What can we learn from imaging ellipsometry analysis of plasmonic nanocomposite materials ?

Michel Voué

University of Mons
Physics of Materials and Optics Unit
Research Institute for Science and Materials Engineering
Mons – Belgium

TUTORIAL bePOM 21

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Outline of the presentation

- Introduction and research context
- Basics of ellipsometry
- (Spectroscopic) Imaging ellipsometry (SEI)
- Applications to plasmonic nanocomposites
- Take-home message

Literature : What to read at the beginning ?

1. Tompkins, H.G. (1993) A users 's guide to ellipsometry, Academic Press
2. Tompkins, H.G and McGahan W.A. (1999) Spectroscopic ellipsometry and reflectometry – A user's guide, John Wiley
3. Tompkins, H.G and Hilfiger J.N. (2016) Spectroscopic Ellipsometry: Practical Application to Thin Film Characterization, Momentum Press

4. Tompkins, H.G. and Irene, E. (Eds) (2005) *Handbook of Ellipsometry*, William Andrew Publishing
5. Fujiwara, H (2007) *Spectroscopic Ellipsometry: Principles and Applications*, Wiley
6. Azzam, R.M.A. and Bashara, N.M. (1996) *Ellipsometry and polarized light*, North-Holland.

Measuring the thickness of a thin film using light …

Gris de fer	0,040	Jaune vif	0,332	Vert	0,747	Indigo	1,151
Gris lavande	0,097	Jaune brun	0,430	Vert plus clair	0,826	Bleu	
Bleu gris	0,158	Orangé rougeâtre	0,505	Vert jaunâtre	0,843	(teinte verdâtre)	1,258
Gris plus clair	0,218	Rouge chaud	0,536	Jaune verdâtre	0,866	Vert de mer	1,334
Blanc verdâtre	0,234	Rouge plus foncé	0,551	Jaune pur	0,910	Vert brillant	1,376
Blanc	0,259	Pourpre	0,565	Orangé	0,948	Jaune verdâtre	1,426
Blanc jaunâtre	0,267	Violet	0,575	Orangé rougeâtre		etc.	
Jaune paille pâle	0,275	Indigo	0,589	vif	0,998		
Jaune paille	0,281	Bleu de ciel	0,664	Rouge violacé foncé	1,101		
Jaune clair	0,306	Bleu verdâtre	0,728	Violet bleuâtre clair	1,128		

Soap bubbles, Newton's colors and associated thickness

- R. Boyle (1627-1691) : Colors of soap bubbles
- I. Newton (1643-1727) : Interference rings
- **E. Malus (1775-1812) : Polarized light (1810)**

Robert Boyle (1627-1691)

The early age of ellipsometry

Paul Karl Ludwig Drude (1863-1906)

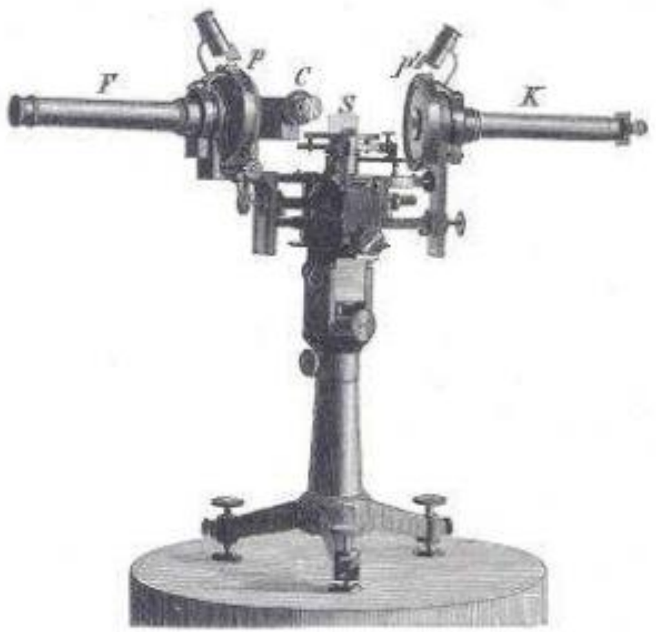


Fig. 81.

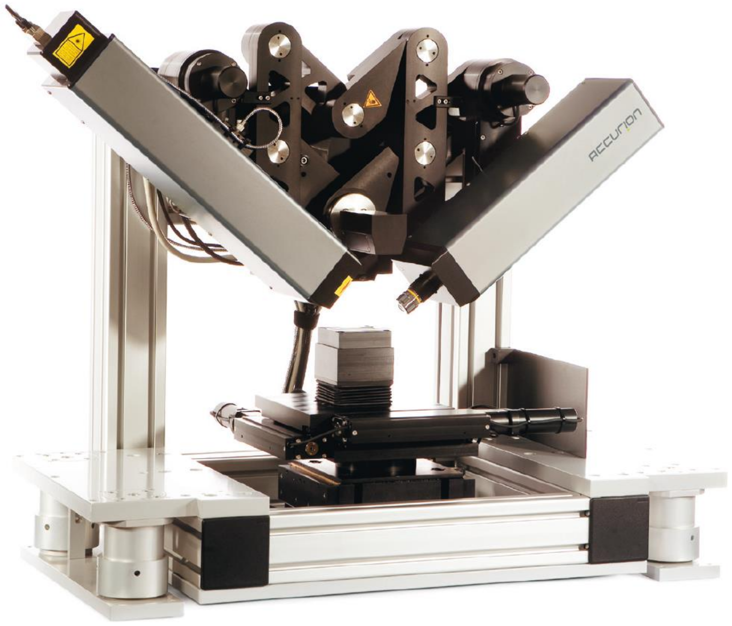
Figure 1. Historical setup of an ellipsometer [Paul Drude, *Lehrbuch der Optik*, Leipzig, 1906]

P. Drude (1863-1906)

Additional phase difference between 2 orthogonally polarized beams upon reflection on a sample

Spectroscopic ellipsometry (SE).

A set of **non-destructive optical analysis techniques** for surfaces, interfaces and multilayer materials, based on the variation of the state of polarization of light after reflection from the surface.



Ellipsometer is NOT a crystal globe …

You only merely get out what you decided to put in …

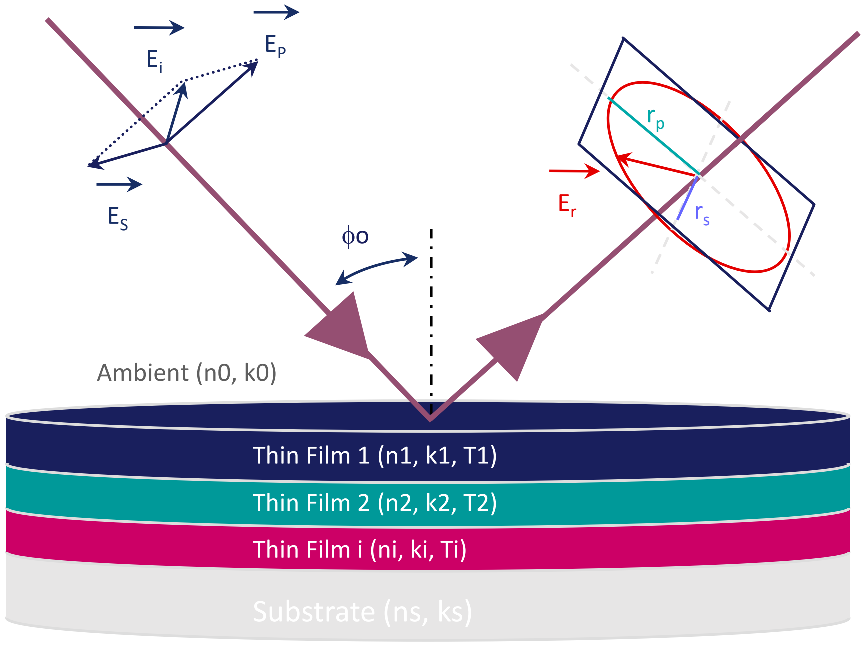
What do we really measure in ellipsometry ?

Basic principle :

Reflection at the interface

=

Polarization change



$$\rho = \frac{r_p}{r_s} = \tan\Psi \; e^{i\,\Delta} \quad \text{with} \quad \tan\Psi = \frac{|r_p|}{|r_s|} \quad \text{and} \quad \Delta = \delta_p - \delta_s$$

Ellipsometry is …

… a set of non destructive methods based on measuring the change in the state of polarization of light after reflection at non-normal incidence on the surface to be studied.

- The measurement gives 2 independent angles Ψ and Δ.
- This is an absolute measure: no benchmark required
- This is an indirect technique: it does not give direct access to the physical parameters of the sample (thickness, indices, concentrations, etc.)
- It is always mandatory to use a model to describe the sample.

Some bibliometric information (23/9/2021) :

- *Ellipsometry (130k) – SE (60k) – IE (2820) – SIE (185)*
- *MME (1300) – MMIE (44)*

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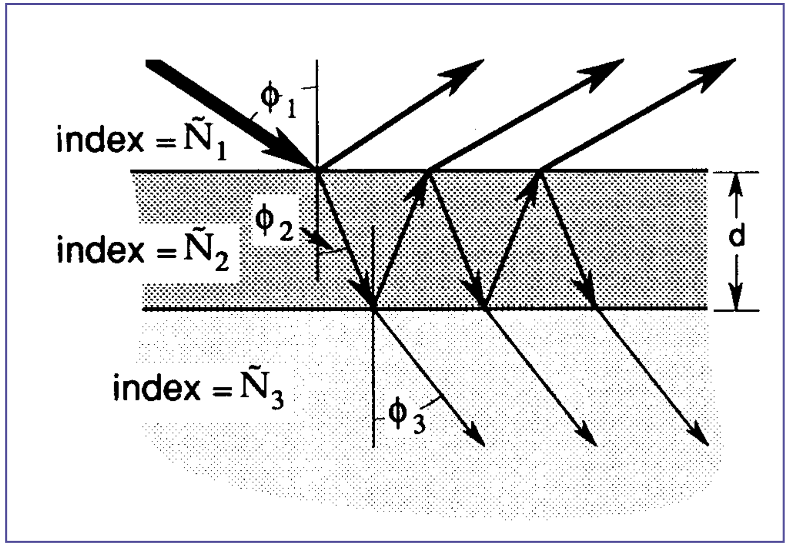
Film / substrate : multiple reflections and optical contrat



$$R^p = \frac{r_{12}^p + r_{23}^p \exp(-2j\beta)}{1 + r_{12}^p r_{23}^p \exp(-2j\beta)} \qquad R^s = \frac{r_{12}^s + r_{23}^s \exp(-2j\beta)}{1 + r_{12}^s r_{23}^s \exp(-2j\beta)}$$

$$\beta = 2\pi \left(\frac{d}{\lambda} \right) \tilde{N}_2 \cos\phi_2$$

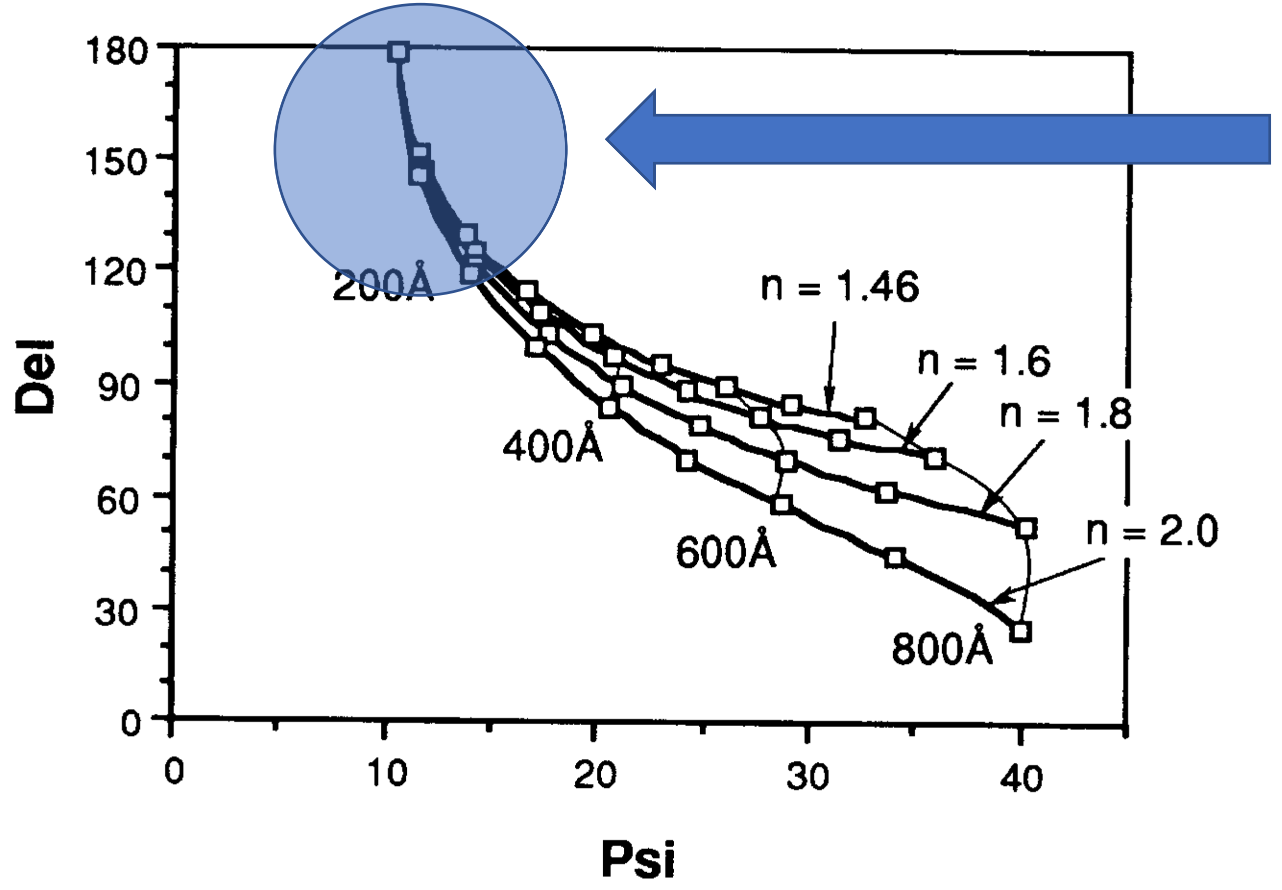
R_p differs from r_{12} if the exponential factor compensates the lack of optical contrast

THICKNESS NEEDED

$r_{23} \sim 0$

AMBIENT – AIR (n = 1)
THIN ORGANIC LAYER (**2 nm**, n ~1.45)
SUBSTRATE - GLASS (n ~1.51)

Thickness effects …



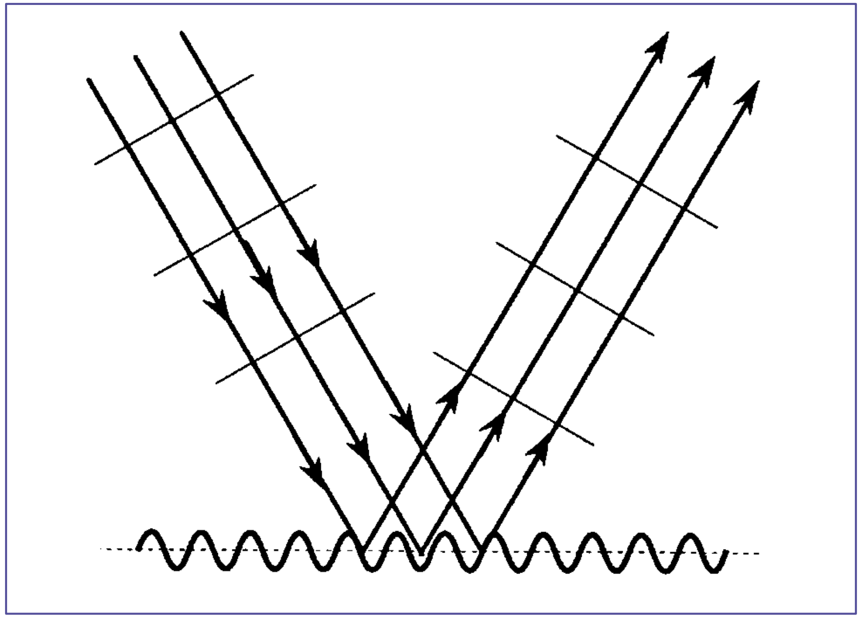
No way to measure the differences between very thin layer optical response if the optical indices of the layers are close to each other

OPTICAL CONTRAST or THICKNESS requested !!!

Roughness effects …

Microscopic roughness :

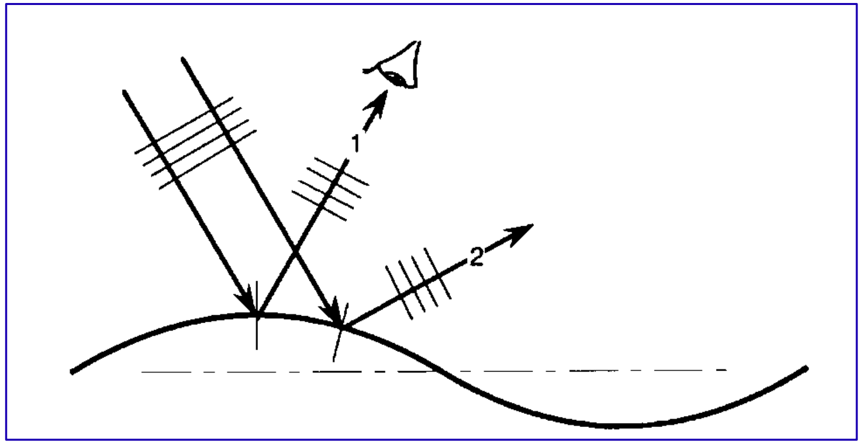
Rough surface (with respect to the wavelength of the probing light)



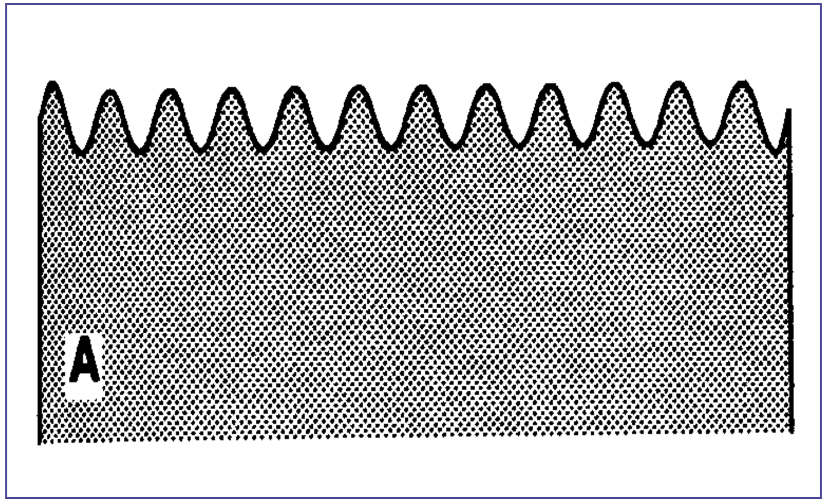
Macroscopic roughness (waviness) :

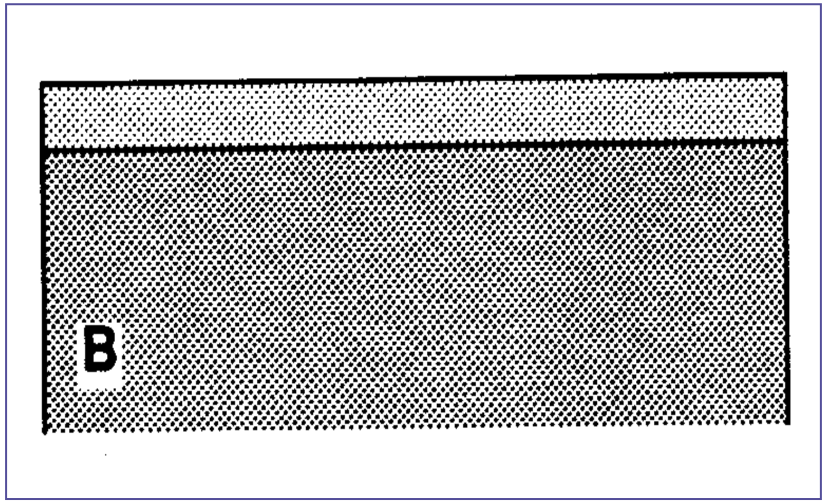
a) Loss of intensity due to light scattering

b) Effect dependding of the wavelength (more important in the UV/Blue region of the spectrum



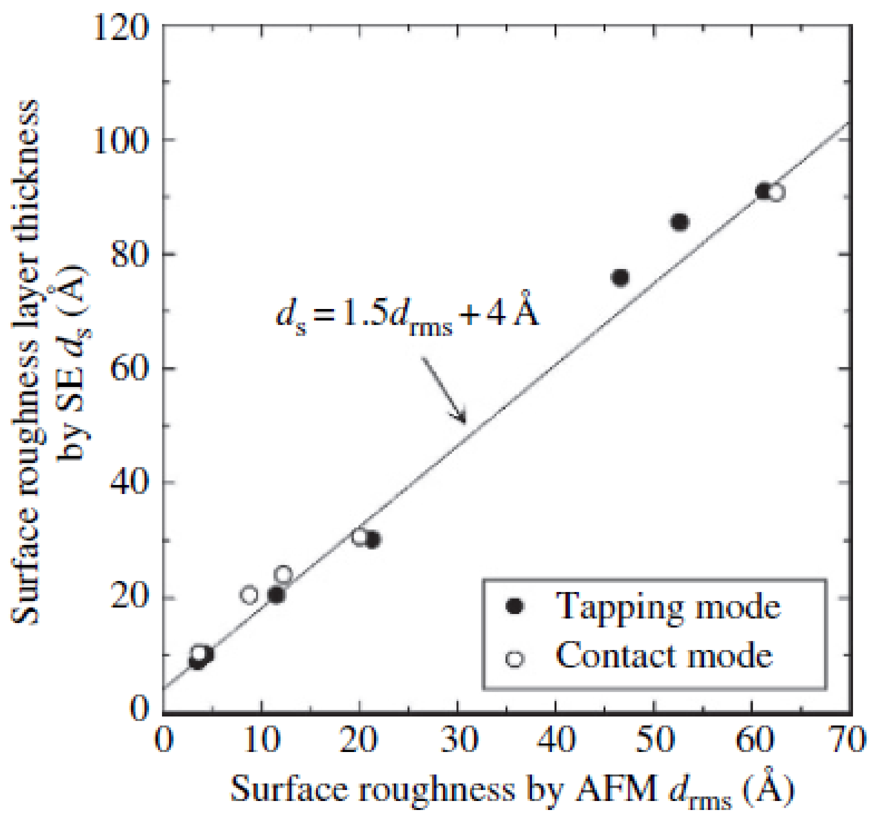
Solution : Effective medium approximation (Bruggeman, Maxwell-Garnett, …)





$$\frac{\tilde{N}_{eff}^{2}-\tilde{N}_{host}^{2}}{\tilde{N}_{eff}^{2}+2\,\tilde{N}_{host}^{2}}=\sum_{i=1,N} f_i\,\frac{\tilde{N}_{i}^{2}-\tilde{N}_{host}^{2}}{\tilde{N}_{i}^{2}+2\,\tilde{N}_{host}^{2}} \quad avec \sum_{i=1,N} f_i=1$$

Yes but … Roughness caracterization needed …



Rougness of semiconductors samples :

Overestimation of the '*ellipsometric*' roughness with respect to the *rms* roughness as measured by AFM

One step further :

Complex link between ***rms roughness*** and ***correlation length*** of the surface

J. Koh et al., *Applied Physics Letters, 69, 1297–1299 (1996).*

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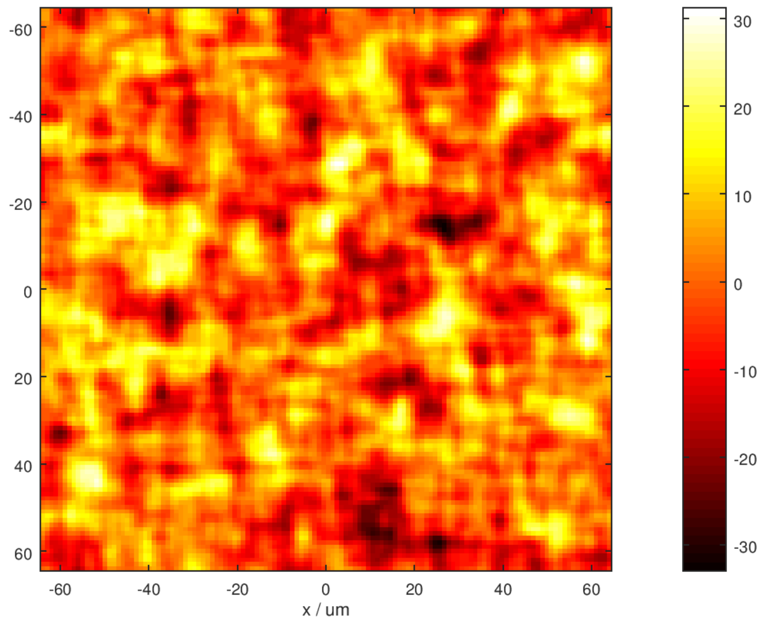
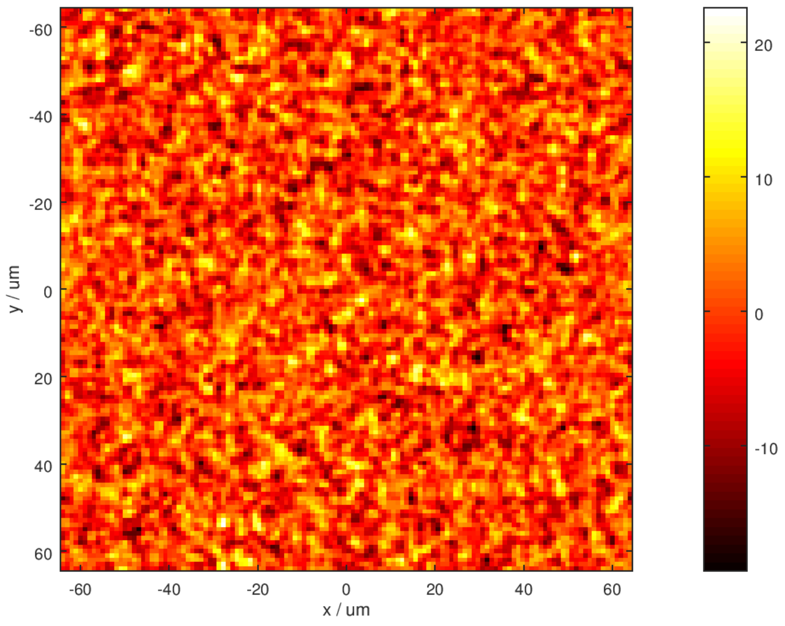
Correlation length effects …



L_{corr} = **5** nm
R_{rms} = 10nm



L_{corr} = **1** nm
R_{rms} = 10nm

Rayleigh-Rice theory (RRT)

Normalized PSD

$$w(K) = \frac{\xi^2}{4\pi} e^{-K^2\xi^2/4}$$

Fresnel's coefficients for the **rough** surface

$$r_{s,p} = r_{s0,p0} + \sigma^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_{s,p}(K_x, K_y) \times w(K_x - n_0 k_0 \sin\theta_0, K_y)\, dK_x dK_y \quad (1)$$

Fresnel's coefficients for the **smooth** surface

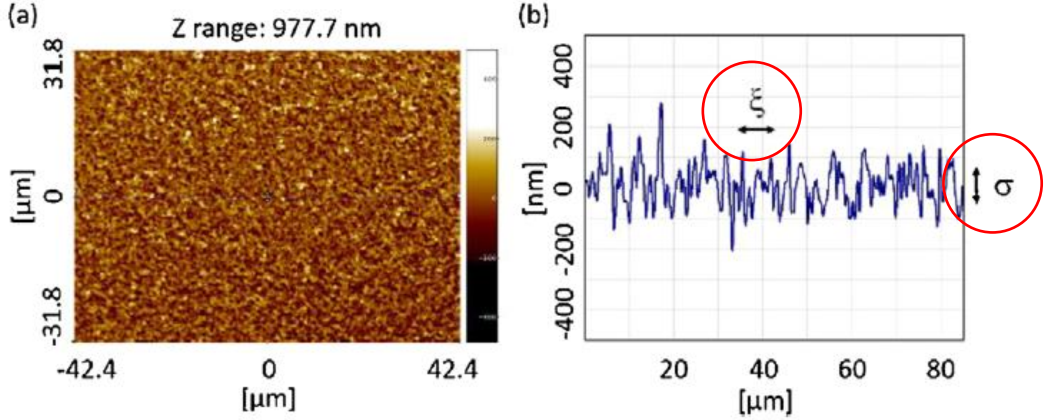
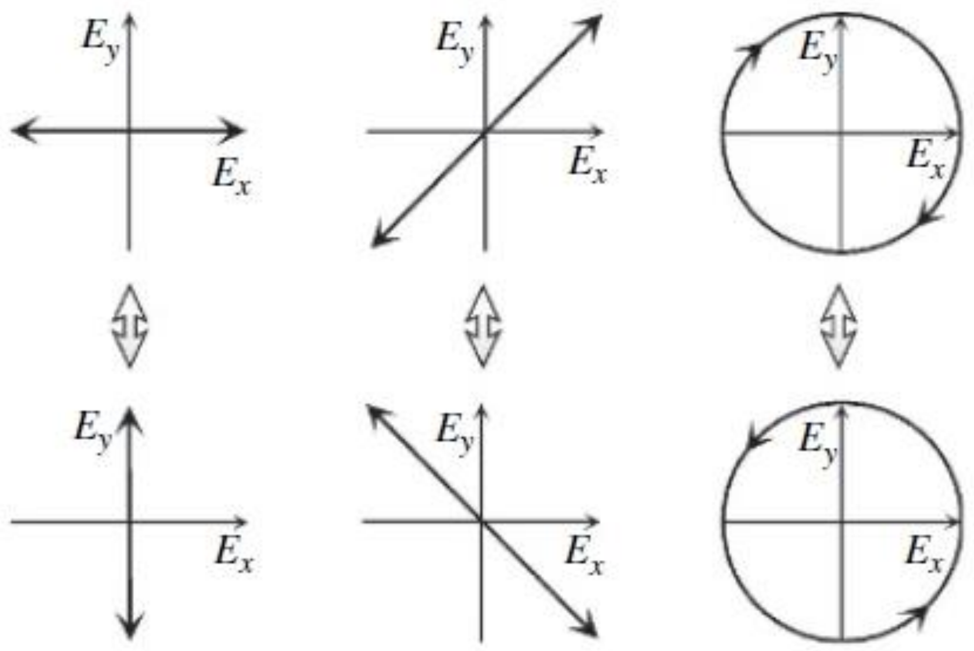


Figure 1. Confocal microscopy image of the CIGS film (a) and cross section illustrating the rms roughness σ and autocorrelation length ξ (b).

Jensen et al (2017) DOI: 10.1002/pssc.201700217

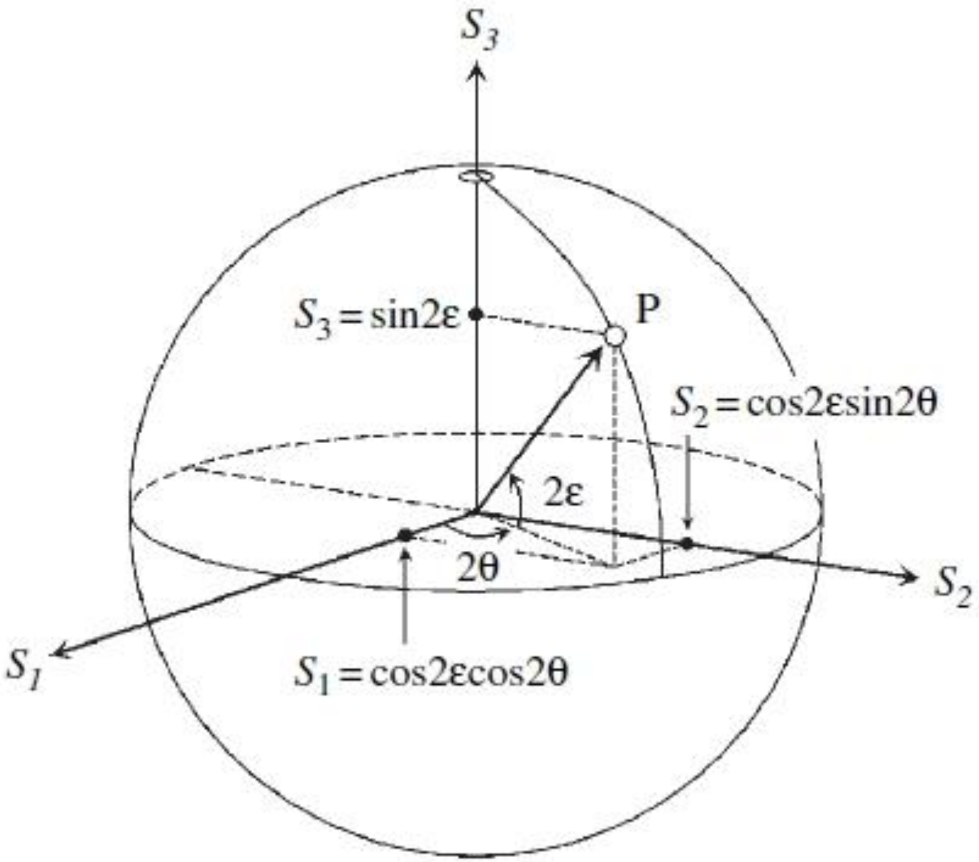
Stokes coefficients

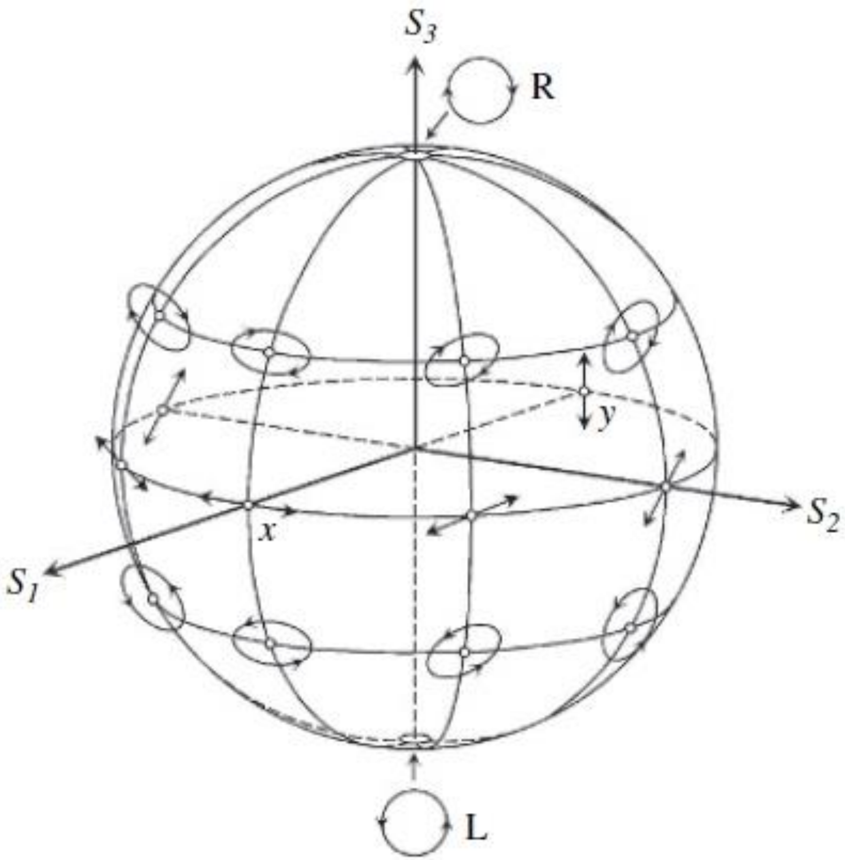


(a) $S_1 = I_x - I_y$ (b) $S_2 = I_{+45°} - I_{-45°}$ (c) $S_3 = I_R - I_L$

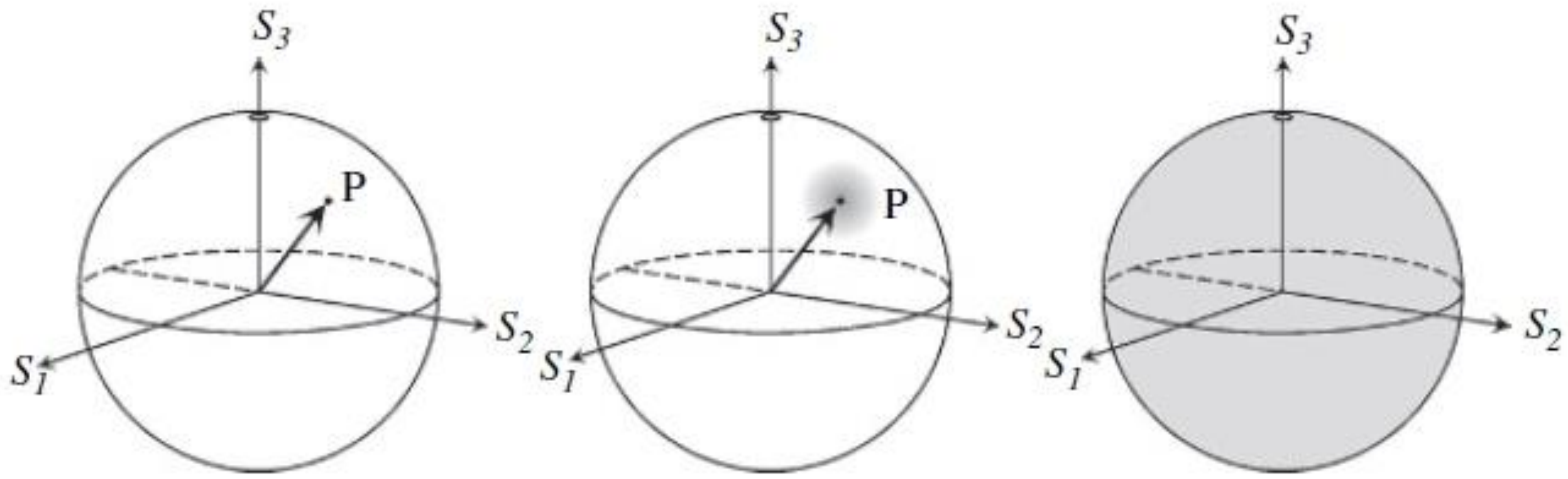
$$
\begin{aligned}
S_0 &= I_x + I_y = E_{x0}^2 + E_{y0}^2 = E_x E_x^* + E_y E_Y^* \\
S_1 &= I_x - I_y = E_{x0}^2 - E_{y0}^2 = E_x E_x^* - E_y E_Y^* \\
S_2 &= E_{45} E_{45}^* - E_{-45} E_{-45}^* = E_x E_y^* - E_x^* E_y \\
&= 2 E_{x0} E_{y0} \cos \Delta \\
S_3 &= -2 E_{x0} E_{y0} \sin \Delta
\end{aligned}
$$

Polarization of light and Stokes coefficients





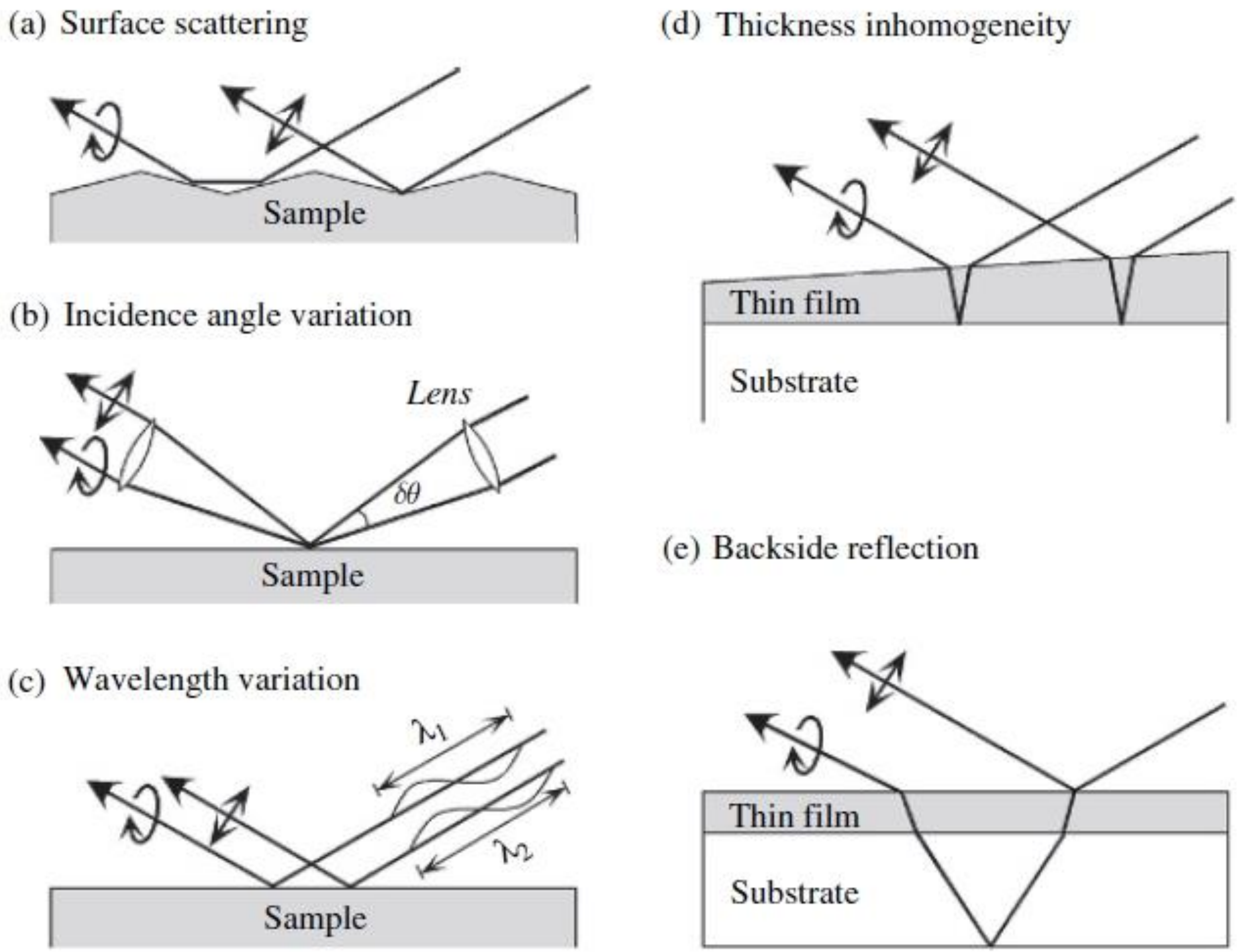
Polarization of light and Stokes coefficients



(a) Totally polarized light (b) Partially polarized light (c) Unpolarized light

Light depolarization

Occurs more often than you expect …



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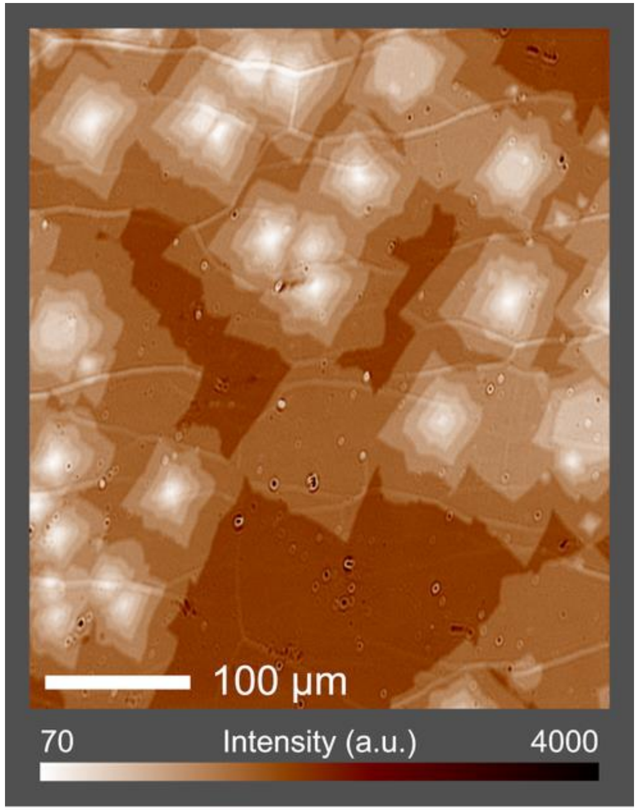
What is (spectroscopic) imaging ellipsometry ?

- IE combines optical microscopy and ellipsometry for spatially resolved layer-thickness and refractive index measurements of micro-structured thin-films and substrates.
- An Imaging Ellipsometer produces <u>after optical modelling</u> images of the measured quantities (maps) (thickness, refractive index, composition) at a spatial resolution of 1 µm/pixel



Sample courtesy of the Hofmann Group at the University of Cambridge

(Graphene by CVD on silicon surface)

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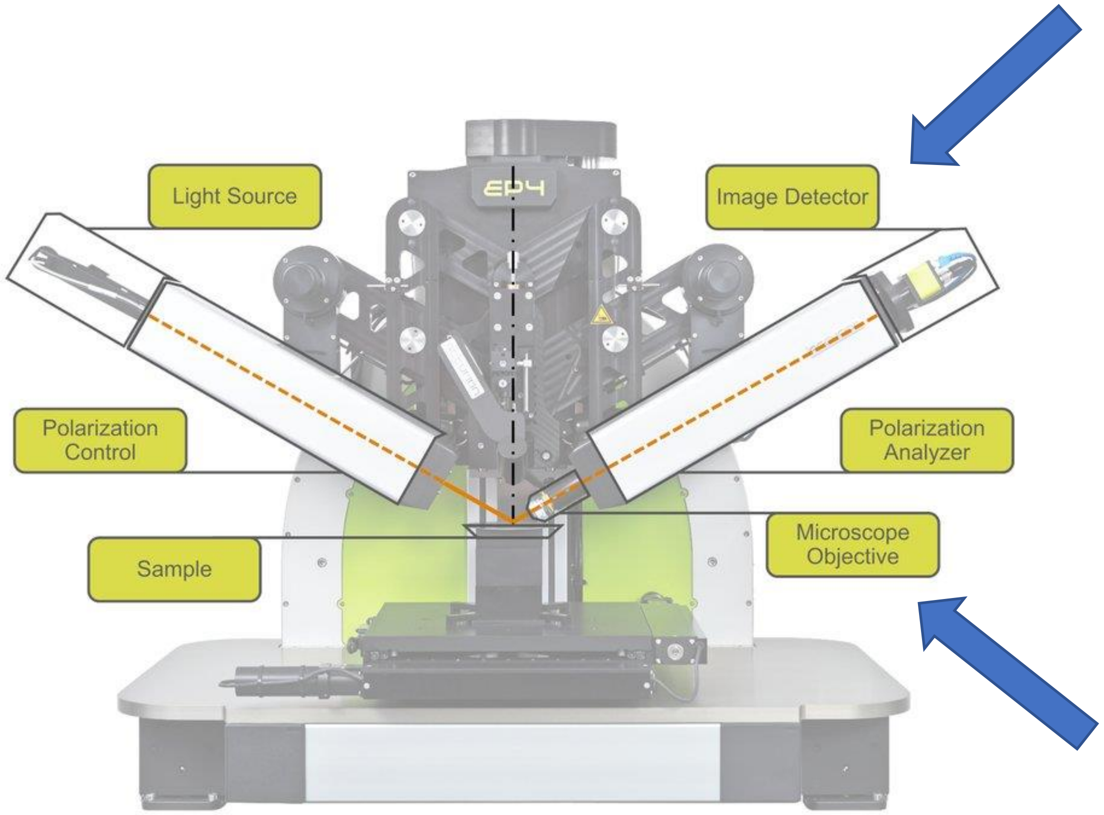
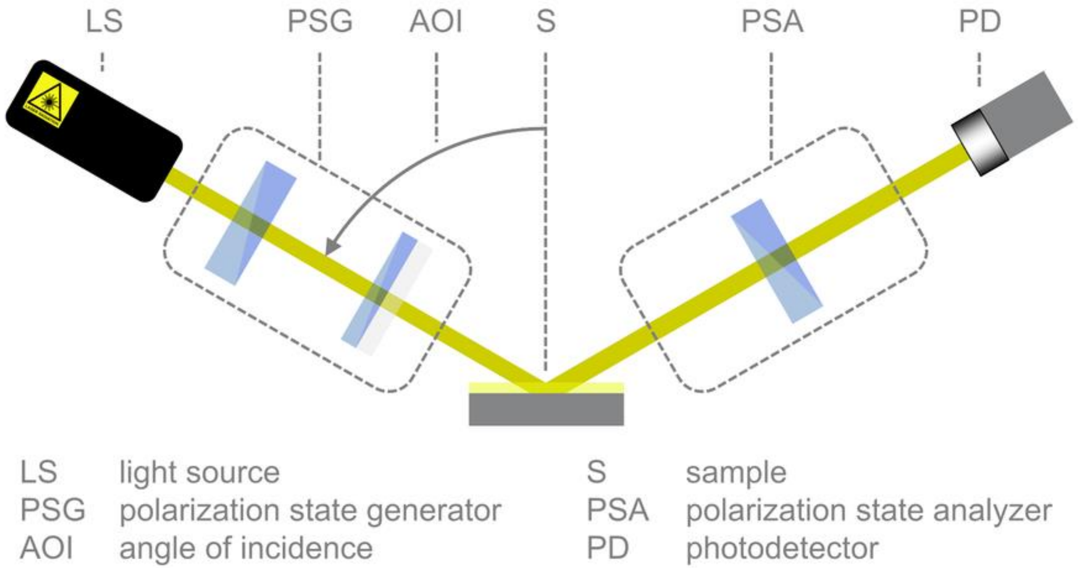
What does an IE ellipsometer look like ?





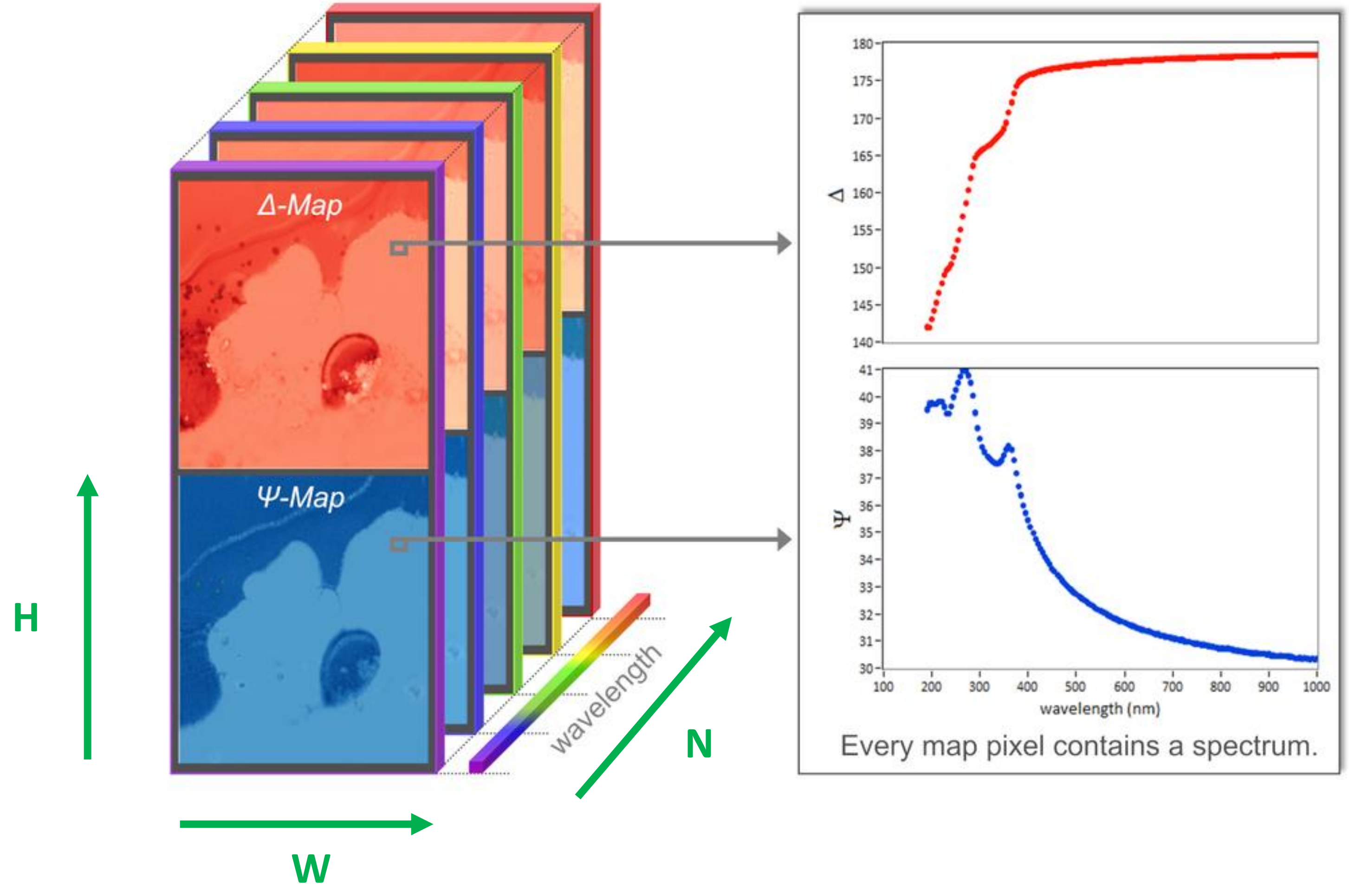
Spectroscopic means “Huge data cubes”

Raw SIE data

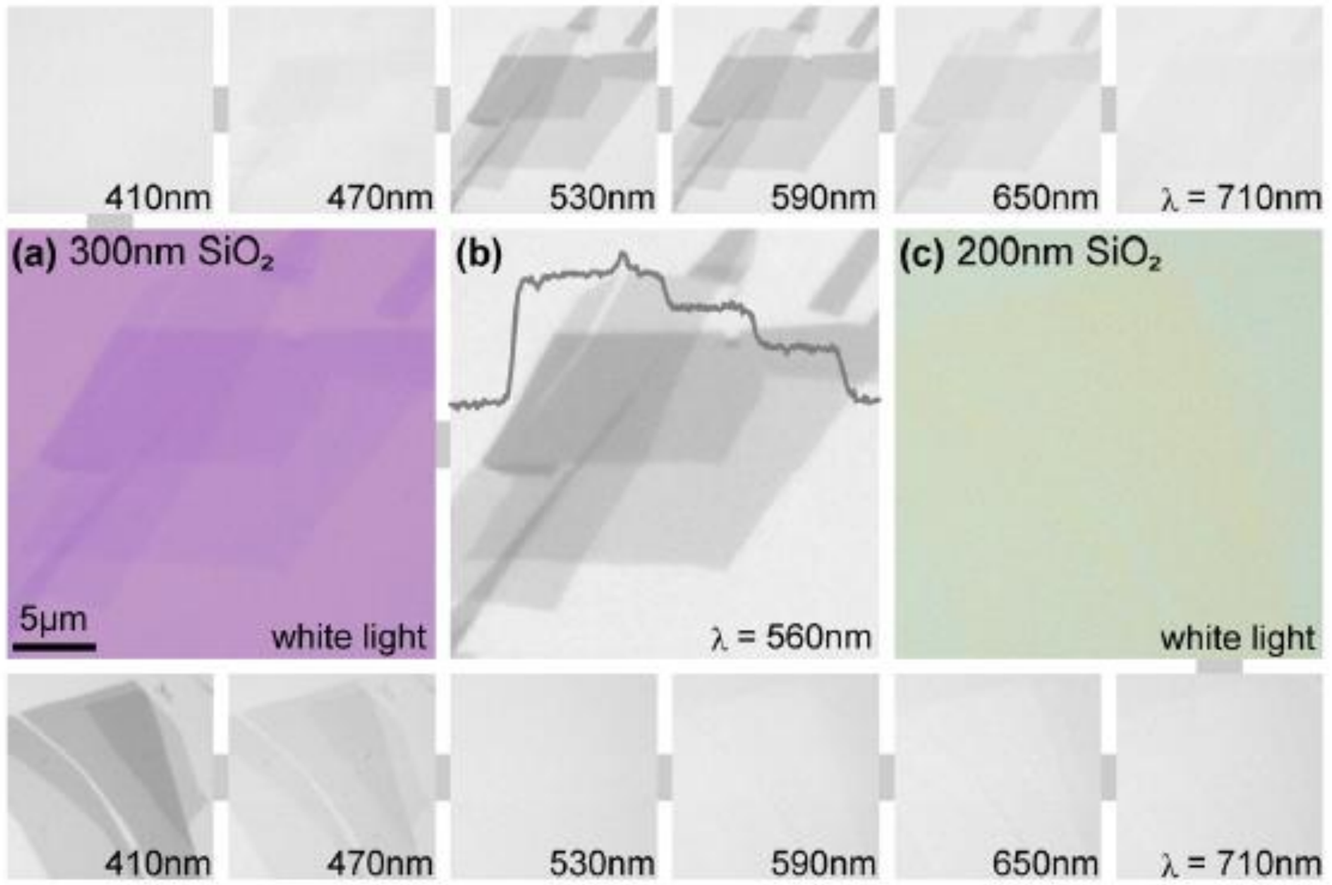
Local SIE data to be interpreted …

Number of data : N x W x H

A playground for hyperspectral analysis techniques and artificial intelligence



Making graphene visible … (Blake, 2007)



- Graphene crystallites on 300 nm SiO2 imaged with white light (a), green light (b) and another graphene sample on 200 nm SiO2 imaged with white light (c). Image sizes are 25x25µm.
- Top and bottom panels show the same flakes as in (a) and (c), respectively, but illuminated through various narrow bandpass filters with a bandwidth of '10 nm.
- The flakes were chosen to contain areas of different thickness so that one can see changes in graphene's visibility with increasing numbers of layers.
- This proves that the contrast can also be used as a quantitative tool for defining the number of graphene layers on a given substrate.

Blake, P., K. S. Novoselov, A. H. Castro Neto, D. Jiang, R. Yang, T. J. Booth, A. K. Geim, et E. W. Hill. « Making Graphene Visible ». *Applied Physics Letters* 91, nº 6 (6 août 2007): 063124. https://doi.org/10.1063/1.2768624.

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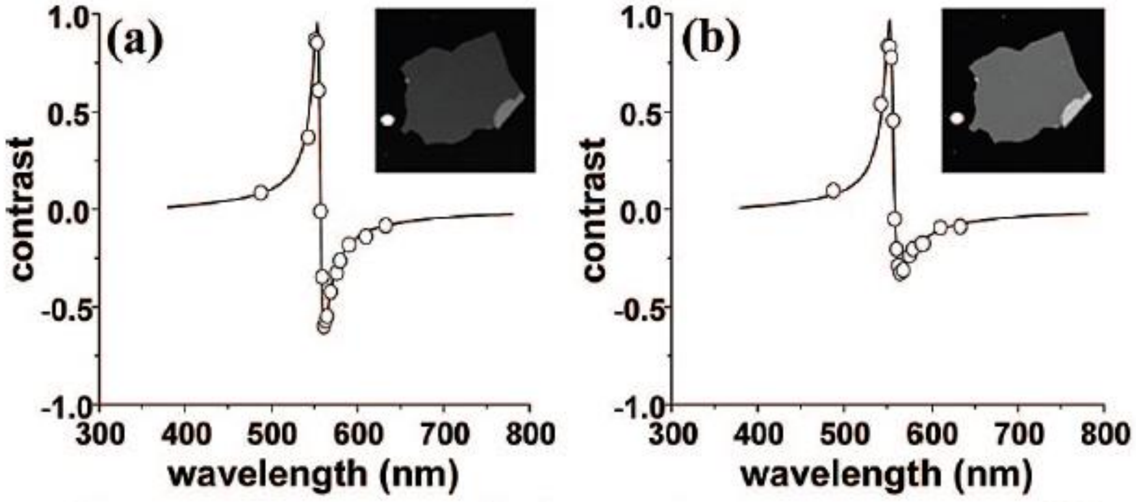
Oxidized graphene (GO) in Imaging ellipsometry (Jung, 2008)

Characterization of Thermally Reduced Graphene Oxide by Imaging Ellipsometry

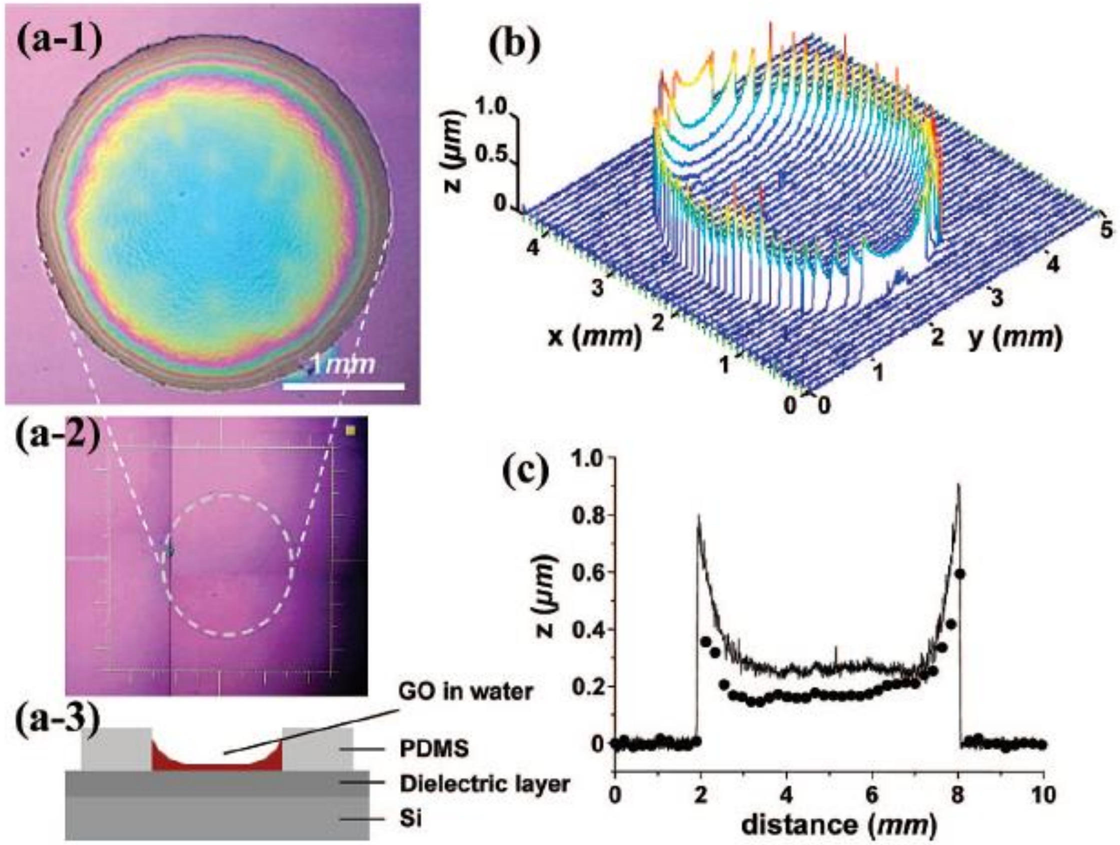
Inhwa Jung,[†] Matthias Vaupel,[‡] Matthew Pelton,[§] Richard Piner,[†] Dmitriy A. Dikin,[‖] Sasha Stankovich,[‖] Jinho An,[†] and Rodney S. Ruoff[*,†]

Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, 78712, Nanofilm Technologie GmbH, Anna-Vandenhoeck-Ring 5, Göttingen, 37081 Germany, Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Mechanical Engineering, Northwestern University, Evanston, Illinois 60208

Received: March 12, 2008; Revised Manuscript Received: April 28, 2008



Before and after annealing (200°C, vacuum)



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APPLIED PHYSICS LETTERS **97**, 231901 (2010)

Imaging ellipsometry of graphene

Ulrich Wurstbauer,[1,a),b)] Christian Röling,[2] Ursula Wurstbauer,[1,b)] Werner Wegscheider,[1,c)] Matthias Vaupel,[2,d)] Peter H. Thiesen,[2] and Dieter Weiss[1]
[1]*Institut für Experimentelle und Angewandte Physik, Universität Regensburg, 93040 Regensburg, Germany*
[2]*Accurion GmbH, Stresemannstr. 30, 37079 Göttingen, Germany*

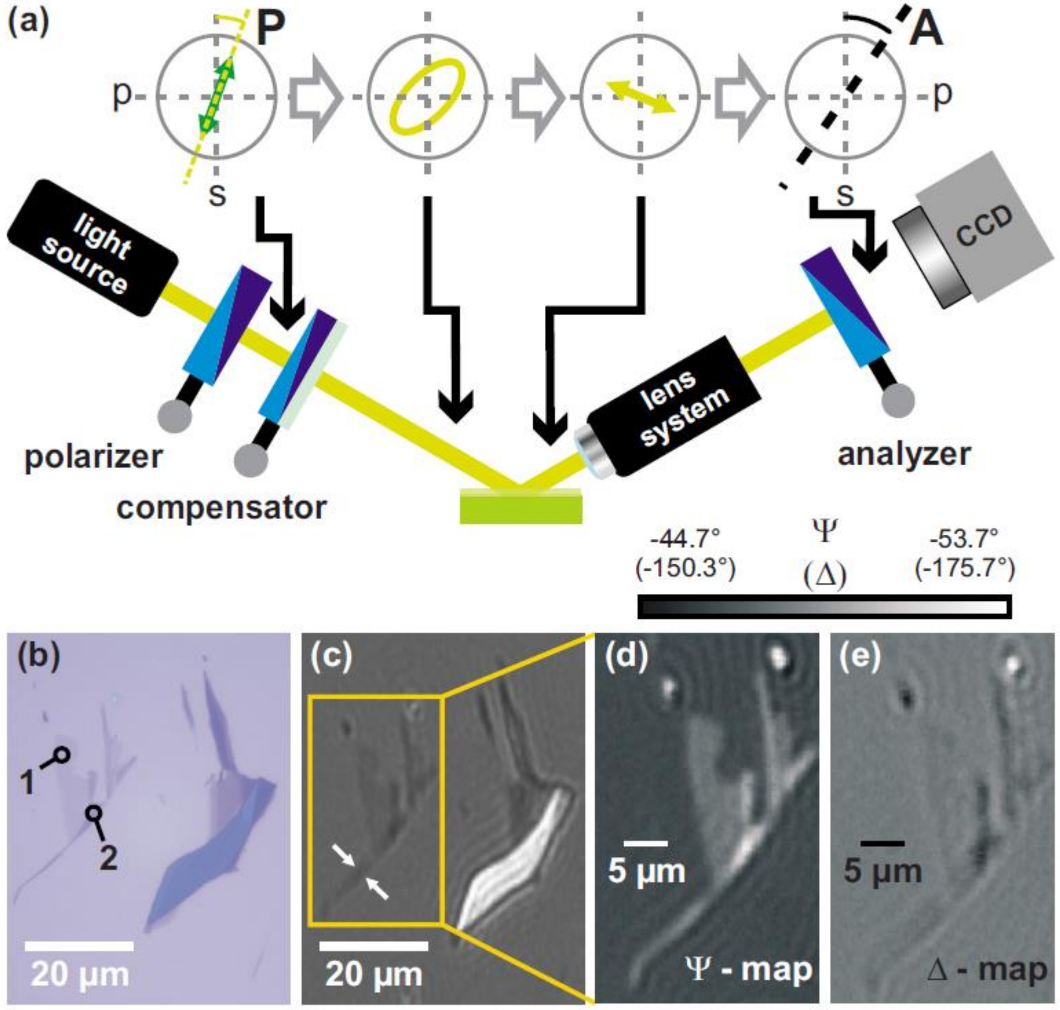


FIG. 1. (Color online) (a) Schematic imaging ellipsometry setup. The lens system mounted between the sample and analyzer allows imaging with submicron lateral resolution. (b) Optical image and (c) imaging ellipsometric intensity image of a sample on SiO_2/Si showing regions with graphene monolayer covering up to thin graphite. Numbers in (b) correspond to the layer number. (d) Ellipsometric Ψ map and (e) the corresponding Δ map of the boxed region display graphene mono- and bilayer areas with higher resolution.

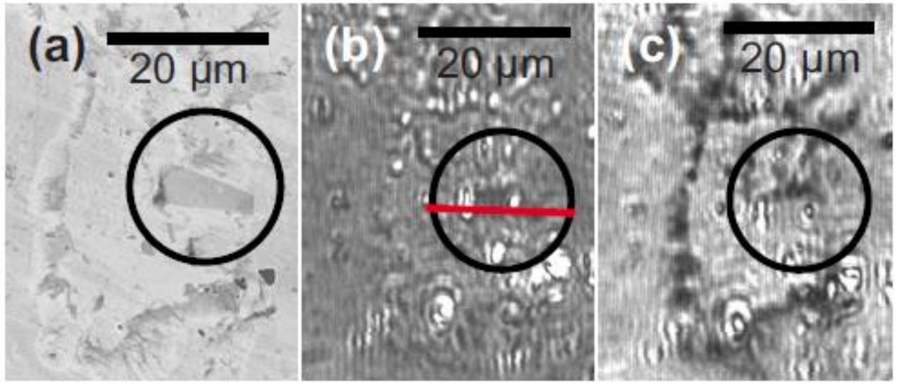


FIG. 2. (Color online) (a) SEM image of few-layer graphene on a GaAs substrate. The flake is centered in the circle and in the surroundings are resist/tape residues. (b) and (c) are IEI plots of the same region. In (b) the contrast is optimized for the graphene layer such that the adhesive tape residues vanish, while in (c) the contrast of the immediate vicinity is enhanced.

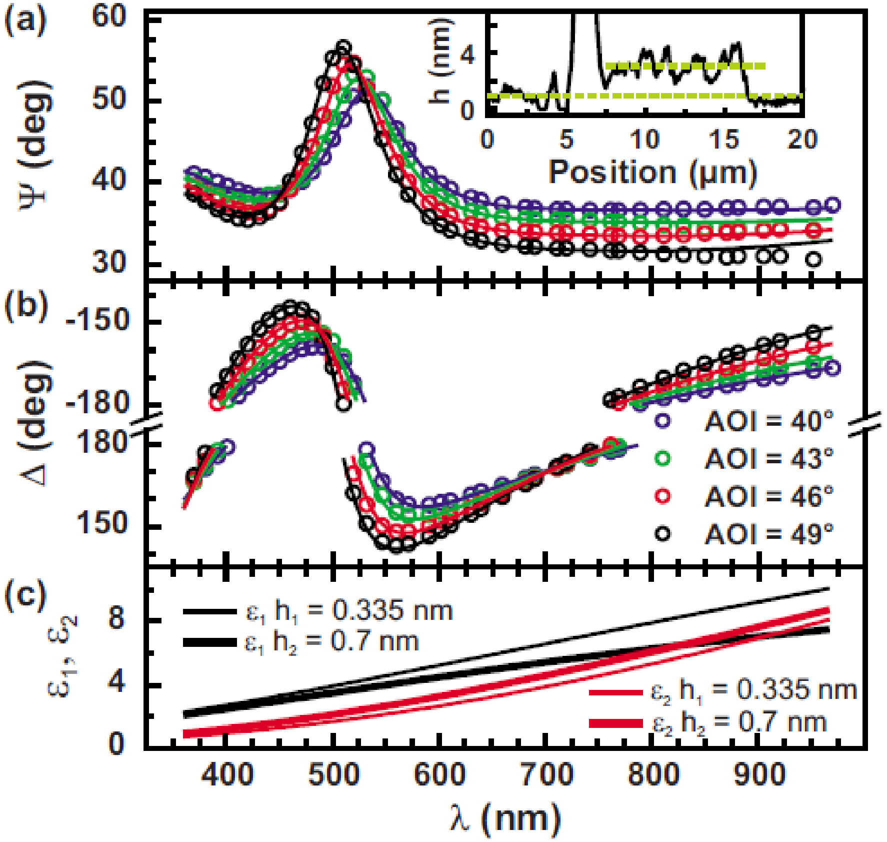


FIG. 3. (Color online) (a) Wavelength dependent Ψ-angle of a graphene monolayer for different AOIs. Inset: height profile of the flake on GaAs shown in Fig. 2. (b) Wavelength dependency of the Δ-angle for the same AOI as in (a). (c) Dielectric coefficients ϵ_1 and ϵ_2 of graphene for both theoretical layer height h_1=0.335 nm (thin lines) and AFM measured height h_2=0.7 nm (thick lines).

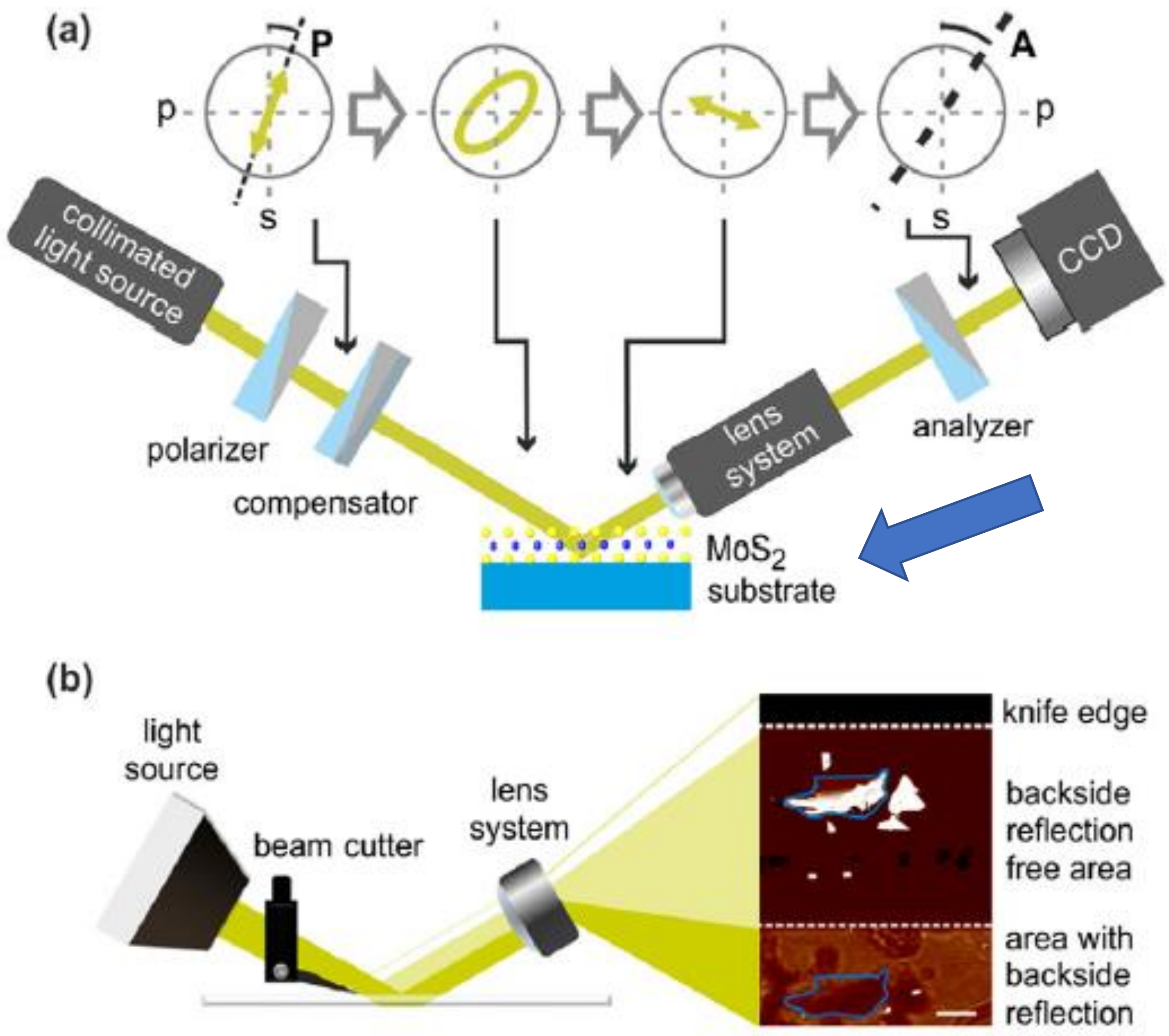


Figure 1. Imaging ellipsometry setup. (a) Scheme of the imaging ellipsometry setup. The polarizer-compensator-sample-analyzer configuration for the reflected light is used. The sample is illuminated by collimated light. The additional lens system between sample and analyzer allows imaging with micrometer resolution. The lateral resolution is only limited by the optical system on the detector side, defined by the lens system and the CCD-camera. (b) The optional beam cutter alignment between light source and sample utilizing a knife edge suppresses effectively signal from reflections stemming from the back side of the transparent substrates. The picture on the right displays a large area view of the imaging ellipsometry contrast picture taken of a MoS2 flake on double-sided polished sapphire using the beam cutter. In the dark region on top, the incoming light is blocked. In the middle area, reflections from the back side are selectively blocked with a sharp image of the MoS2 flake and silicon alignment marker, while the lower part shows a blurred image of the MoS2 flake that is a reflection from the flake on the back side of the substrate (scale bar denotes 50 μm).

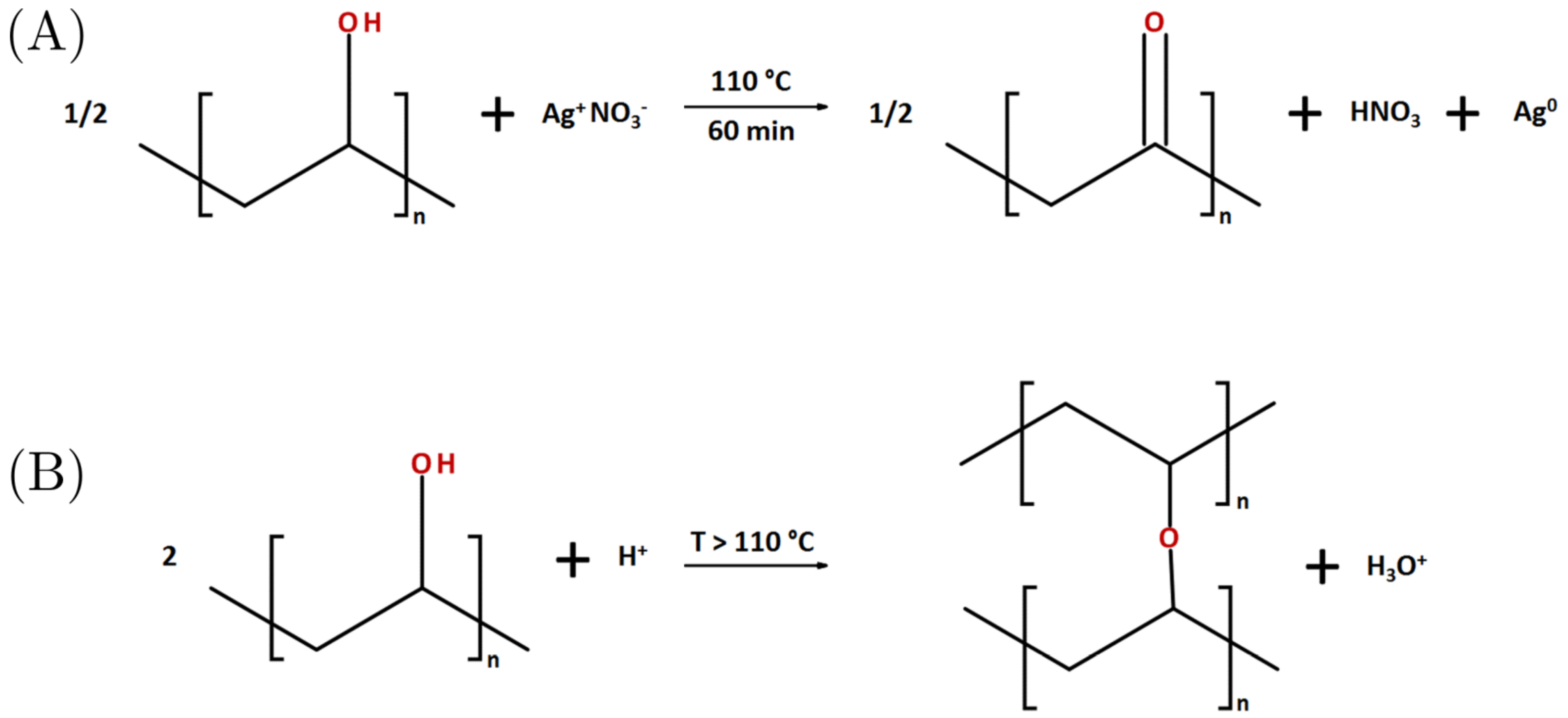
What are the benefits of imaging ellipsometry ?

- Spatial resolution down to 1 µm, easily beating the resolution limits of conventional ellipsometers.
- A 2D map with more than 500000 points is created within a single measurement. Conventional ellipsometers need to scan and move the sample to measure an areal 2D map.
- The intrinsic Ellipsometric Contrast-enhanced Microscopy (ECM) allows for a very fast detection of film-thickness and refractive index variations without the need to run a full ellipsometric measurement.
- “First find, then measure”: Identify the relevant sample spots of interest prior to the ellipsometric measurement.
- A Region-of-Interest concept (ROI concept) allows focusing the measurement and the data analysis on several selected features within the field of view.
- The spatial resolution is independent of the probing spot size. Hence, no tight beam focusing is required.

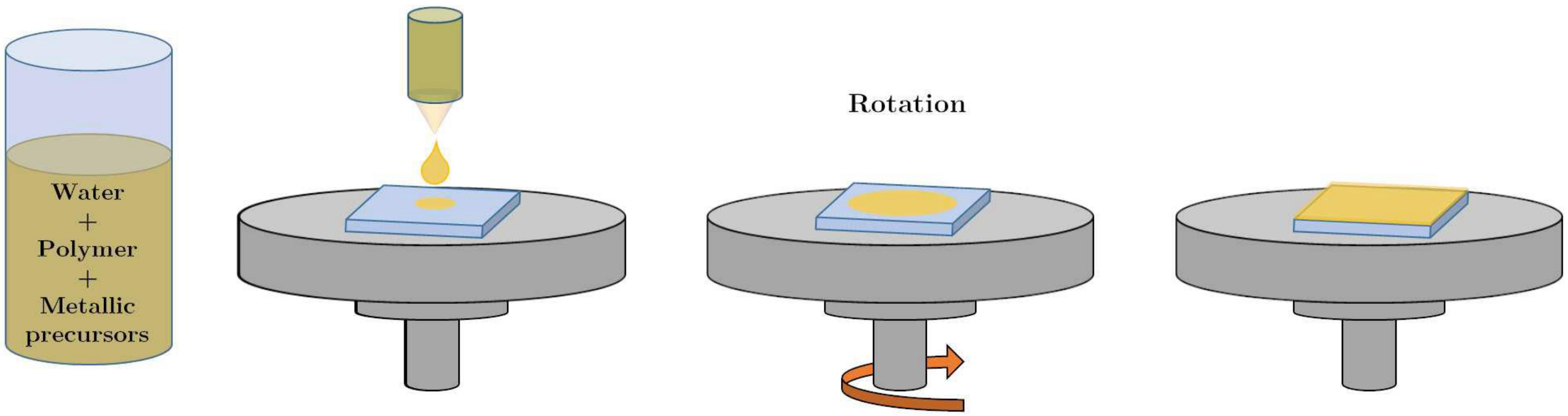
Plasmonic nanocomposite (PNC) materials

PNC
=
matrix
+
Dispersed or *in situ* grown plasmonic material

Model system : Au or Ag PVA films

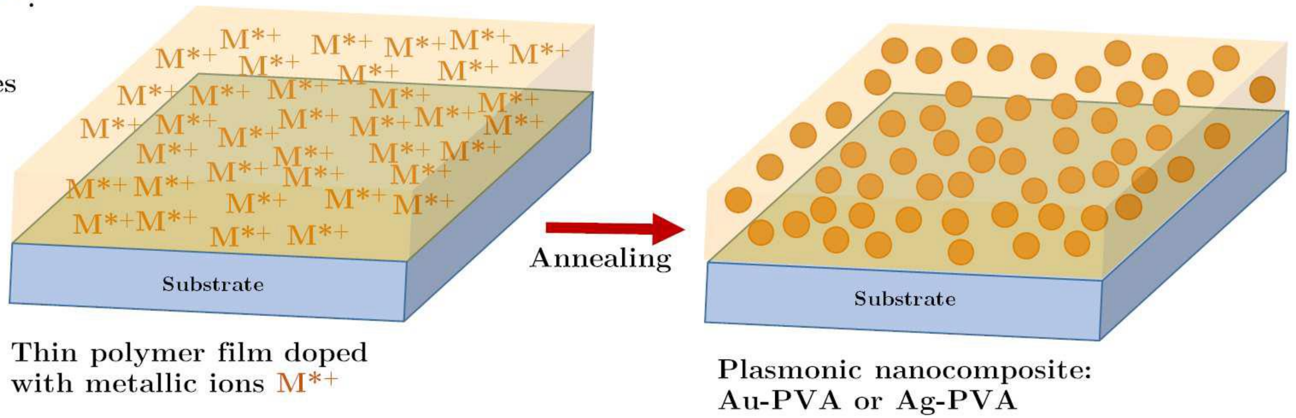


How to prepare them ?

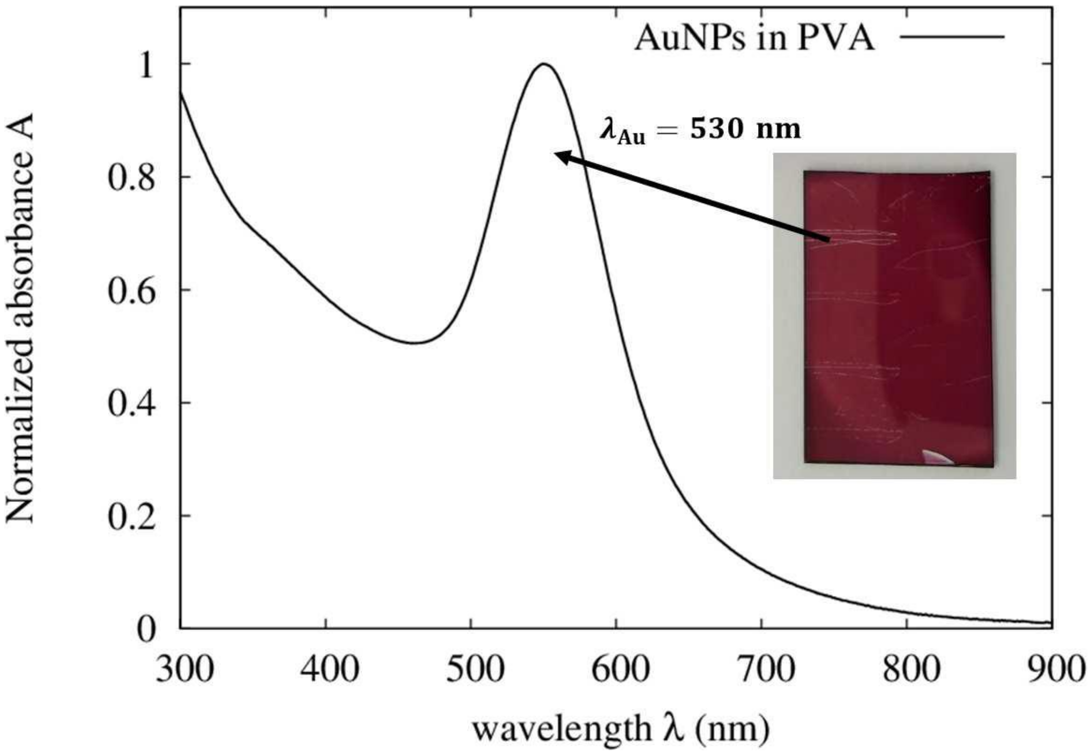


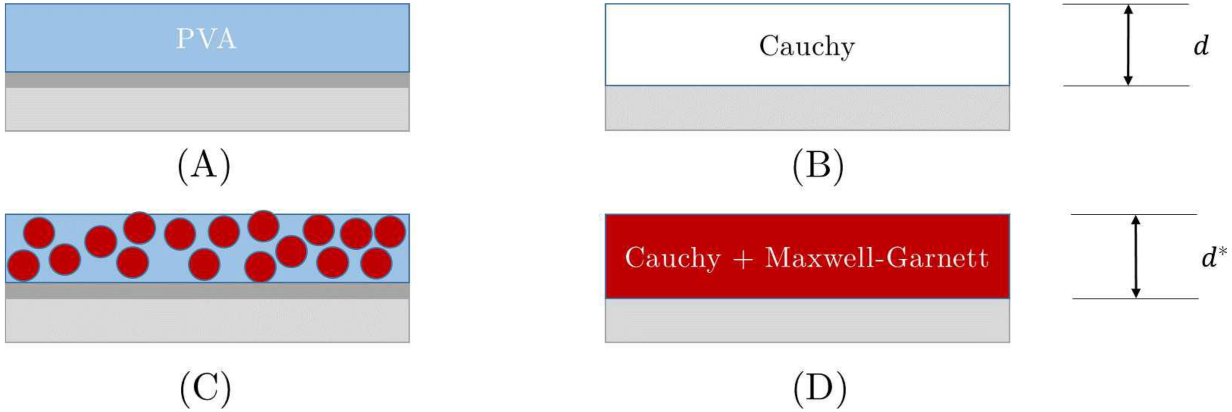
Metallic precursors M^{*+}:

- $HAuCl_4.3H_2O$ for gold nanoparticles
- $AgNO_3$ for silver nanoparticles

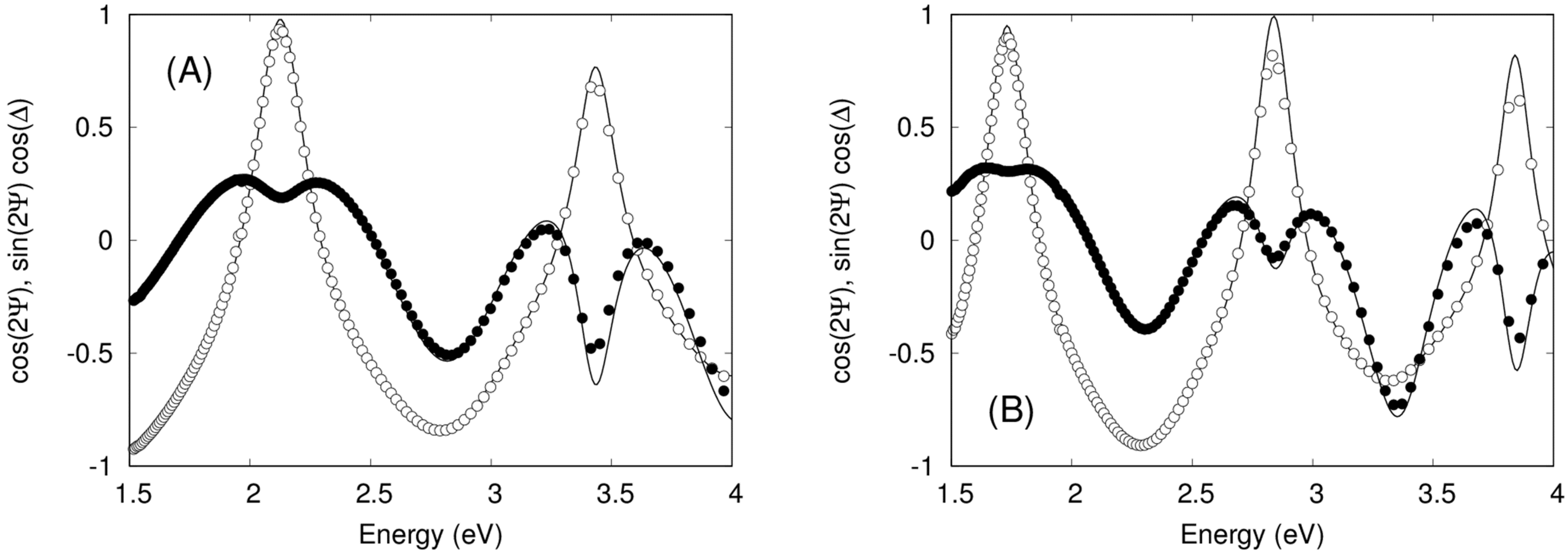


UV-Vis optical response





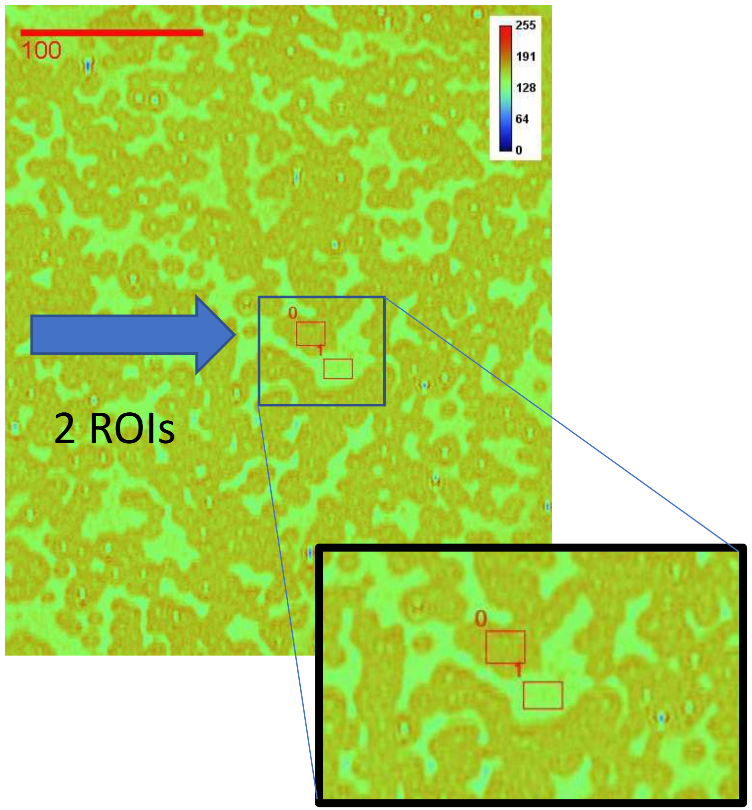
Au-PVA films (f_{Au} = 0.13%) in conventional SE

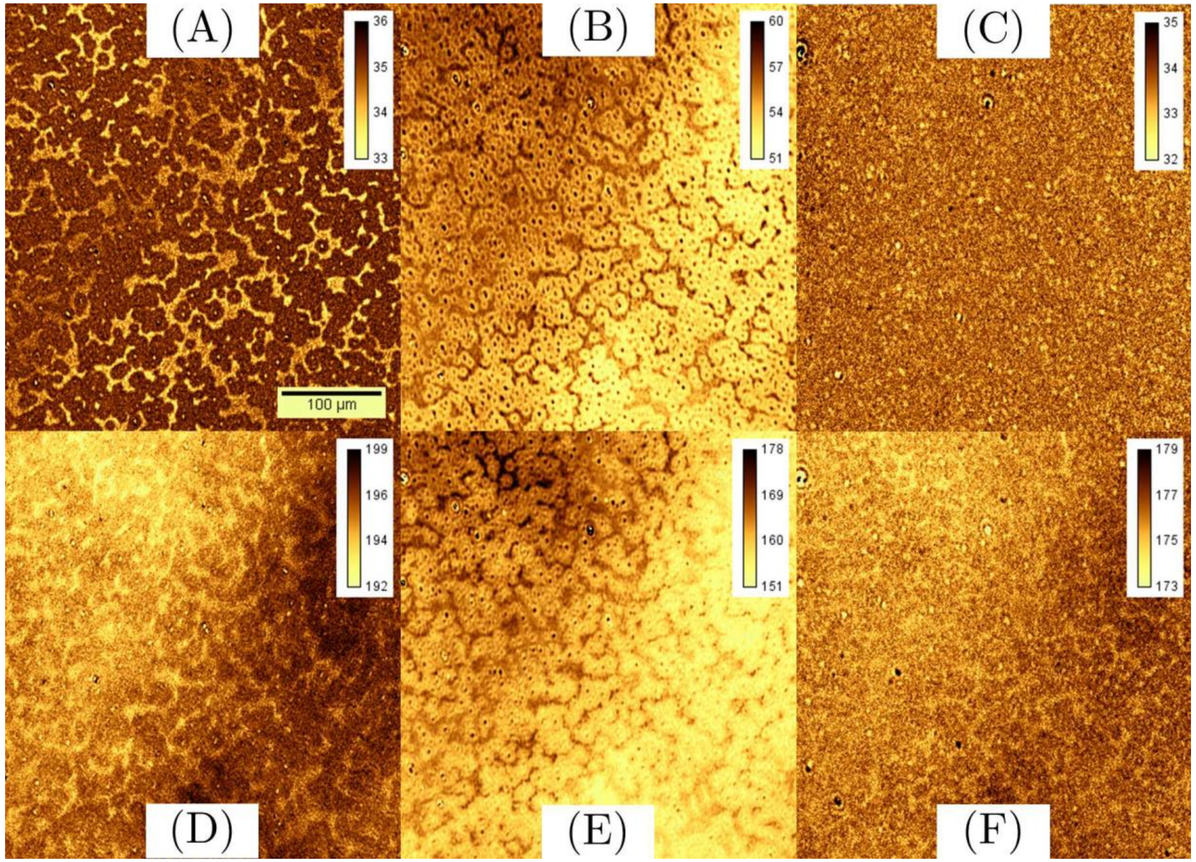


Au nanocomposite film (A : 358 nm thick , B : 441 nm) : **No difference in modelling by Cauchy or MG-EMA)**

Now spectroscopic imaging ellipsometry…

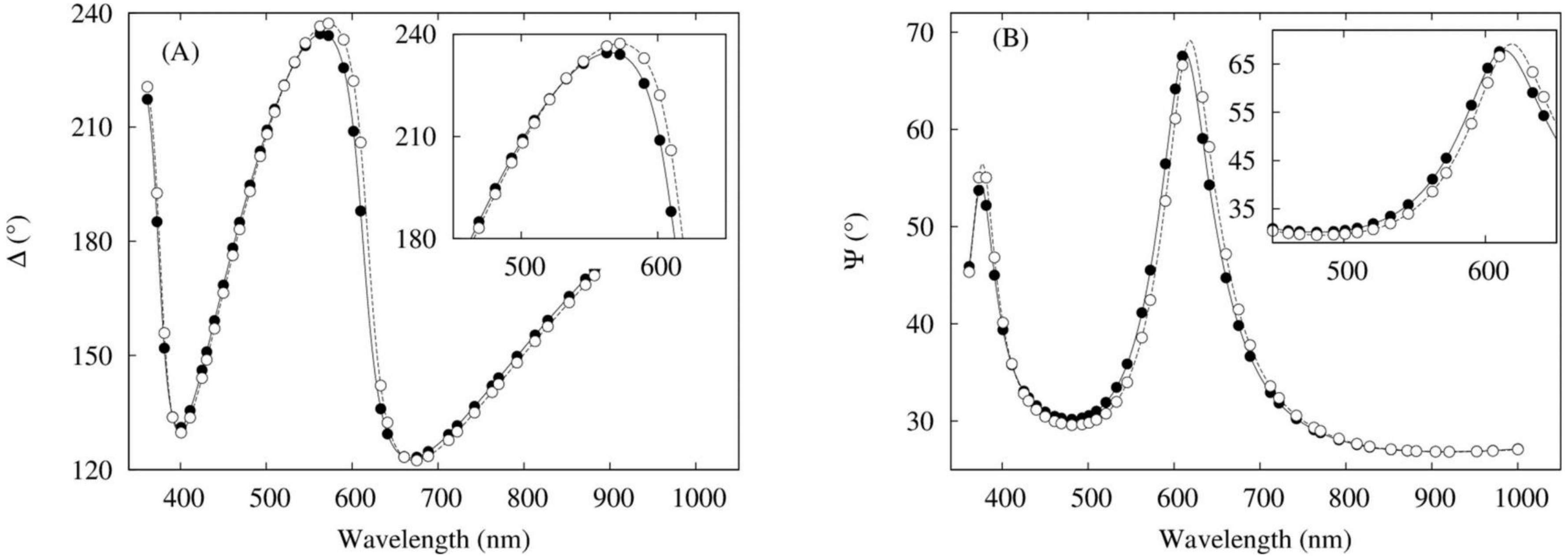
Enhanced Contrast image (653 nm)





(A-B-C) and (D-E-F) images of the Au-PVA films (AOI = 45). Each image corresponding to a different incident light wavelength: (A) and (D) = 533 nm, (B) and (E) = 660 nm, (C) and (F) = 920 nm. (Image size: 430 µm x 400 µm and color scale in (°))

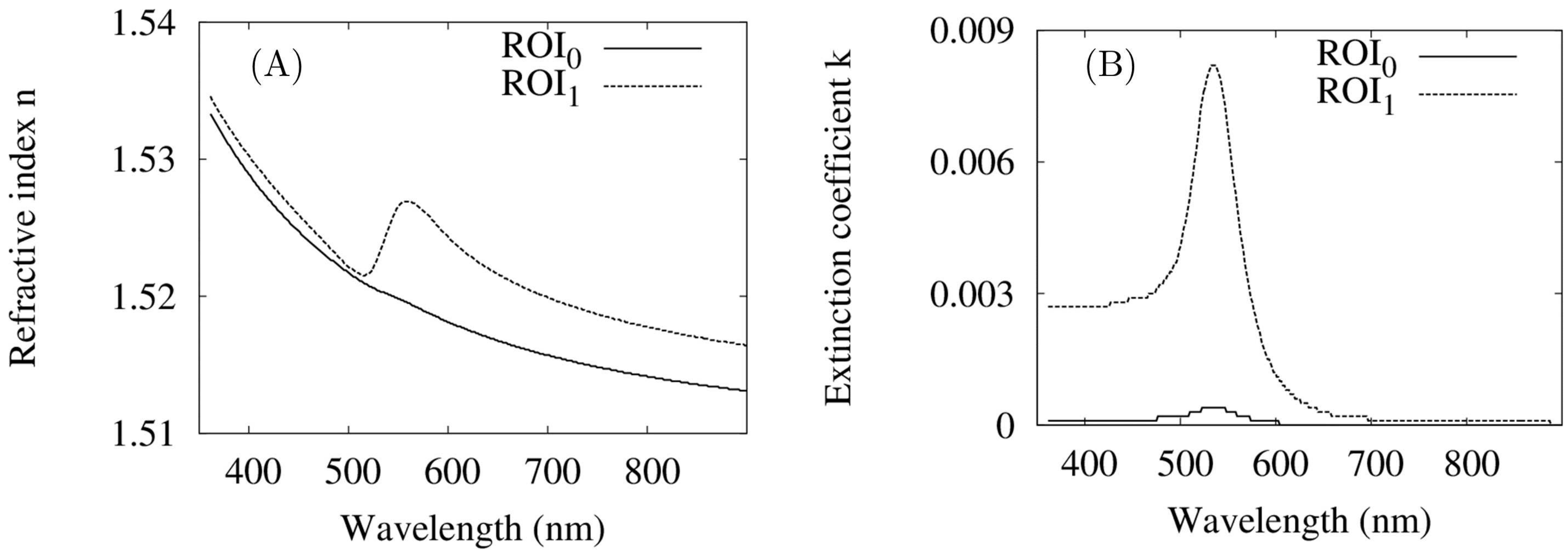
Local ellipsometric analysis over each ROI



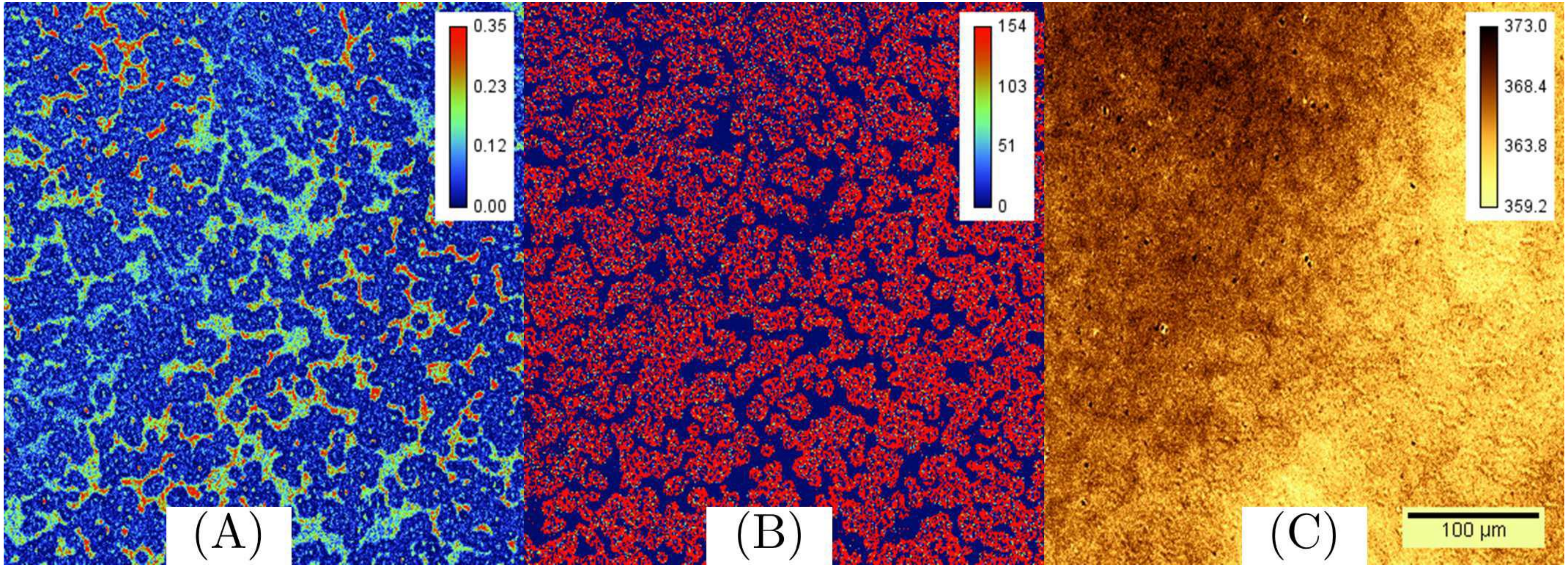
ROI	Thickness (nm)	Gold fraction f_{Au} (%)	RMSE	Correlation
0	359.8 ± 0.2	0.006 ± 0.013	0.682	-0.736
1	360.8 ± 0.1	0.103 ± 0.013	0.688	-0.730

Equivalent thickness
Different local gold fractions

Local refractive index and gold fractions



From spectra to maps …



(A) Gold fraction

(B) Error on gold fraction

(C) Thickness of the layer

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About the experimental technique :

- Spectroscopic Imaging ellipsometry : provides much more information than conventional SE but generates huge data sets
- Interesting for LOCAL optical properties (spectroscopic or not)
- Model-free Enhanced Contrast mode : “first find and then measure” and “regions-of-interests” concepts
- Can be extended to Mueller Matrix approach

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About the plasmonic nanocomposites :

- Not suitable for conventional SE at low metal fraction (limit at 1%)
- LOCAL optical properties and thickness obtained from ECM et SEI measurements
- Inhomogeneous growth of the gold NPs
- Local gold fraction measured with a limit of detection close to 0.1%

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