Optical methods : spectroscopic ellipsometry

Workshop "Non-Conventional Materials Characterization Methods"

FPMs – Mons – 24/04/2012

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Outline of the presentation

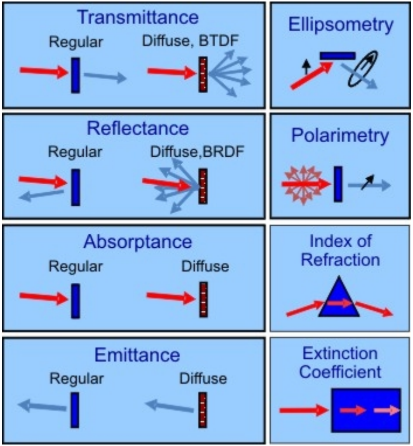
Optical properties of materials

- Optical processus in materials : reflexion, propagation, transmission
- Propagation modes : refraction, absorption and luminescence, diffusion (elastic or inelastic)
- Restricted (and more precise) meaning : complex frequency dependent refractive index or dielectric tensor

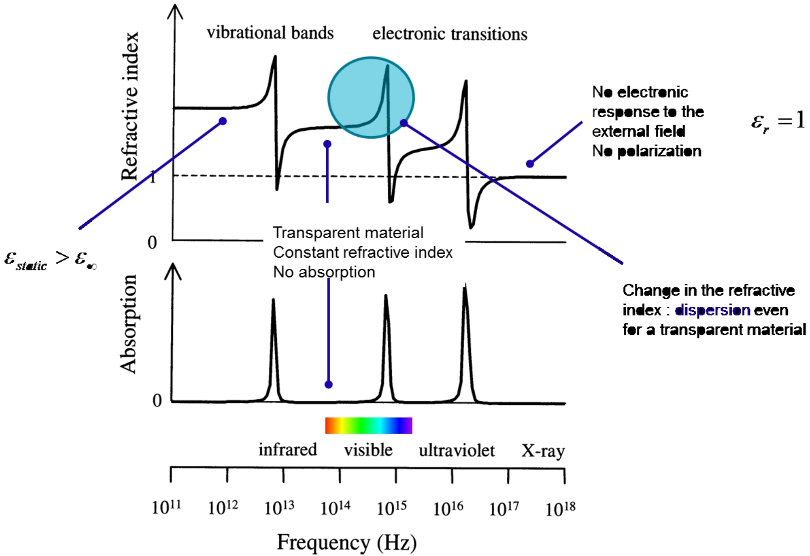
$$\tilde{\epsilon}(\omega) = [n(\omega) - j\, k(\omega)]^2$$

$$\alpha(\omega) = \frac{4\pi}{\lambda} k(\omega)$$

- Need for absolute experimental methods



What in which spectral range ?



$\varepsilon_{static} > \varepsilon_{\infty}$

Transparent material
Constant refractive index
No absorption

No electronic
response to the
external field
No polarization

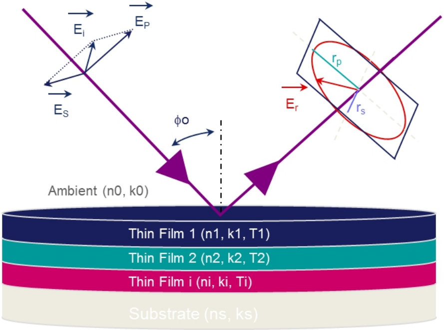
$\varepsilon_r = 1$

Change in the refractive
index : dispersion even
for a transparent material

Ellipsometry : a powerful tool to probe layer thickness and optical properties

Paul Karl Ludwig Drude (1863-1906)

Different behavior of two light beams with orthogonal polarizations after reflexion (1890)



$$\rho = \tan \Psi e^{i\Delta}$$

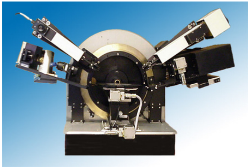
$$\tan \Psi = \frac{|R_p|}{|R_s|} \quad \text{and} \quad \Delta = \delta_p - \delta_s$$

Spectroscopic ellipsometry at UMONS and MATERIA NOVA

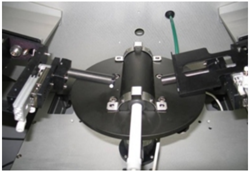
Rudolph Auto EL III SWE

Rudolph S2000 SE

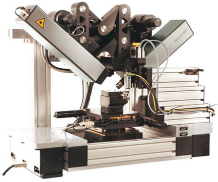
SOPRA GESP5 NUV-VIS-NIR (2001)



SOPRA FTIR-SE (2003)



SOPRALAB ellipsometric porosimeter (2009)



ACCURION Imaging Ellipsometer (03/2012)

Overall spectral range : 250 nm – 18000 nm with control of temperature (-196 K – 650 K), determination of nano- and mesoporosity and spacial resolution better than 1 micron

Optical properties of nickel-chromium oxide layers

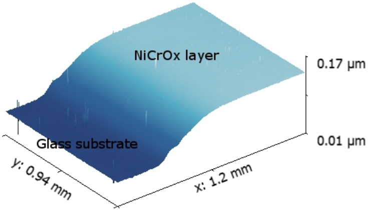
Importance of $NiCrO_x$:

- Interest in solar absorbers manufacturing
- High absorbance
- Good stability in a wide range of oxidizing/reducing environments
- High thermal resistance

Materials and methods :

- Films deposited by magnetron sputter deposition (Materia Nova) on glass substrates
- Roughness by optical profilometry
- Optical properties in VIS-NIR $(350 - 1700 \text{ nm})$ and mid-IR $(600 - 6000 \text{ cm}^{-1})$ by SE analysis

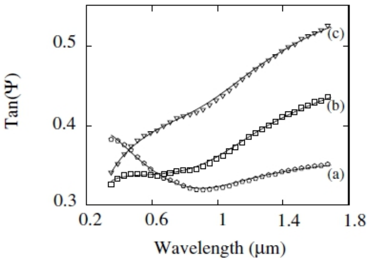
Optical properties of nickel oxide chromium thin films as a function of their chemical composition

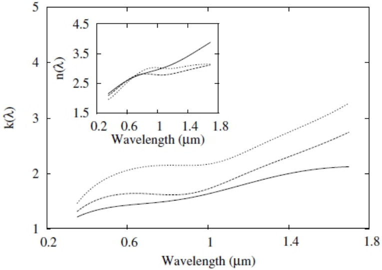


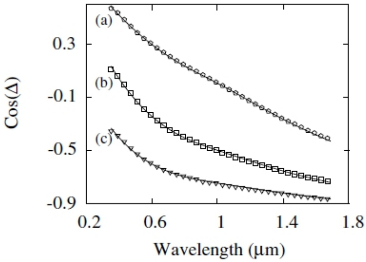
Optical profilometry of a $\simeq$ 170 nm-thick $NiCrO_x$ film on model substrate (glass) [Magn. 5x – Area : $0.94 \text{ mm} \times 1.2 \text{ mm}$]

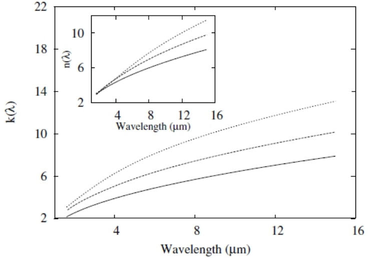
- Roughness parameters $\leq 1 \text{ nm}$
- One-layer model for SE data modeling

Optical properties of nickel-chromium oxide layers









Optical properties of nickel-chromium oxide layers

- Optical modeling with non-interacting Lorentzian oscillators and Drude term for conductivity in the IR range
- Importance of the metal-oxide transition
- Equivalence between electrical conductivity (4-points method) and optical conductivity (FTIR-SE results)

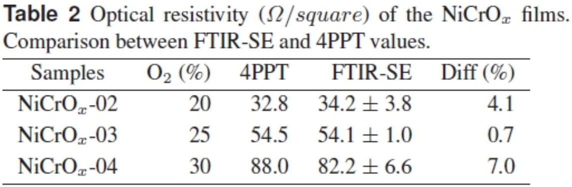
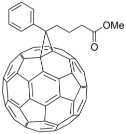


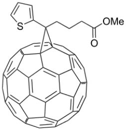
Table 2 Optical resistivity ($\Omega/square$) of the NiCrO$_x$ films. Comparison between FTIR-SE and 4PPT values.

Samples	O$_2$ (%)	4PPT	FTIR-SE	Diff (%)
NiCrO$_x$-02	20	32.8	34.2 ± 3.8	4.1
NiCrO$_x$-03	25	54.5	54.1 ± 1.0	0.7
NiCrO$_x$-04	30	88.0	82.2 ± 6.6	7.0

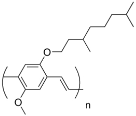
Materials for organic solar cells (OPV) : P3HT-PCBM



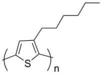
PCBM



ThCBM

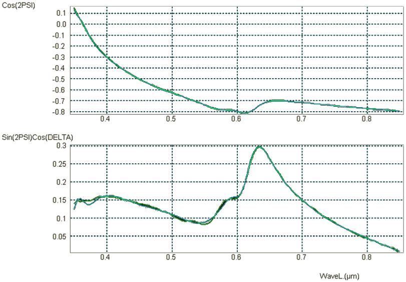


MDMO-PPV

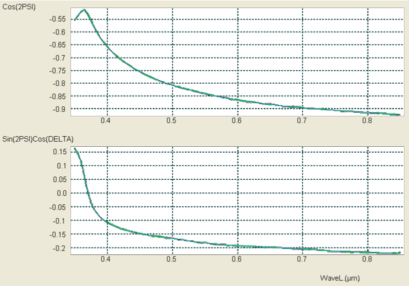


P3HT

- PCBM : n-type organic semiconductor (electron acceptor)
- P3HT : electron donor

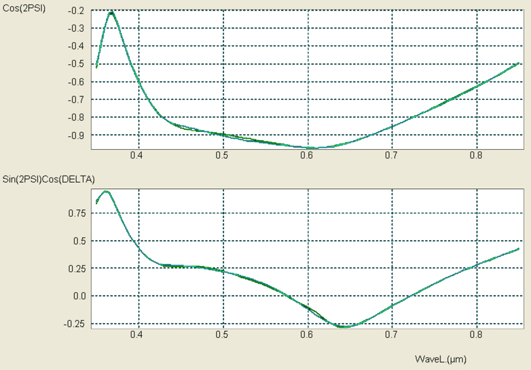


Ellipsometric spectra (Green : data – Blue : fit results) of a 55 nm-thick P3HT film on silicon substrate



Ellipsometric spectra (Green : data – Blue : fit results) of a 21 nm-thick PCBM film on silicon substrate

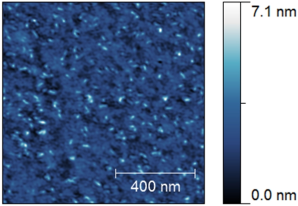
Materials for organic solar cells (OPV) : P3HT-PCBM



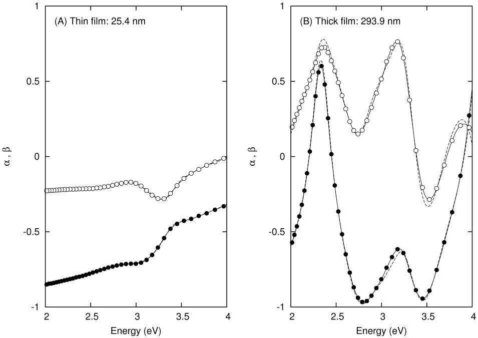
Ellipsometric spectra (Green : data – Blue : fit results) of a mixed P3HT/PCBM (1 :0.7 w :w) 180 nm - thick film on silicon substrate

Optical response of dielectric matrices embedding silver nanoparticles

- Importance of noble metal nanoparticles (embedded or localized at interfaces) or of metallic gratings to enhance solar light absorption using plasmonic modes
- Polyvinyl-alcohol (PVA) films (20 nm) with high silver content (25% $AgNO_3$)

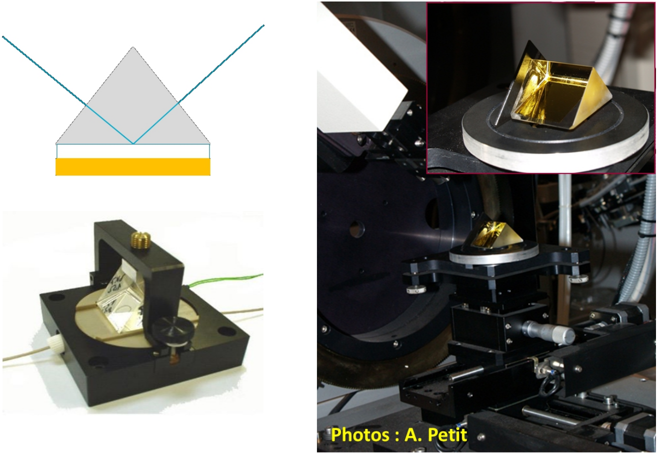


Topography AFM image (non-contact mode) of a 25 nm-thick film



Spectroscopic ellipsometry data (symbols) and fit results (lines) for (A) thin and (B) thick films

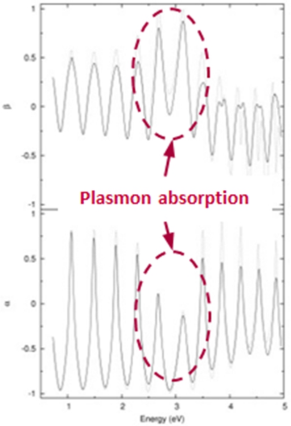
TIRSE : Total Internal Reflexion SE



Photos : A. Petit

Experimental setup for TIRSE experiments

Optical response of nanocomposites : plasmonic effects

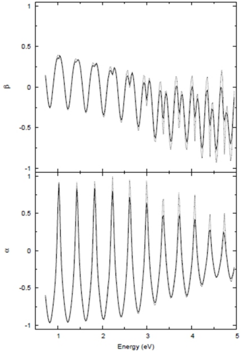


Plasmon absorption

Optical model :
one layer
(Cauchy) and
Lorentzian
absorption

PVA film annealed 10
min at 90°C (SE data
and regression
results)

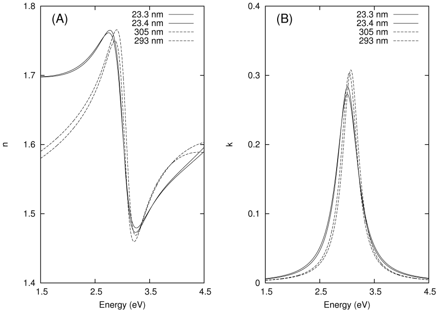
Pure PVA

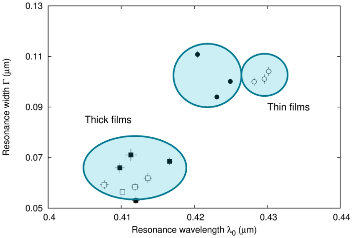


Comparison between pure PVA film and Ag NPs doped films : optical response

Optical response of dielectric matrices embedding silver nanoparticles

- Polymer films (PVA) embedding silver nanoparticles : behavior of thin and thick films at low (2.5%, open symbols) and high (12.5%, plain symbols) doping levels
- Significant difference in the refractive index of thin and thick films at high constant doping levels
- Need for modeling beyond the classical effective media theories (Bruggeman) : island models ('optical percolation')

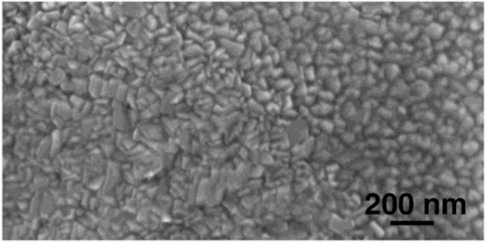




Smart materials with tunable optical properties for control of the solar reflectance/transmittance

Vanadium VO_2 :

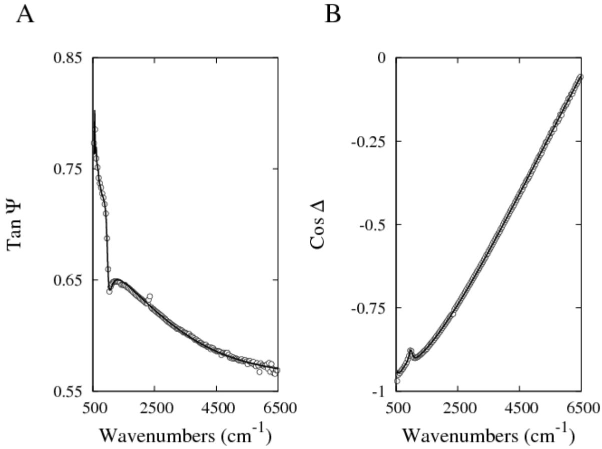
- Thermochromic material with tunable transition temperature (doping)
- Oxyde–Metal transition



(Lafort et al, Thin Solid Films 2011)

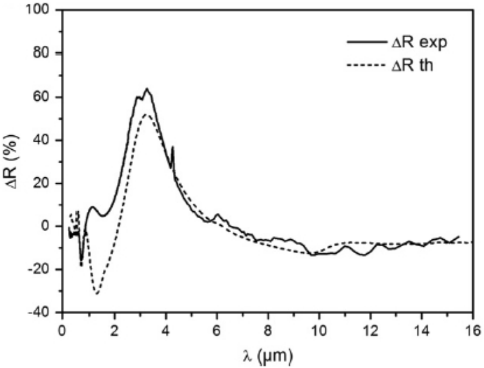
Vanadium oxide : SE data and fit results

mid-IR spectral range and FTIR-SE analysis



SE data for a 200 nm-thick VO_2 film

Vanadium oxide : reflexion contrast in the VIS-NIR and MidIR spectral domains



Integrated reflectance :

$$IR = \frac{\int_{\text{spectral range}} R(\lambda)S(\lambda)d\lambda}{\int_{\text{spectral range}} S(\lambda)d\lambda}$$

with $S(\lambda)$: solar spectrum (*e.g. AM 1.5*)

Imaging ellipsometry

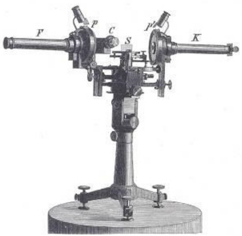
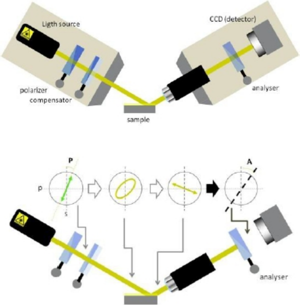


Fig. 81.

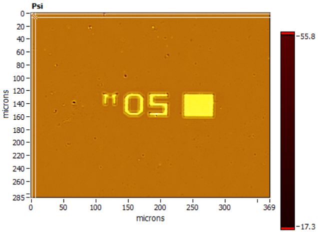
Figure 1. Historical setup of an ellipsometer [Paul Drude, *Lehrbuch der Optik*, Leipzig, 1906]



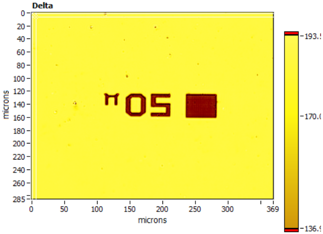
Principles of IE : optical components (top) and polarization states of light (bottom)

Advantages : ellipsometry and IMAGES !
Drawbacks : Increasing number of data, complexity of the analysis
Applications : materials science, biosensors . . .

SiO_2 boxes on silicon substrate with native oxide



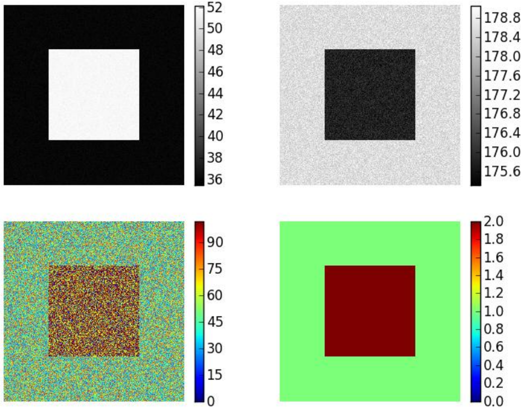
Ψ image



Δ image

Direct inversion of the ellipsometric data fails !

Multivariate analysis : sorting pixels is better !

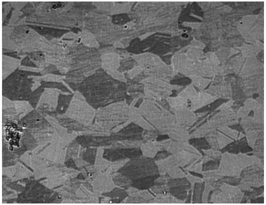


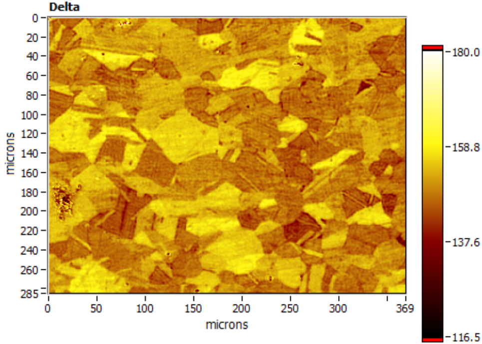
Top : simulated data with noise added
Bottom : Classified pixels (k-means and hierachical cluster analysis)

Vanadium oxide

100-nm thick VO_2 film on stainless steel substrate

Local information required on optical properties : IMAGING ELLIPSOMETRY



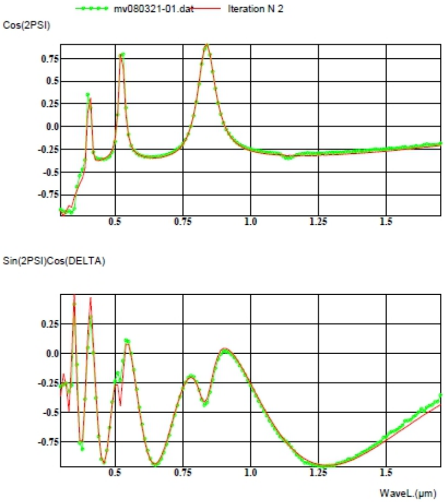


White light image (polarization mode) → : structural information and contours

Imaging ellipsometry data (Δ image) → : optical properties at the micron scale but increa sing number of data (hypercube)

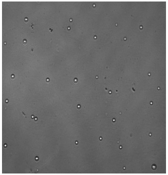
Multivariate analysis methods required

Tungstene oxyde on stainless steel

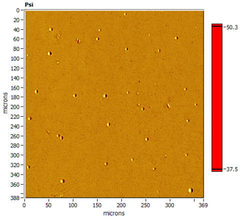


- Optical properties described by Cauchy law
- Thickness : $\simeq$ 320 nm

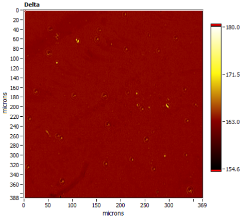
Tungstene oxyde on stainless steel



White light image



Ψ image



Δ image

320nm-thick WO_3 film on stainless steel

Resume and conclusions

Resume

- Non-destructive analysis of optical properties
- Large spectral domain covered by spectroscopic ellipsometry
- Determination of porosity, temperature effects and local effects at the (sub)micron scale

Conclusions

- Experimental technique suitable for investigating the optical bahavior of solar energy materials (solar absorbers, PV-OLED, smart materials . . .)
- Need of advanded models for metallic layers, metal-oxide transition and link between AFM and ellipsometric roughness parameters

Thank you for your attention !
Questions ?

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