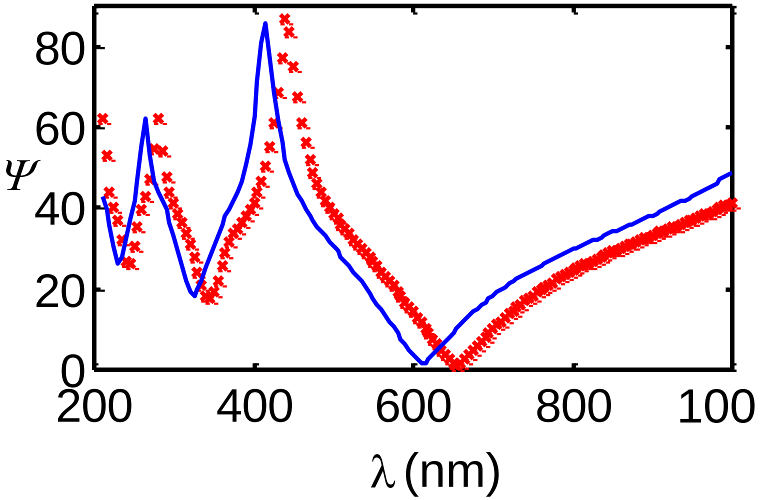
J. A. Woollam Co., « Ellipsometry tutorial », www.jawoollam.com.

Choice of the appropriate initial values – An example

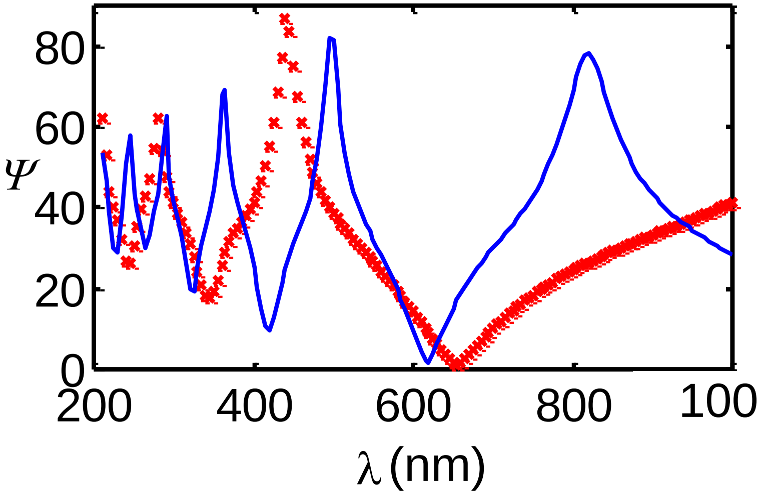
Bad starting point



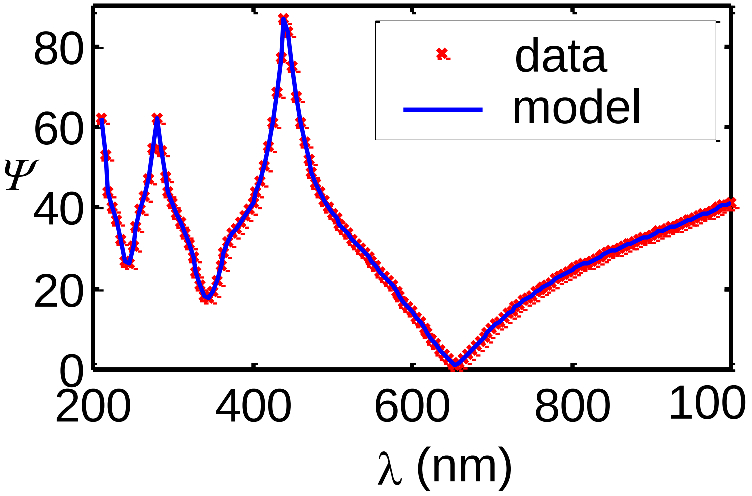
Good starting point



Bad optimization



Good optimization



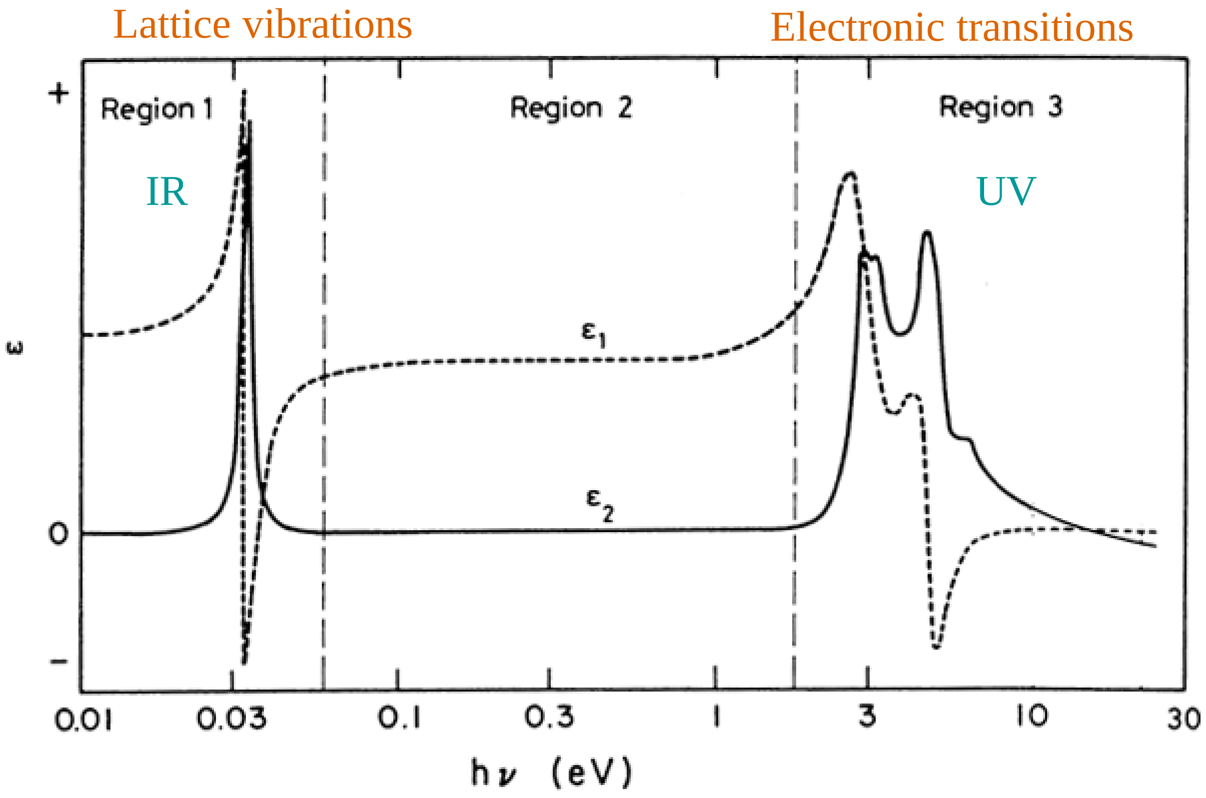
Evaluating the results

- Before accepting the obtained results following optimization, it is important to ask oneself the following questions:
  - Does the model reproduce the experimental data?
  - Are the obtained parameter values reasonable?
    - Positive thicknesses;
    - Normal dispersion curves;
    - Positive absorption coefficients;
    - …
  - Is the MSE sufficiently low? Can it be significantly reduced by the addition of additional parameters?
  - Is there any correlation between parameters (see the correlation matrix)?

ÉCOLE
POLYTECHNIQUE
MONTRÉAL

Using dispersion models

- The refractive index varies as a function of the wavelength; in addition, it varies in a continuous fashion. This dispersion is the result of the interaction of light with the material; at specific frequencies, absorption bands will appear; these can be modeled using oscillators (lorentzian, gaussian, …) and adjusting their position, amplitude and broadness. It then becomes possible to model the refractive index using a limited number of parameters.



Corey L. Bungay and James N. Hilfiker, Slides from *Spectroscopic Ellipsometry Short Course*.

ÉCOLE POLYTECHNIQUE MONTRÉAL

Cauchy/Urbach dispersion models

- In the low absorption region, the refractive index varies quite slowly and is often modeled using the empirical Cauchy formula:

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

where λ is given in micrometers.

- The beginning of the absorption band (absorption tail), can be modeled using the Urbach model:

$$k(\lambda)=A_k\exp\left(12400\,E\left[\frac{1}{\lambda}-\frac{1}{\lambda_{\text{Edge}}}\right]\right).$$

amplitude

exponent

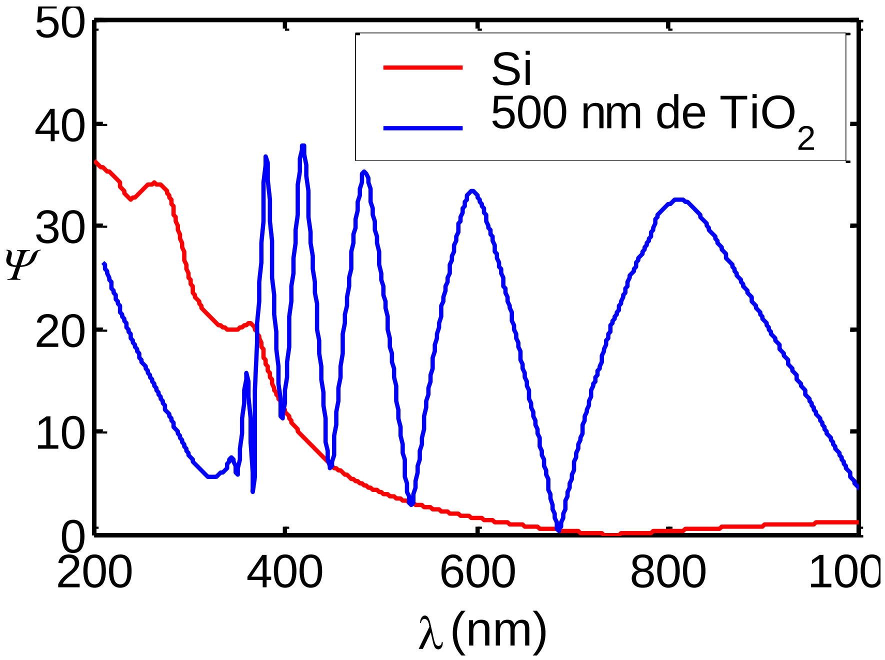
band edge

Acquisition strategies

- To determine the optical properties of a **semi-infinite transparent substrate**:
  - Measure at multiple angles to determine the Brewster angle;
  - Measure at several wavelengths to determine the dispersion curve;
  - Use transmission measurements to decorrelate the effect of absorption of that of the surface roughness.
- To determine the optical properties of an **absorbing substrate**:
  - Make a spectroscopic measurement at an angle near the Brewster angle.
- To determine the properties **of a single layer** on a substrate:
  - Determine the substrate's properties;
  - Make a spectroscopic measurement at an angle close to the Brewster angle of the substrate;
  - Make a measurement at a second angle if there are signs of correlation between some of the model's parameters.
- To determine the properties of **multiple layers** on a substrate:
  - Determine the substrate's properties;
  - If possible, characterize each layer separately;
  - Make spectroscopic measurements at several angles below, near and above the Brewster angle; this will vary the optical path thus helping to decorrelate the thicknesses and refractive indices of the different layers.

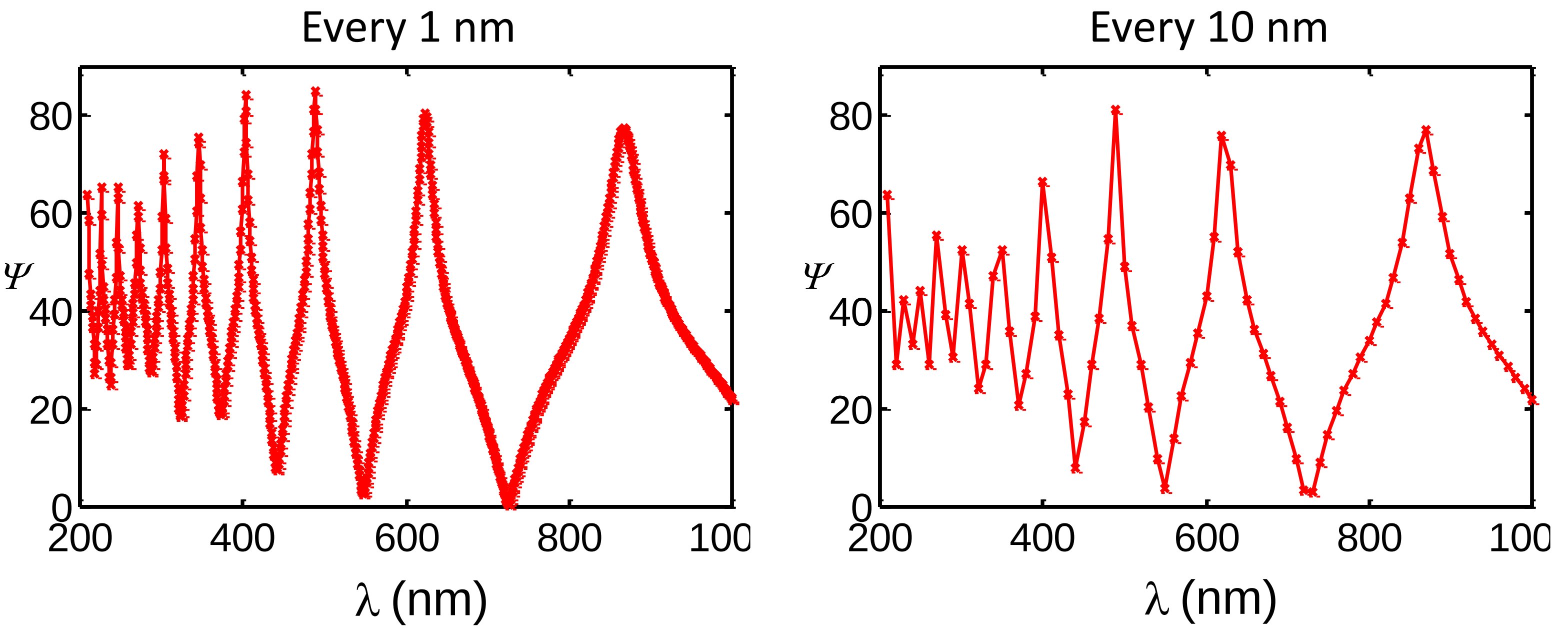
Which wavelength region should I choose?

- Obviously, the region where we wish to obtain the optical properties.
- If we want to obtain the film's thickness, we must choose a region where the film is transparent.



Resolution

- The thicker the film, the closer the interference fringes; one must therefore measure at a higher number of wavelengths.
- Keep the system's spectral resolution in mind.

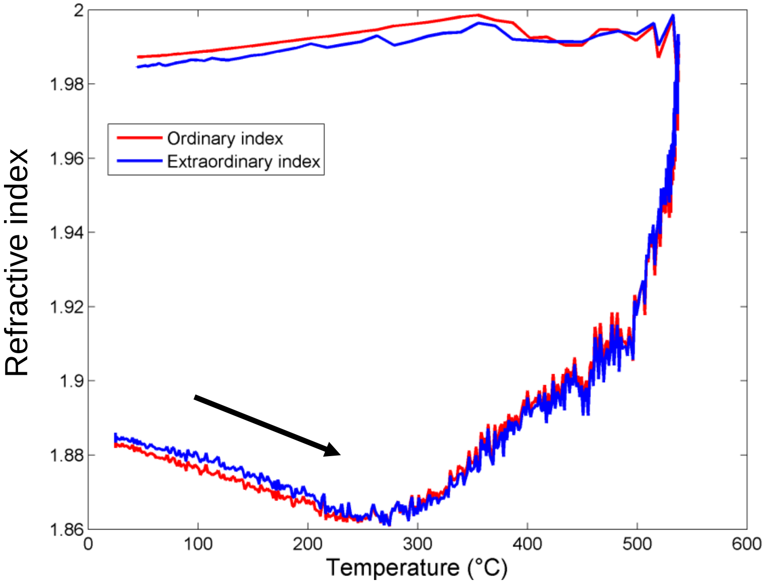

Every 1 nm

Every 10 nm

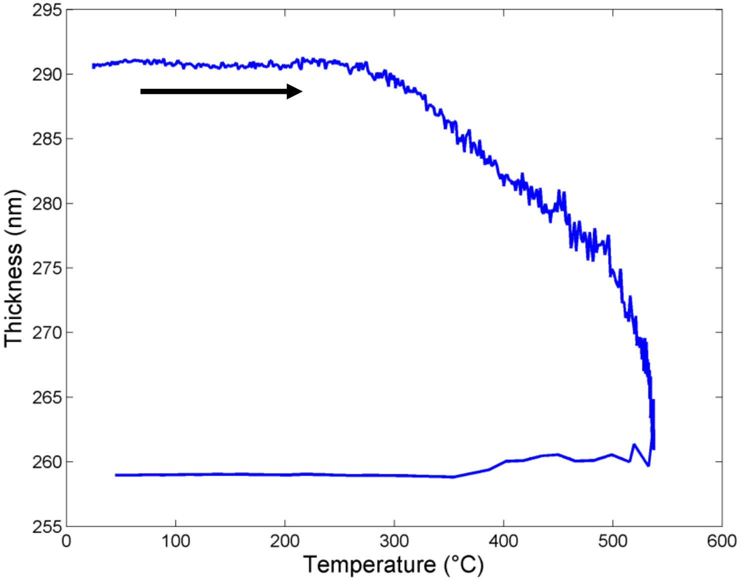
ÉCOLE
POLYTECHNIQUE
MONTRÉAL

Applications: *In situ* measurements using a heat cell

Example of *in situ* measurements as a function of temperature using a heat cell on the RC2.



Refractive index of a SiO_2-WO_3 thin film as a function of temperature.



Thickness vs temperature.

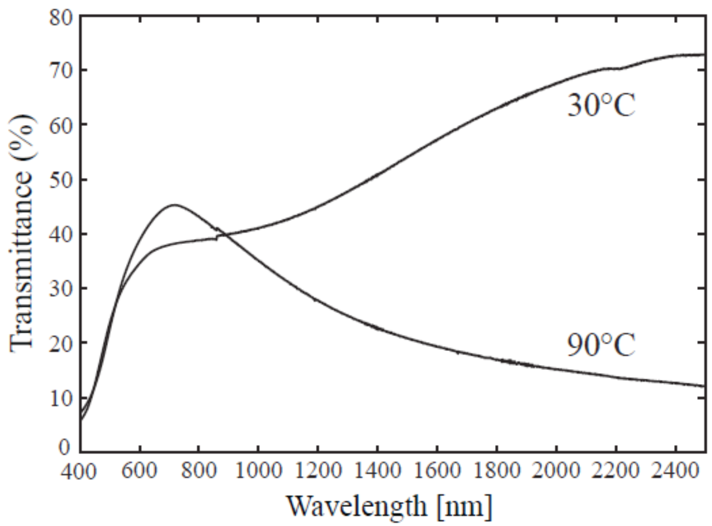
ÉCOLE POLYTECHNIQUE MONTRÉAL

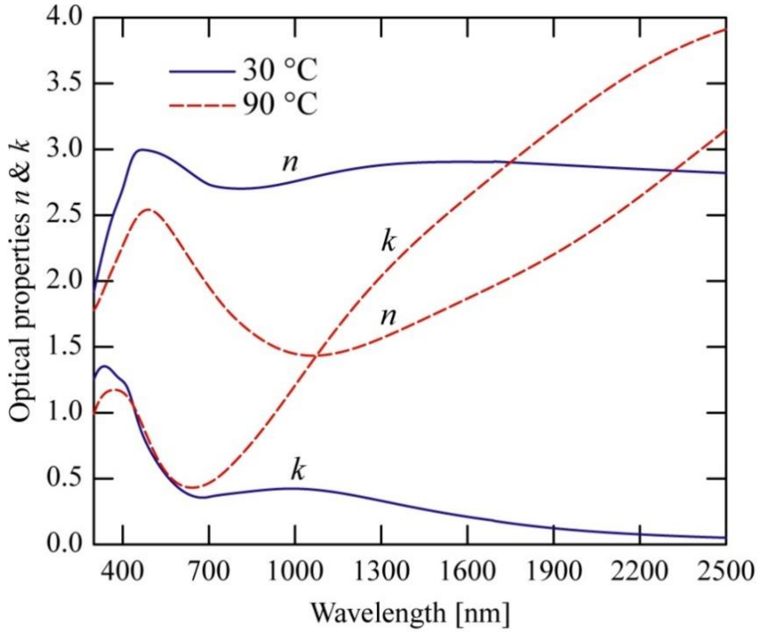
PHS6317 – Nanoengineering of thin films

Chapter 8B

Applications: *In situ* measurements using a heat cell – Thermochromic VO_2

Example of a thermochromic VO_2 coating.





J.-P. Fortier, B. Baloukas, O. Zabeida, J.E. Klemberg-Sapieha, L. Martinu, “Thermochromic VO_2 thin films deposited by HiPIMS,” *Solar Energy Materials and Solar Cells* **125** (2014) 291–296.

Applications: *In situ* measurements using an electrochemical cell – Electrochromic WO_3

ÉCOLE POLYTECHNIQUE MONTRÉAL

Optical properties of electrochromic WO_3 thin films deposited at different pressures under coloration via H^+ insertion.

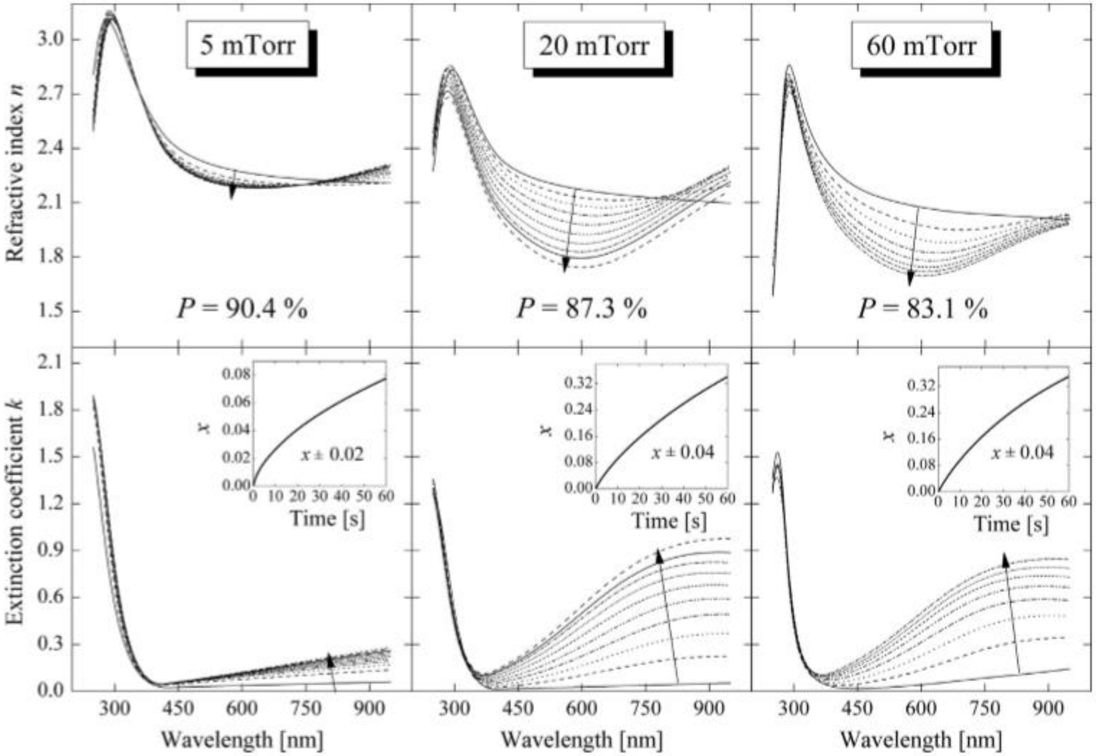


Fig. 4. Dispersion curves (*n* and *k*) for the 5, 20 and 60 mTorr samples. The insets contain the evolution of *x* *vs* time during coloration when passing from 1.0 to −0.6 V *vs* SCE. The dispersion curves are separated by a Δ*t* of 2 s.

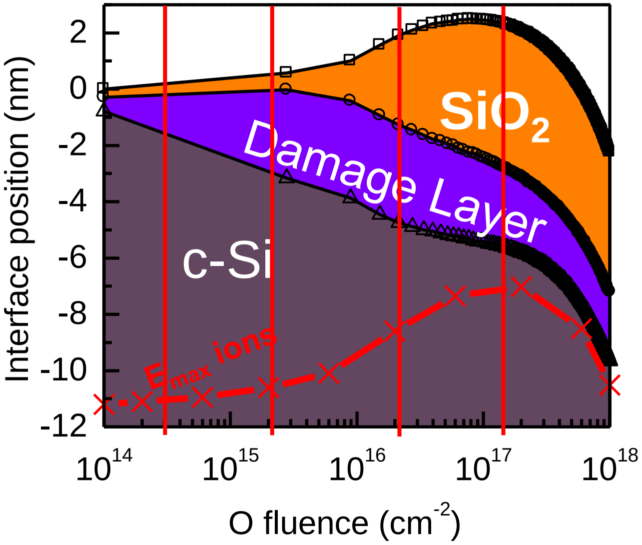
H. Camirand, B. Baloukas, J.E. Klemberg-Sapieha, L. Martinu, "*In situ* spectroscopic ellipsometry of electrochromic amorphous tungsten oxide films," Solar Energy Materials and Solar Cells **140** (2015) 77-85.

Applications: *In situ* measurements during deposition - Dynamics of plasma-induced modifications

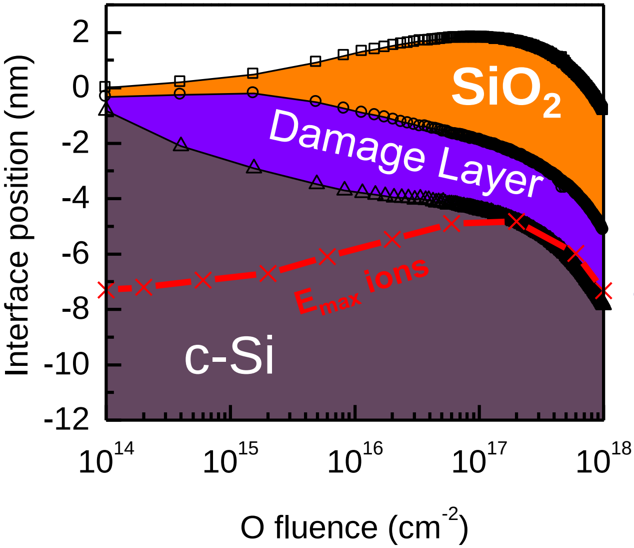
Experiment

V_B = -600 V

E_{max} ≈ 690 eV
E_m ≈ 180 eV
ϕ_I = 2x10^{15} O cm^{-2}



0.1 s 1 s 10 s 1 min



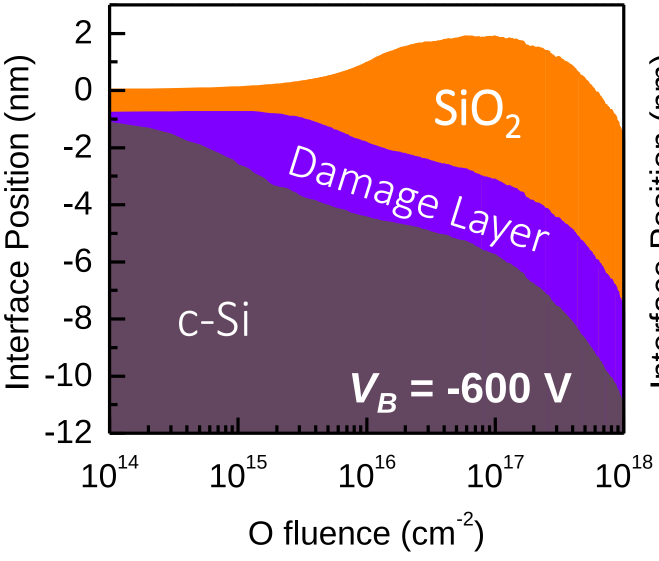
V_B = -300 V

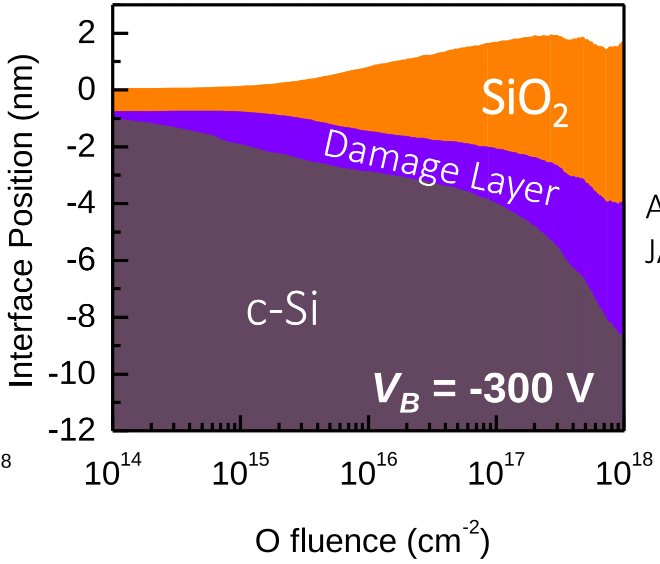
E_{max} ≈ 345 eV
E_m ≈ 90 eV
ϕ_I = 1x10^{15} O cm^{-2}

Simulation

TRIDYN-FZR

No Fitting!



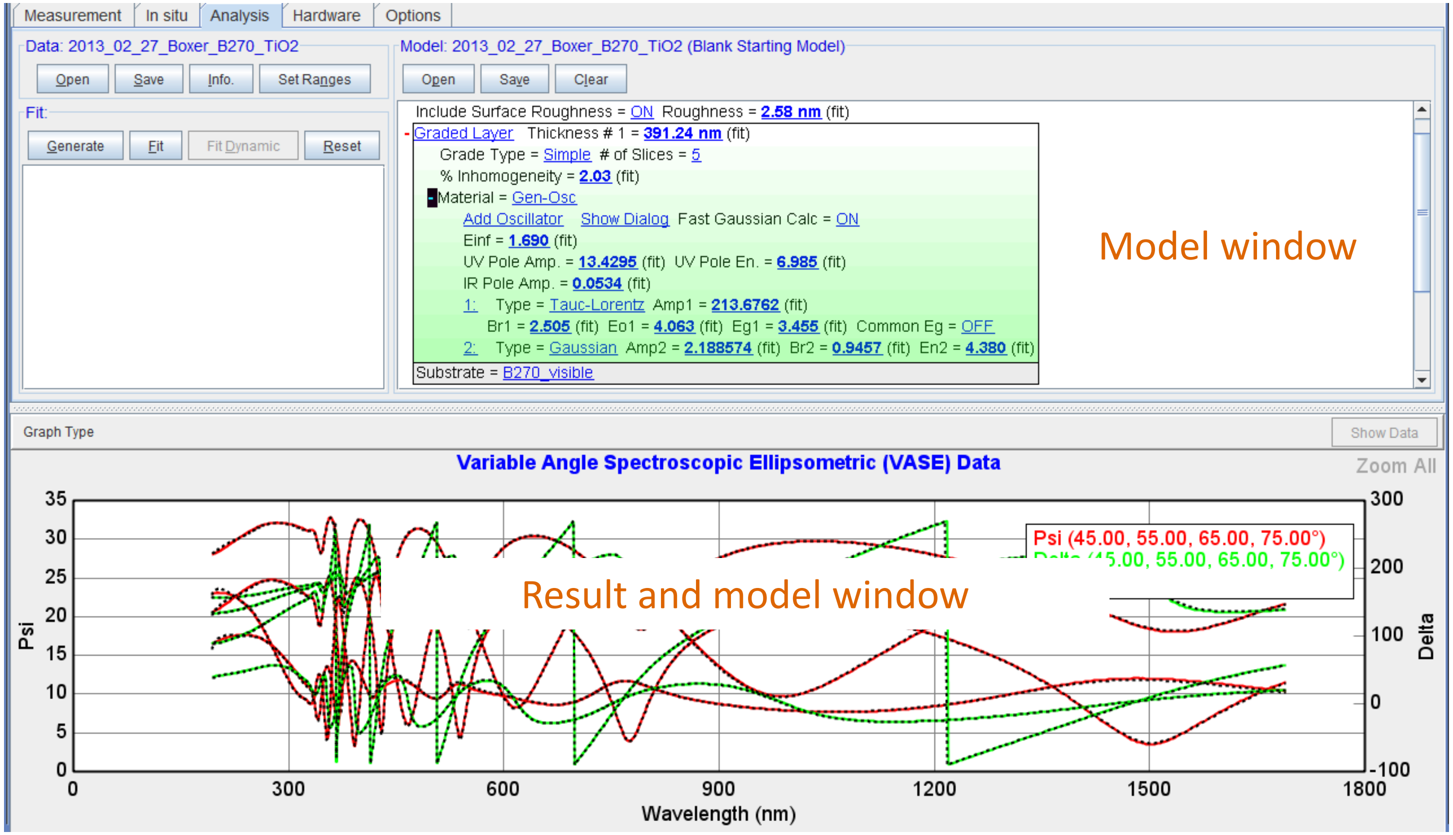


Amassian *et al.*
JAP, 2006

ÉCOLE POLYTECHNIQUE MONTRÉAL

Live example

Live example of using an ellipsometry modeling software (*CompleteEase* from J.A. Woollam Co.).



Data: 2013_02_27_Boxer_B270_TiO2

Model: 2013_02_27_Boxer_B270_TiO2 (Blank Starting Model)

Include Surface Roughness = ON Roughness = **2.58 nm** (fit)
Graded Layer Thickness # 1 = **391.24 nm** (fit)
Grade Type = Simple # of Slices = 5
% Inhomogeneity = **2.03** (fit)
Material = Gen-Osc
Add Oscillator Show Dialog Fast Gaussian Calc = ON
Einf = **1.690** (fit)
UV Pole Amp. = **13.4295** (fit) UV Pole En. = **6.985** (fit)
IR Pole Amp. = **0.0534** (fit)
1: Type = Tauc-Lorentz Amp1 = **213.6762** (fit)
Br1 = **2.505** (fit) Eo1 = **4.063** (fit) Eg1 = **3.455** (fit) Common Eg = OFF
2: Type = Gaussian Amp2 = **2.188574** (fit) Br2 = **0.9457** (fit) En2 = **4.380** (fit)
Substrate = B270_visible

Model window

Result and model window

Using *OpenFilters*

ÉCOLE
POLYTECHNIQUE
MONTRÉAL

PHS6317 – Nanoengineering of thin films

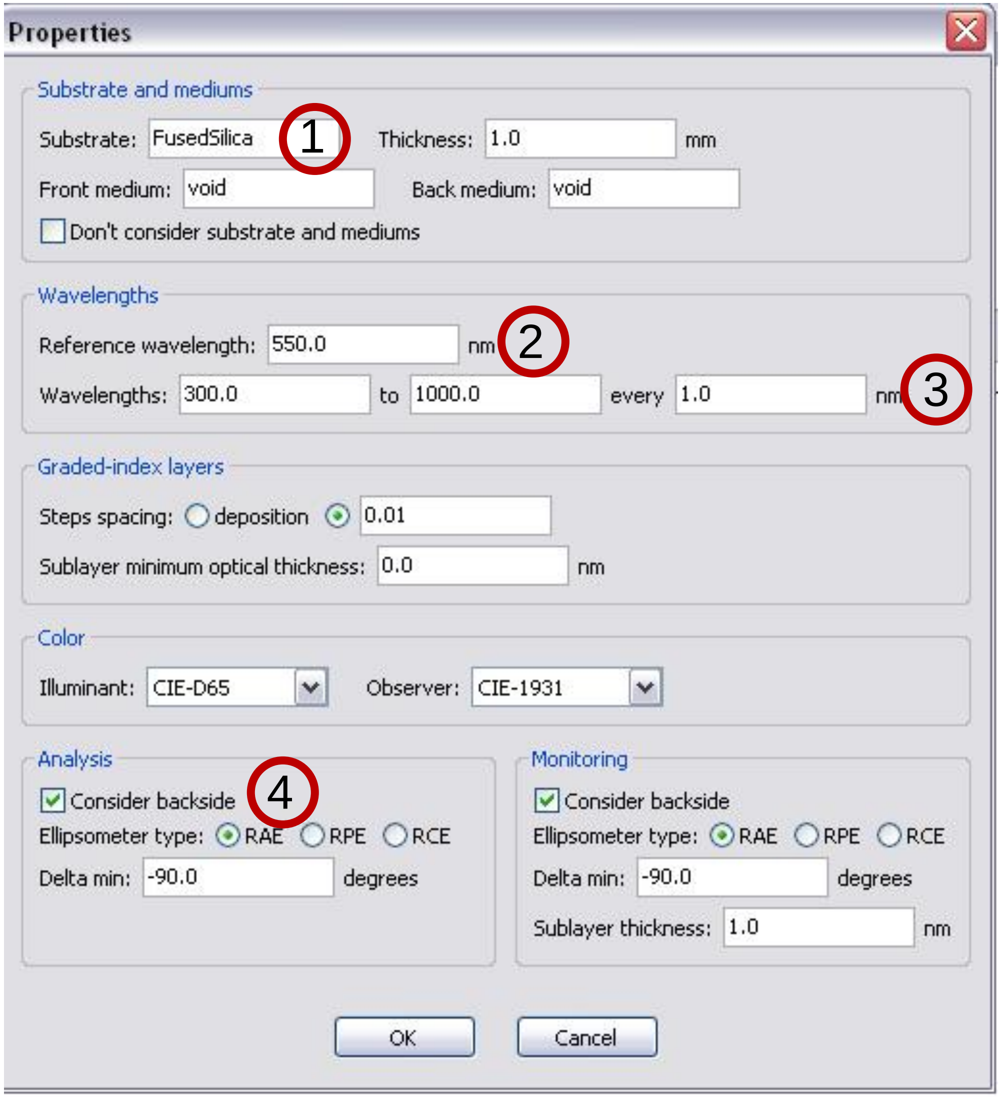
Chapter 8B

In this example, I will be using *OpenFilters,* an Open Source software developed by a former PhD student of Polytechnique Montreal (S. Larouche).

Available at: https://www.polymtl.ca/larfis/en/links

To start: Create a project and add a filter

- Choice of substrate (1)
- Reference wavelength (2)
- Wavelength range (3)
- Backside reflection (4)
- Etc.



Substrate and mediums

Substrate: FusedSilica
Thickness: 1.0 mm
Front medium: void
Back medium: void
☐ Don't consider substrate and mediums

Wavelengths

Reference wavelength: 550.0 nm
Wavelengths: 300.0 to 1000.0 every 1.0 nm

Graded-index layers

Steps spacing: ○ deposition ● 0.01
Sublayer minimum optical thickness: 0.0 nm

Color

Illuminant: CIE-D65
Observer: CIE-1931

Analysis

☑ Consider backside
Ellipsometer type: ● RAE ○ RPE ○ RCE
Delta min: -90.0 degrees

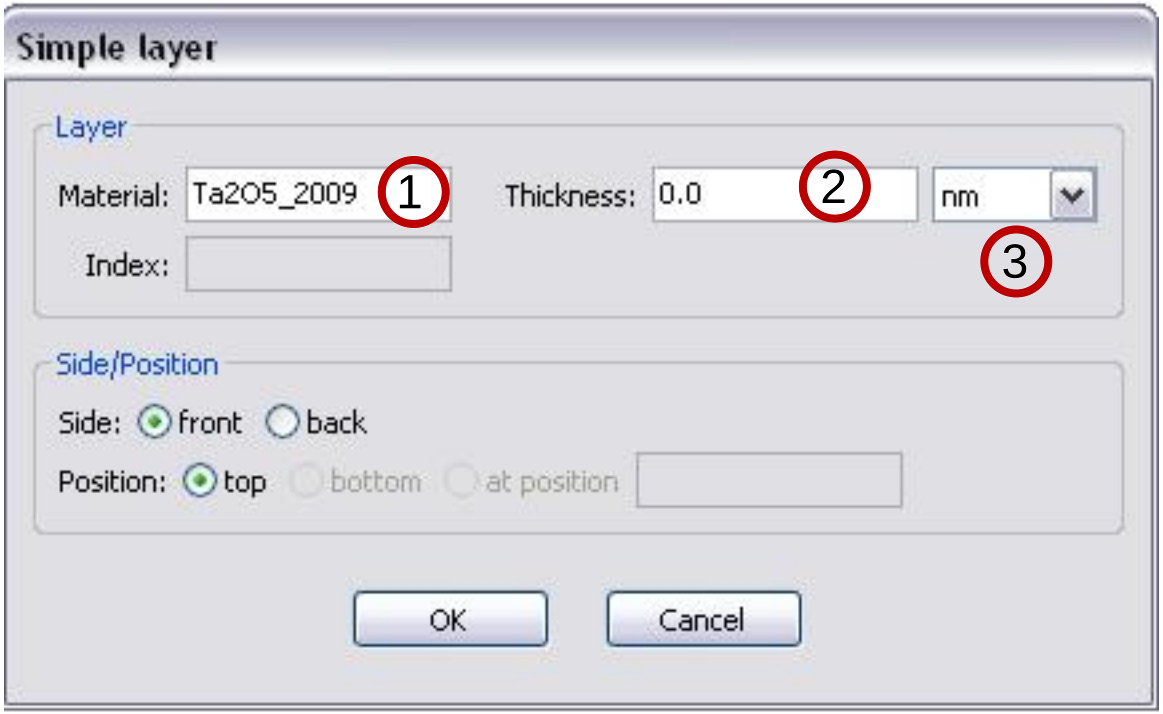
Monitoring

☑ Consider backside
Ellipsometer type: ● RAE ○ RPE ○ RCE
Delta min: -90.0 degrees
Sublayer thickness: 1.0 nm

Using *OpenFilters* – Adding layers

Next: Add layers

- Choice of material (1)
  - **Note:** It is possible to add your own materials.
- Specify thickness (2)
- Choice of thickness definition: nm, quarter-wave, etc. (3)



Simple layer

Layer

Material: Ta2O5_2009

Index:

Thickness: 0.0 nm

Side/Position

Side: ● front ○ back

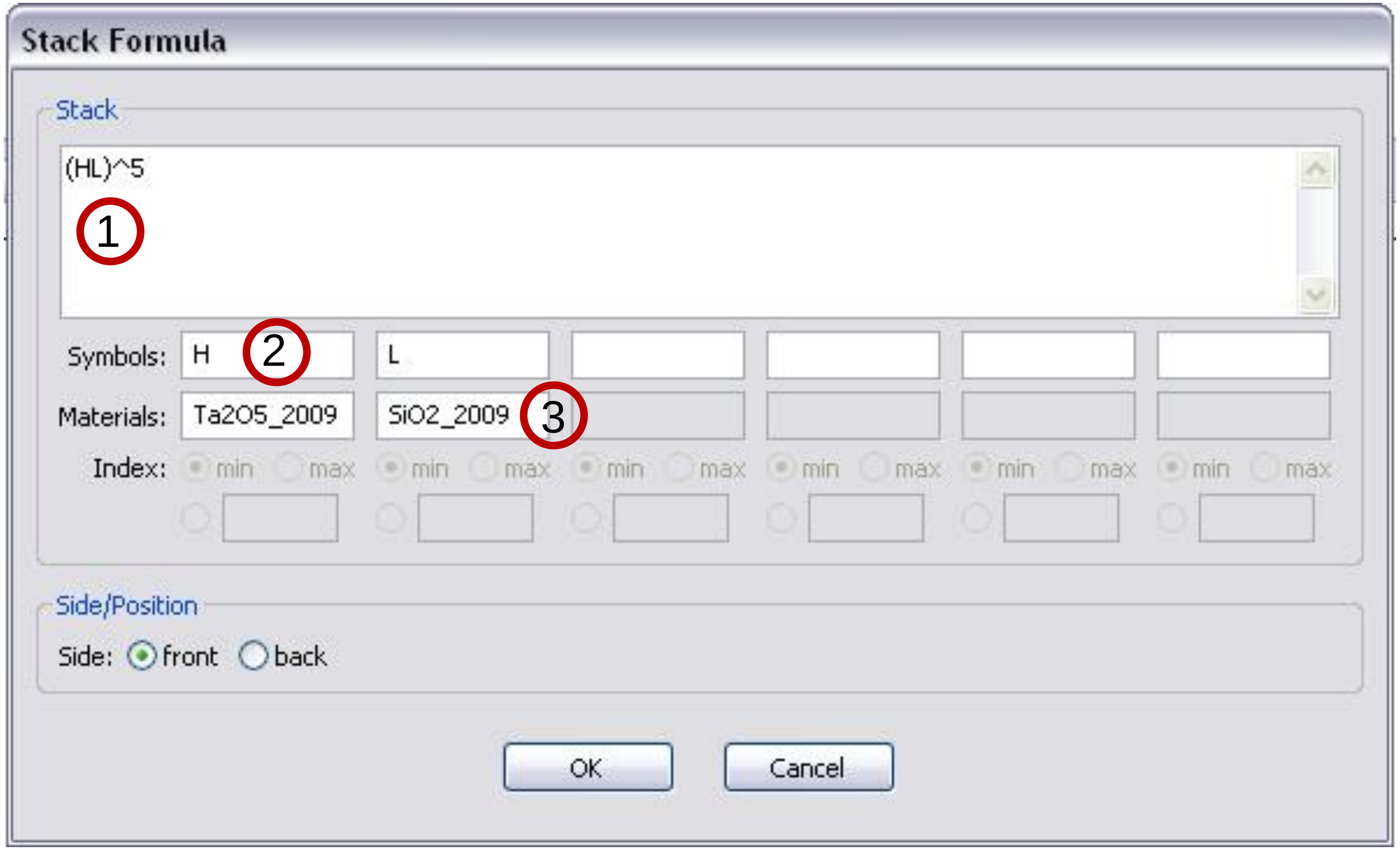
Position: ● top ○ bottom ○ at position

ÉCOLE POLYTECHNIQUE MONTRÉAL

Using *OpenFilters* – Stack formula

To go faster: Adding multiple layers using a stack formula

Structure of the filter (1), define symbols (2) and choice of materials (3)



(HL)^5

Symbols: H | L

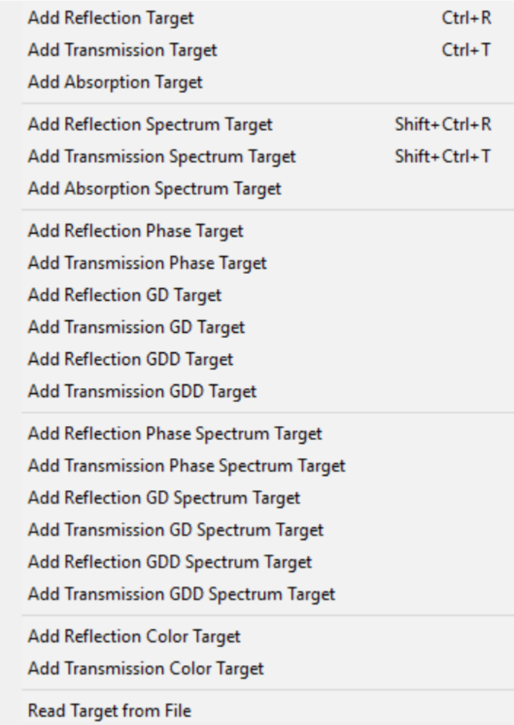
Materials: Ta2O5_2009 | SiO2_2009

Side: ● front ○ back

ÉCOLE
POLYTECHNIQUE
MONTRÉAL

Using *OpenFilters* – Filter optimization

To optimize a filter, one must define targets.



Add Reflection Target Ctrl+R
Add Transmission Target Ctrl+T
Add Absorption Target

Add Reflection Spectrum Target Shift+Ctrl+R
Add Transmission Spectrum Target Shift+Ctrl+T
Add Absorption Spectrum Target

Add Reflection Phase Target
Add Transmission Phase Target
Add Reflection GD Target
Add Transmission GD Target
Add Reflection GDD Target
Add Transmission GDD Target

Add Reflection Phase Spectrum Target
Add Transmission Phase Spectrum Target
Add Reflection GD Spectrum Target
Add Transmission GD Spectrum Target
Add Reflection GDD Spectrum Target
Add Transmission GDD Spectrum Target

Add Reflection Color Target
Add Transmission Color Target

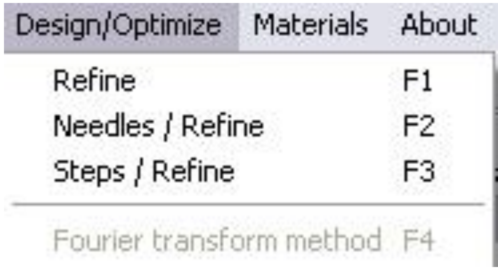
Read Target from File

- Spectral and wavelength specific targets
- Color targets
- Etc.

- It is possible to read targets from a file.

The optimization process can then be launched:

- Refine the thicknesses of the layers already present.
- “Needle” method: Add infinitely thin layers at the most appropriate positions and refine.



Design/Optimize Materials About

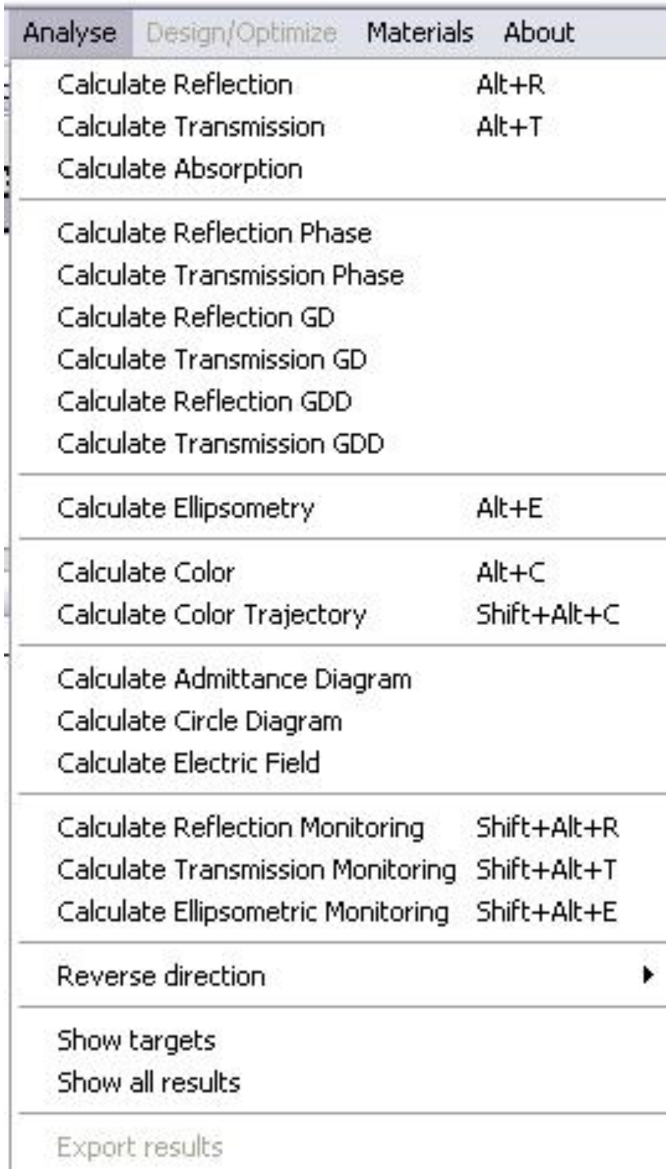
Refine F1
Needles / Refine F2
Steps / Refine F3

Fourier transform method F4

Using *OpenFilters* – Filter analysis

Possibilities: Analyse filter

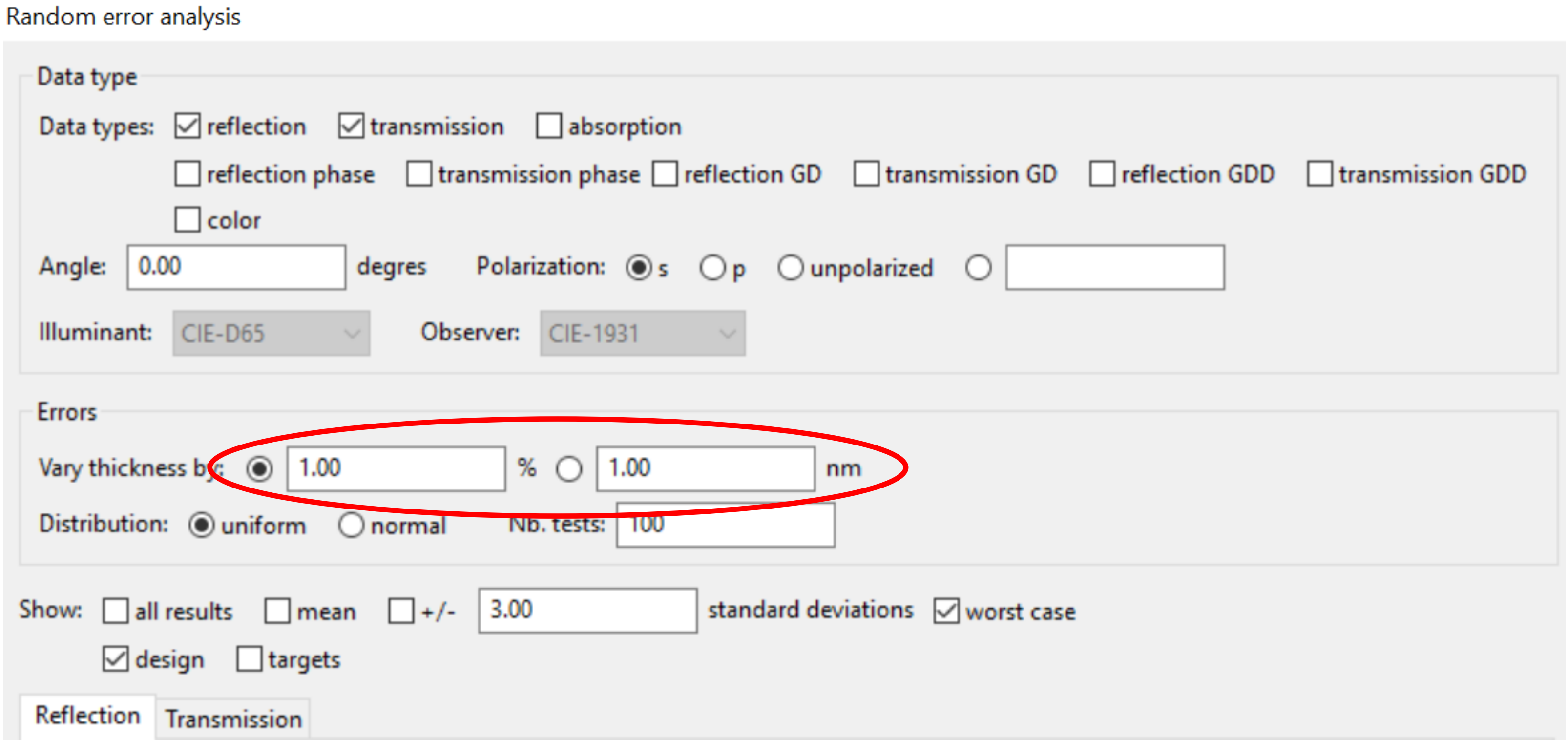
- Spectral reflection
- Spectral transmission
- Spectral absorption
- Color calculations
- Angular color variations
- Optical monitoring
- Ellipsometry
- Electric field intensity
- Etc.



Using *OpenFilters* – Preproduction

ÉCOLE POLYTECHNIQUE MONTRÉAL

Random error analysis – Filter sensitivity to deposition errors



Random error analysis

Data type

Data types: ☑ reflection ☑ transmission ☐ absorption
☐ reflection phase ☐ transmission phase ☐ reflection GD ☐ transmission GD ☐ reflection GDD ☐ transmission GDD
☐ color

Angle: 0.00 degres Polarization: ● s ○ p ○ unpolarized ○

Illuminant: CIE-D65 Observer: CIE-1931

Errors

Vary thickness by: ● 1.00 % ○ 1.00 nm

Distribution: ● uniform ○ normal Nb. tests: 100

Show: ☐ all results ☐ mean ☐ +/- 3.00 standard deviations ☑ worst case
☑ design ☐ targets

Reflection Transmission

References

- Harland G. Tompkins, *A user's guide to ellipsometry*, San Diego, Academic Press, 1993.
  - Application examples of ellipsometry. Library (QC 443 T65 1993).
- R. M. A. Azzam and N. M. Bashara, *Ellipsometry and polarized light*, Amsterdam, North-Holland, 1977.
  - Interesting for an in-depth analysis of the mathematics behind ellipsometry.
- *WVASE32 User Guide* from J.A. Woollam Co.