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Optical properties of gold-based plasmonic nanocomposites

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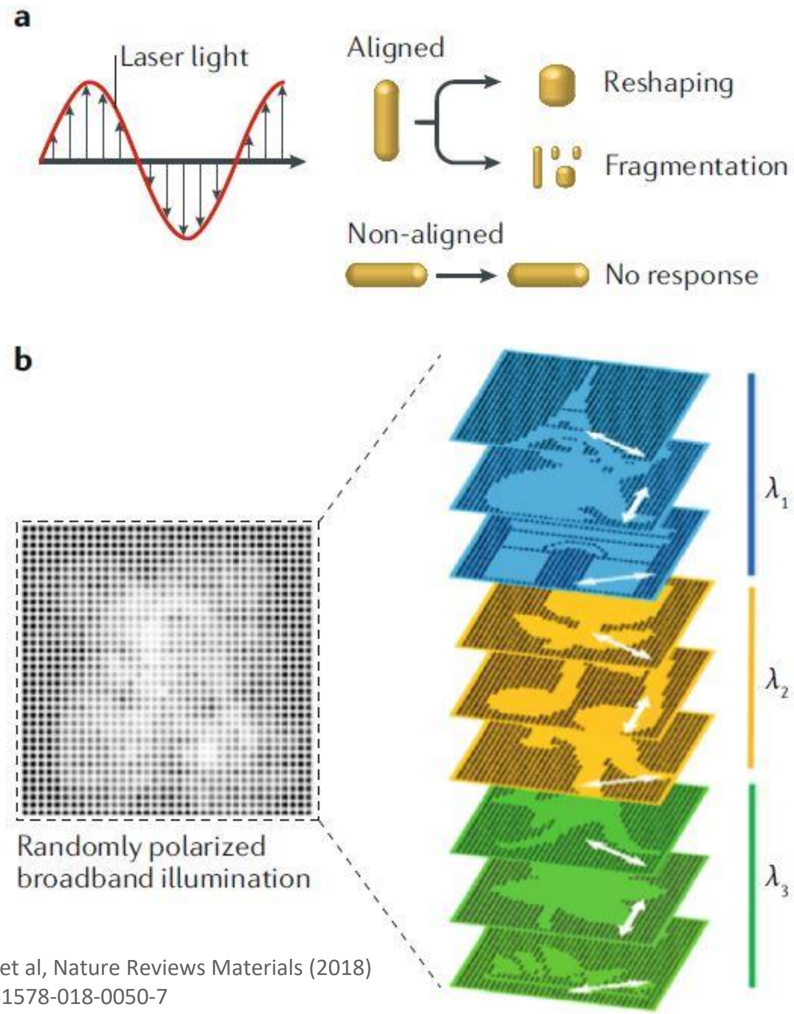
Outline

- **Plasmonic nanocomposites (PNCs)**
- Gold PNCs at high concentration
- Data analysis of SEI data cubes
- Concluding remarks

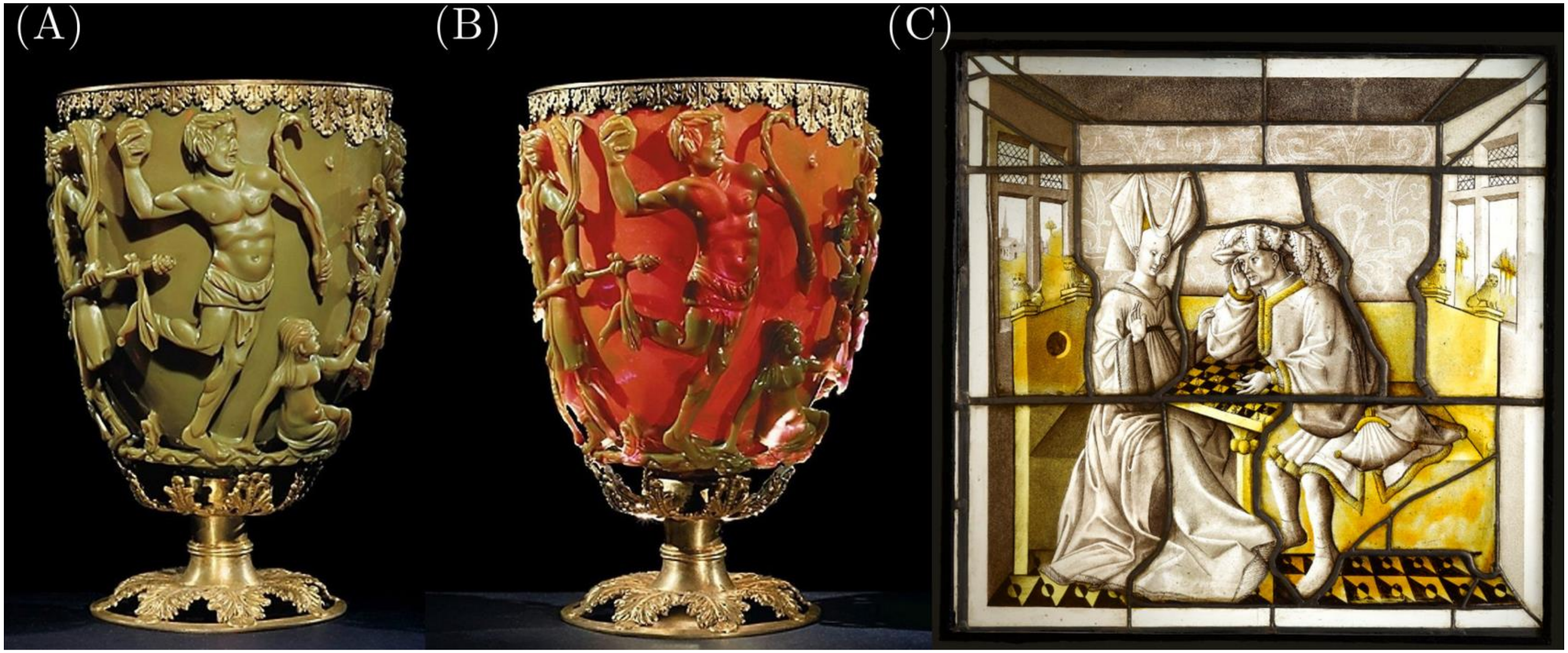
Plasmonic nanocomposites (PNCs)

- Plasmonic nanoparticles have been developed for multiple purposes : detection of chemicals and biological molecule, light-harvesting enhancement in solar cell ...
- PNCs : Hydrid materials synthesized by adding plasmonic nanoparticles to a polymer matrix
- Robustness, responsiveness and flexibility of the system are enhanced
- Intrinsic properties of the nanoparticles preserved
- Applications in optical data storage, sensing and imaging and photothermal gels for in vivo therapy



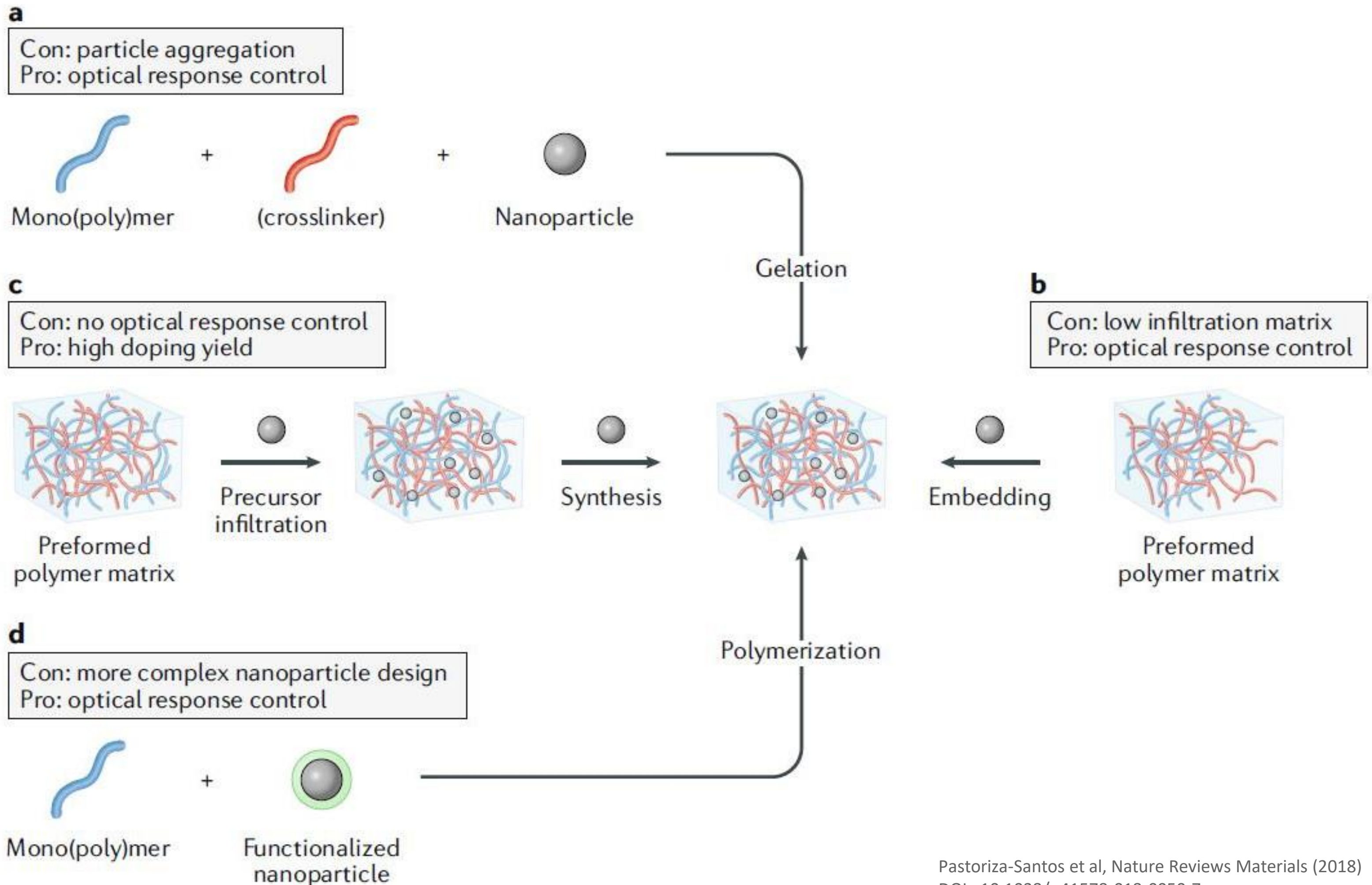
Pastoriza-Santos et al, Nature Reviews Materials (2018)
DOI : 10.1038/ s41578-018-0050-7

PNCs when PNCs were not named "PNC"...



(A) - (B) Pictures of the Lycurgus cup (from the British Museum Images, London). (A) Lit from the outside and (B) illuminated from the inside. (C) Stained glass “Les joueurs d’echecs" from the Cluny Museum, Paris.

Synthesis scheme



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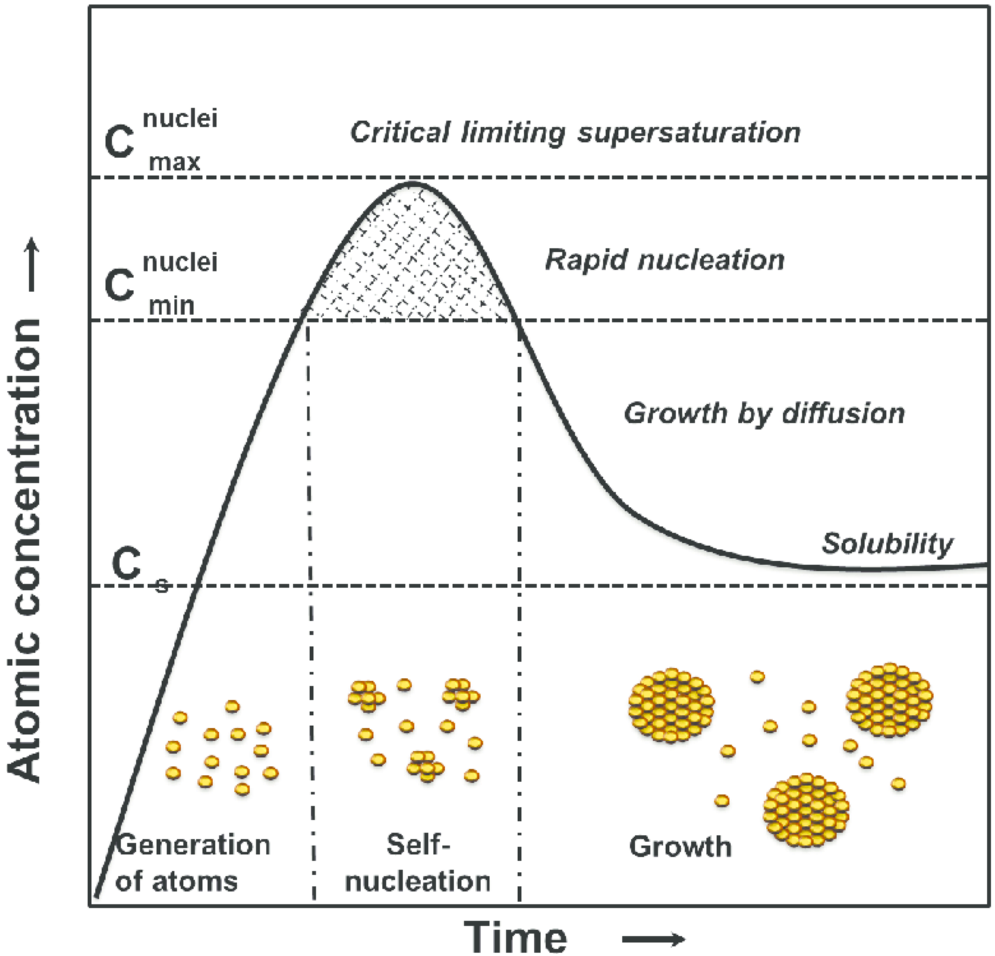
Lamer's diagram for colloidal solutions (1950)



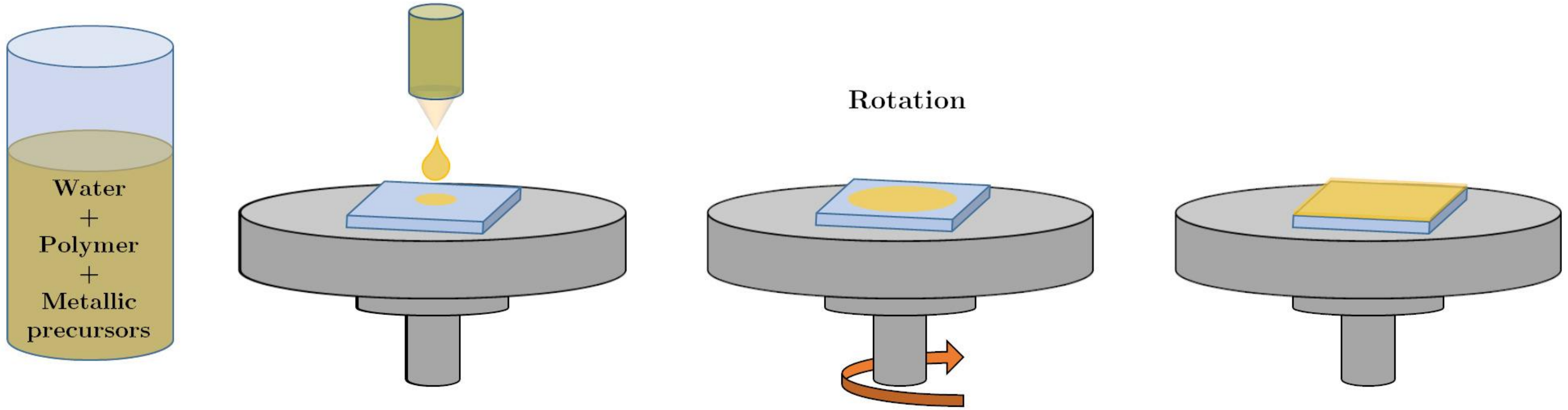
Formation process of monodisperse particles.

C_0 : equilibrium concentration of solute with the bulk solid, $C_{nuclei\ min}$: critical concentration as the minimum concentration for nucleation, respectively.

(I) prenucleation : generation of atoms,
(II) self-nucleation, and
(III) growth stages

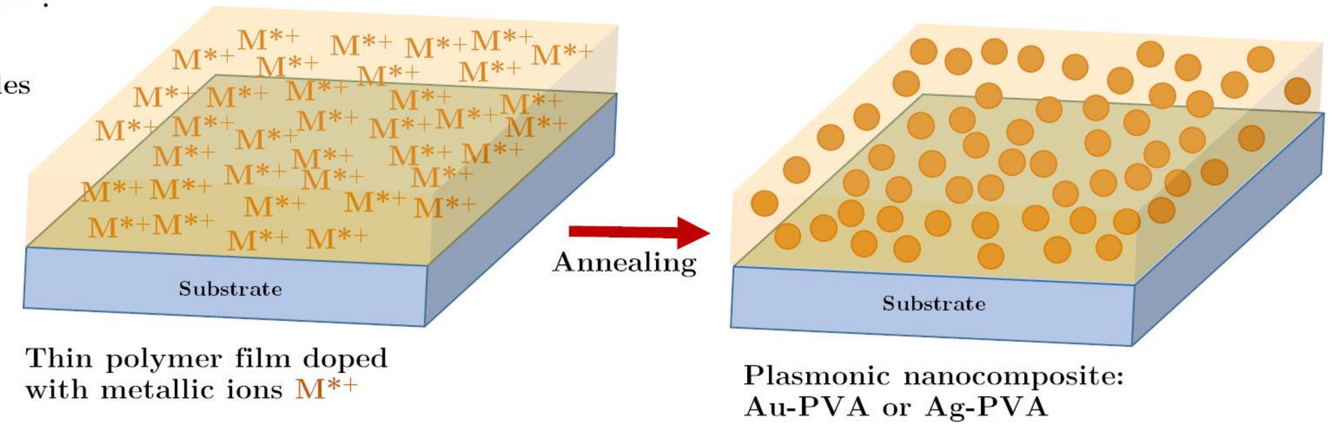
(Lamer and Dinegar, 1950).

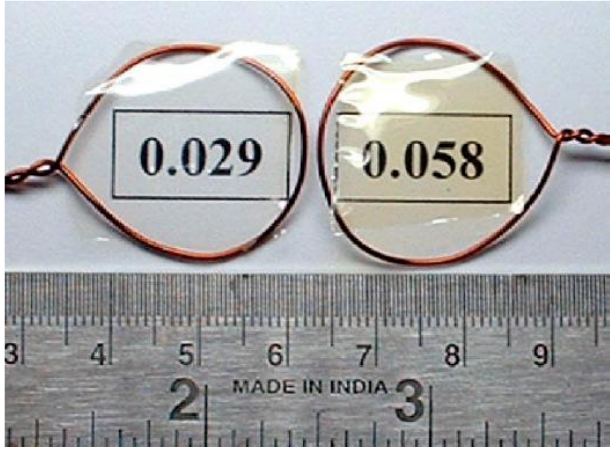
Experimental protocol in more details ...



Metallic precursors M^{*+}:

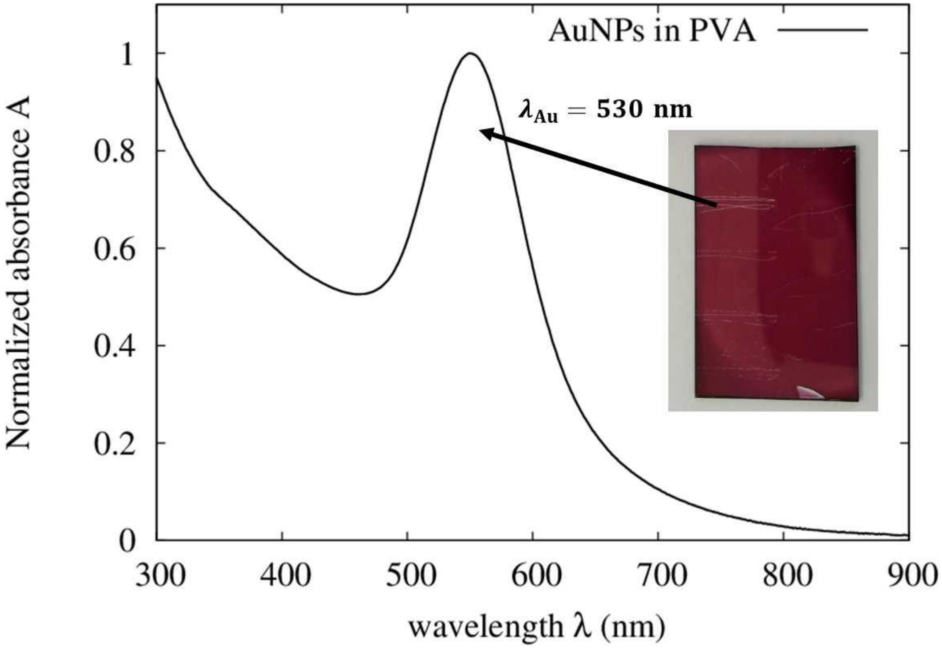
- $HAuCl_4.3H_2O$ for gold nanoparticles
- $AgNO_3$ for silver nanoparticles





First report on in situ synthesized PNCs :

Photographs of free-standing films of AgNPs in PVA matrix ; transparency of the films is demonstrated by placing them on wire frames above a paper on which the corresponding value of the Ag/PVA mass ratio is printed (Porel, 2007).



EXtinction spectrum of a glass coated with AuNPs embedded in a PVA matrix. The inset represents a picture of the analyzed sample. (Guyot, 2020)

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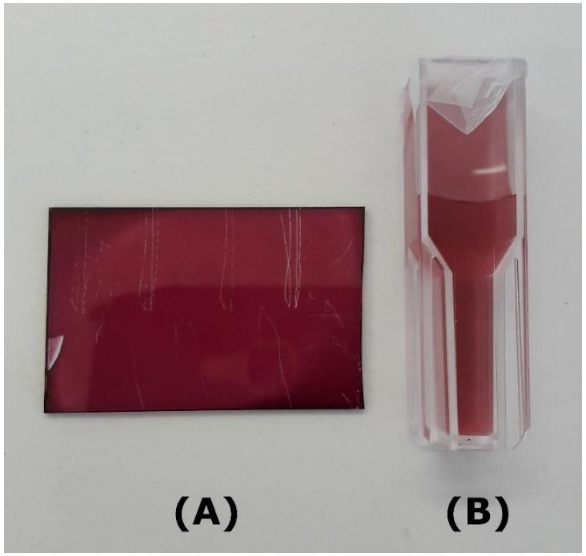
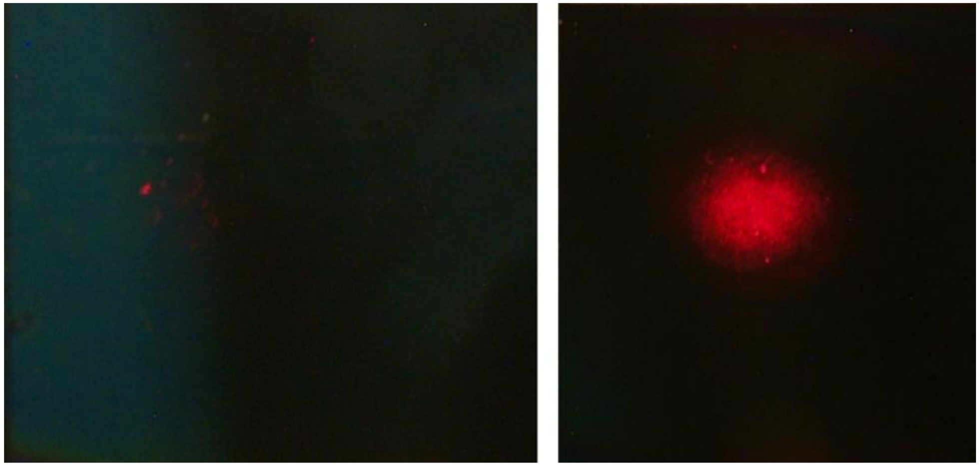
Gold-based PNCs



(A) Thin polymer film with in situ grown AuNPs (optical path: ca. 350 nm, [Au]/[PVA] mass ratio = 50%);
(B) Colloidal solution of AuNPs (optical path: 1 cm).

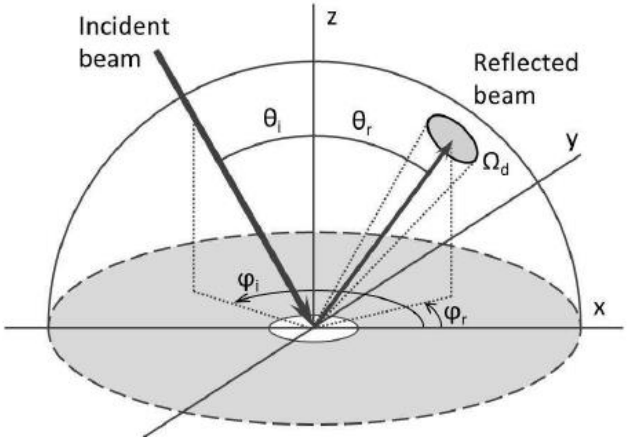
Optical path difference : 350 nm vs 1 cm

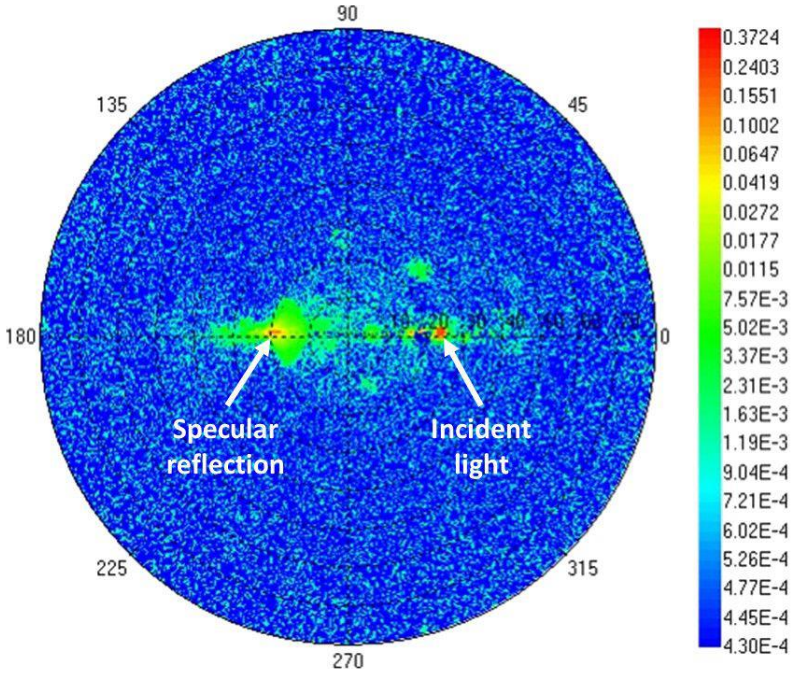


Images at 90° (AOI: 45°C) from the incidence plane. (Left) Before and (Right) After annealing of the sample

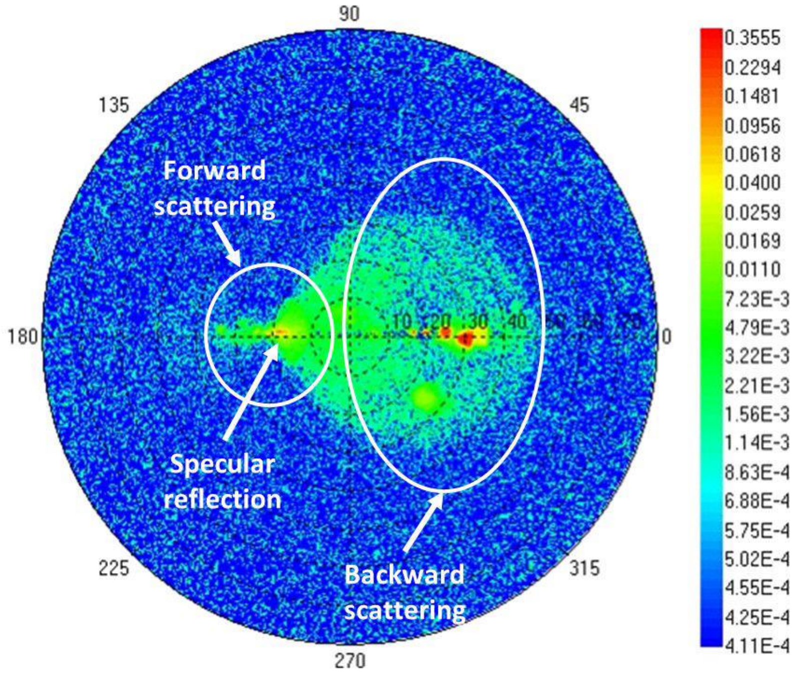
Increase of scattering

Bidirectional reflectance distribution function (BRDF)



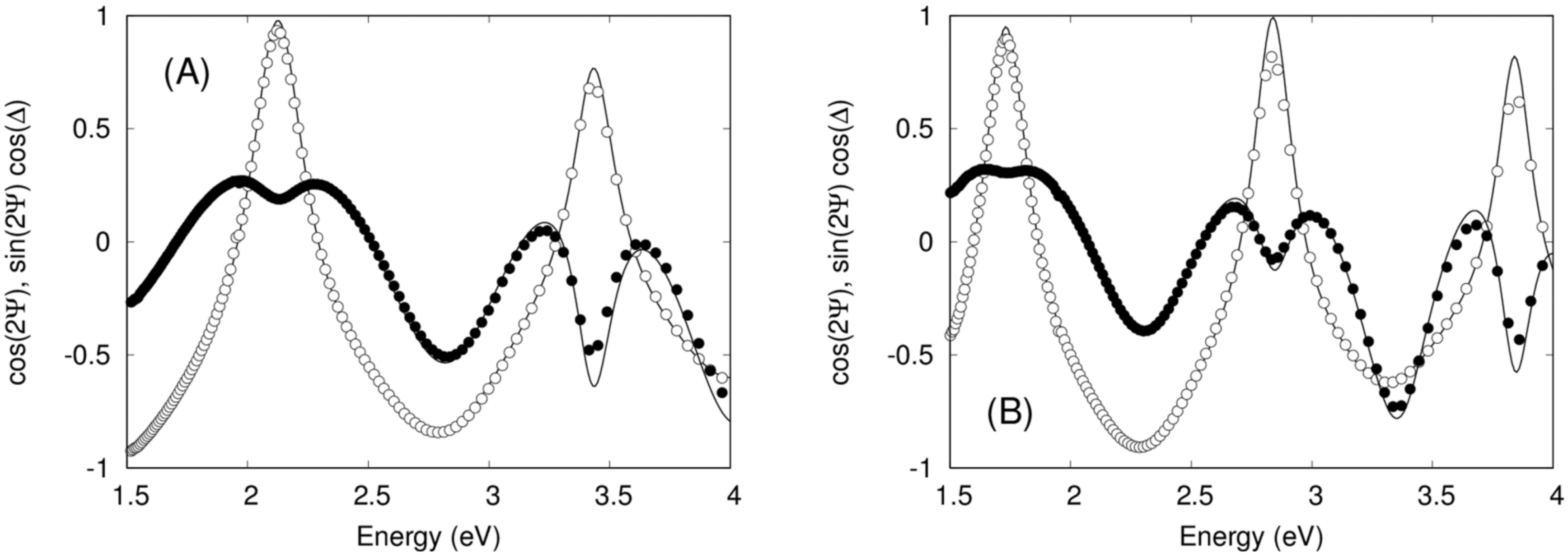


Before annealing



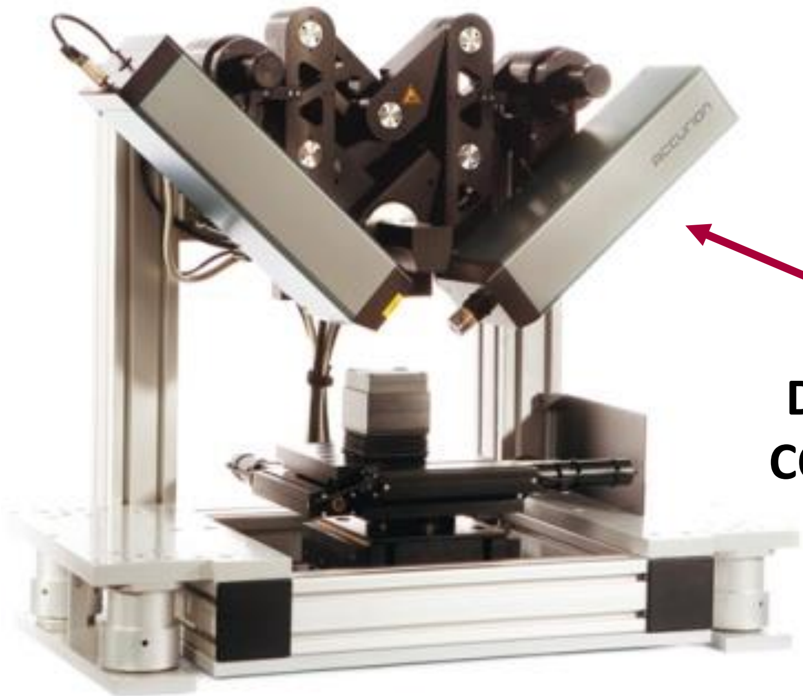
After annealing

Global optical response at low volume fraction



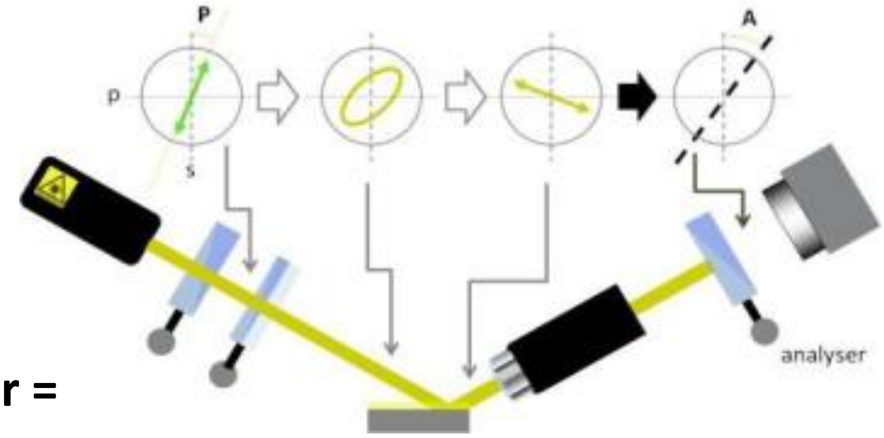
Global ellipsometric response of: (A) a 358 nm-thick undoped-PVA film and (B) a 441 nm-thick AuPVA film with average **f_{Au} = 0.13%**. Open symbols: cos (2Ψ), closed symbols: sin (2Ψ) cos (Δ). Plain lines: best-fit of the experimental data by (A) a Cauchy dispersion law (undoped polymer) or (B) a Cauchy dispersion law and a Maxwell- Garnett approximation that accounts for the contribution of the AuNPs

Imaging ellipsometry



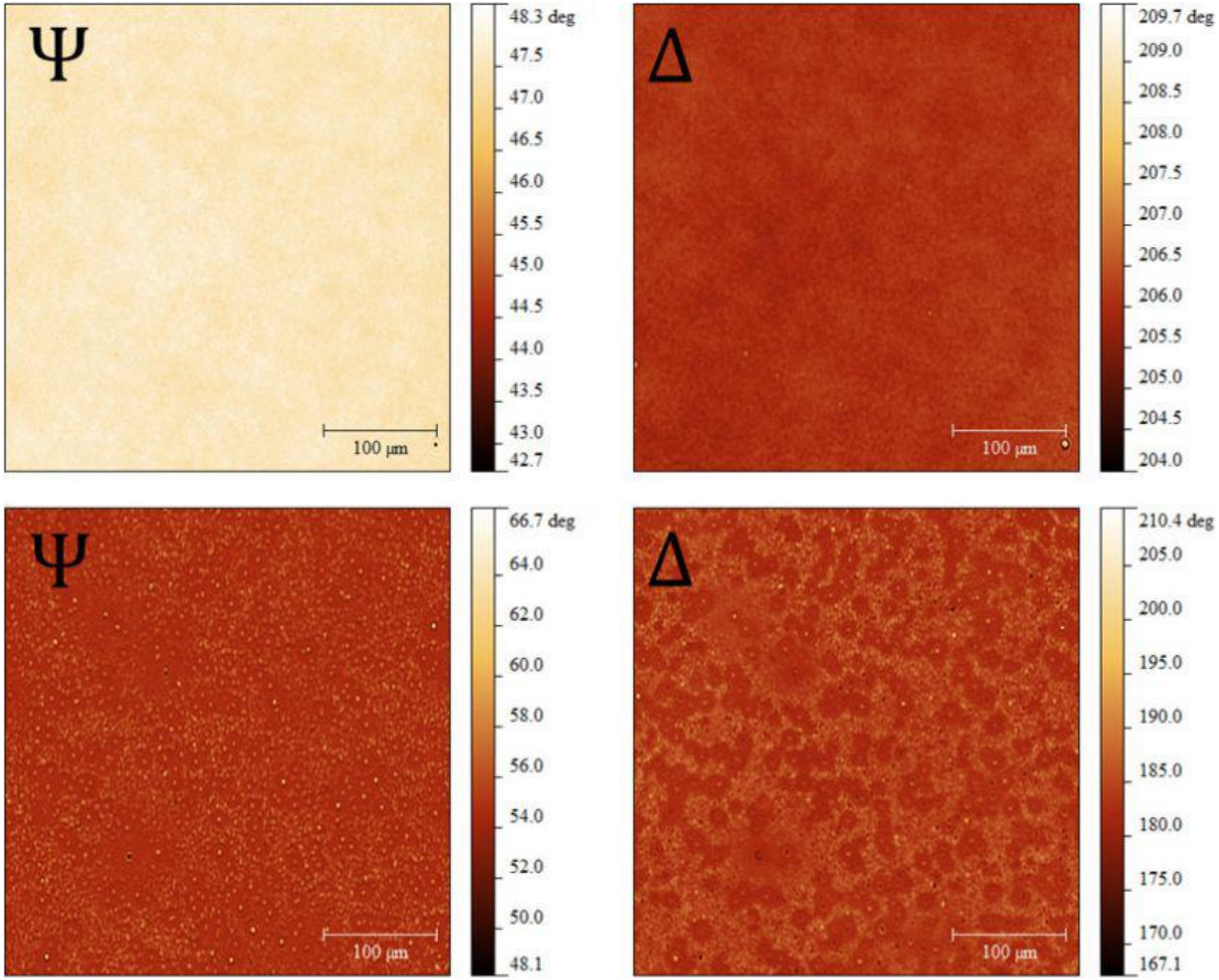
(From : Accurion GmbH)

Detector =
CCD camera



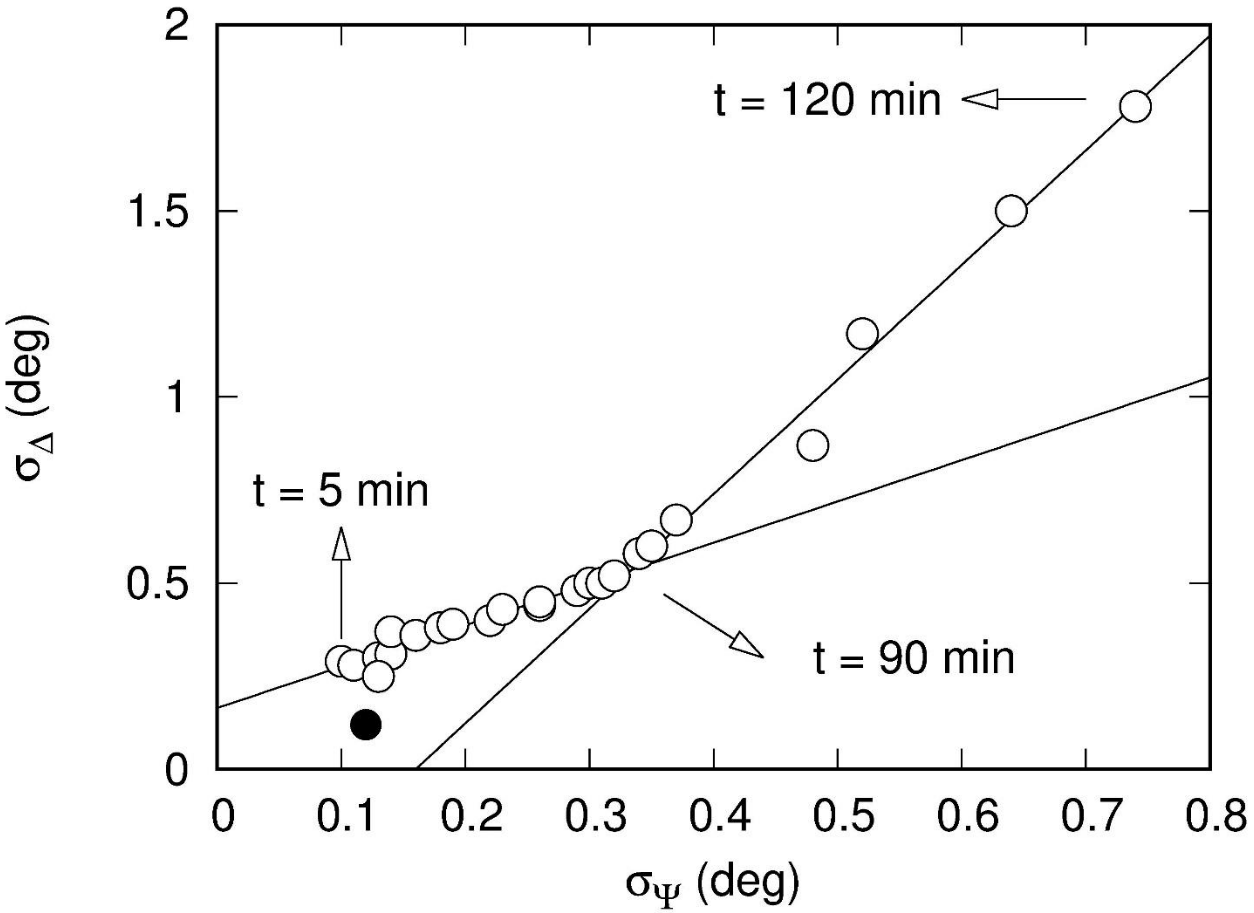
- Nulling ellipsometry
- Same as SE but optical properties at 1µm-scale
- Large number of data (esp. if spectroscopic) : data cube and statistics
- Optical model changes from pixel to pixel

Optical response by IE



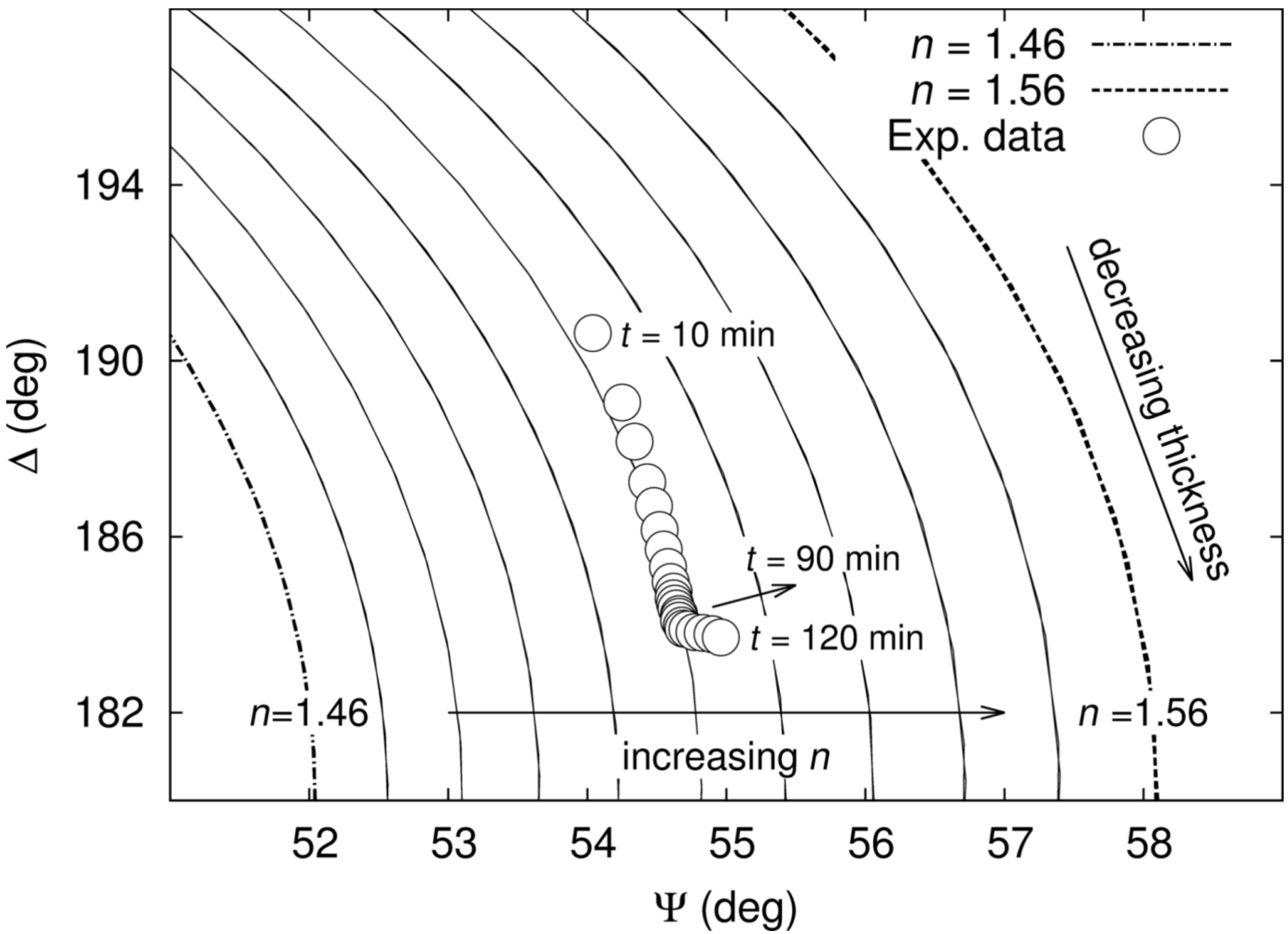
Maps of the ellipsometric angles Ψ and Δ of Au-doped PVA films (λ = 658nm) . (Top) Before annealing. (Bottom) After annealing (135 °C, 120 min).
(Left) Ψ angle. (Right) Δ angle.
(Image size: 450 µm × 380 µm).

Correlation plot of the standard deviations

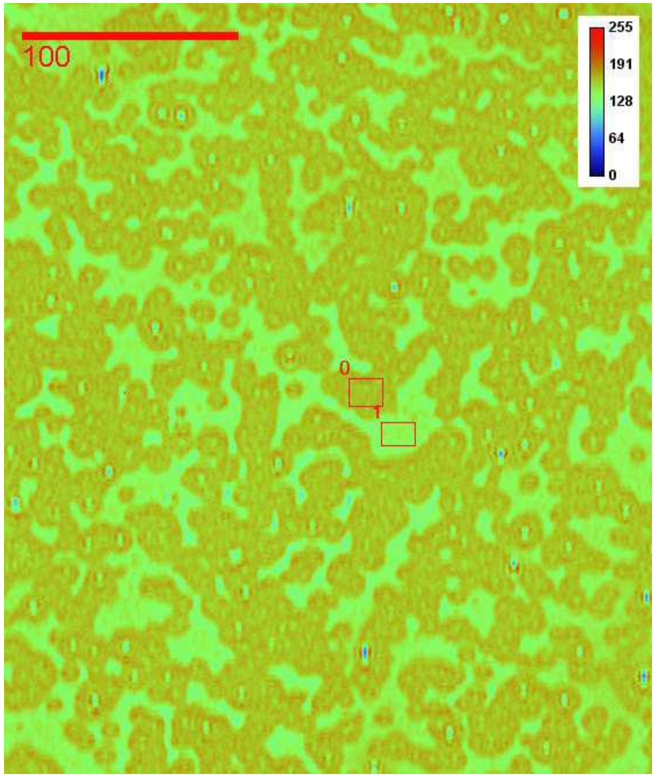


Correlation plot between the standard deviation of the ellipsometric angles Ψ and Δ during film annealing (open circles: experimental data, lines: linear fits).
The filled circle corresponds to *t* = 0 min.

Constant angle of incidence (CAI) curves (Rasheed AZZAM)

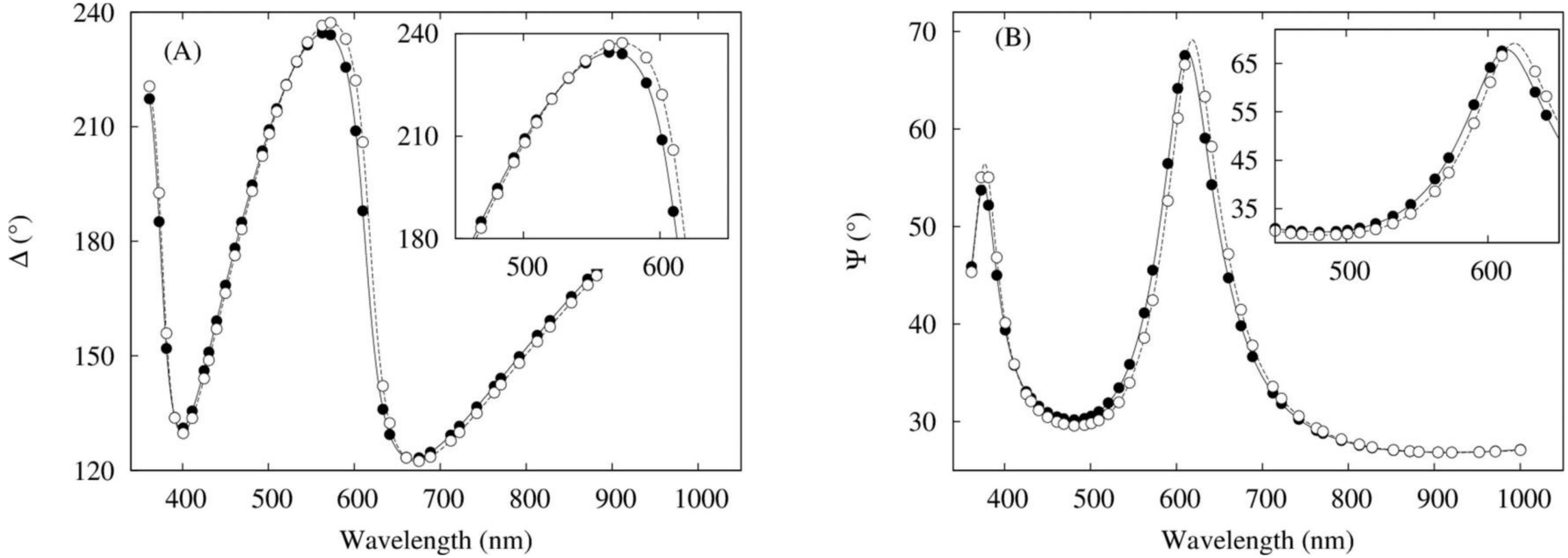


EEC images



Ellipsometric enhanced contrast (grey levels, in false color) image of the AuPVA film at the end of the annealing (Scalebar: 100 m, wavelength: 533 nm, AOI: 55). Red rectangles indicates the regions of interest “0” and “1” used for spectroscopic characterisation.

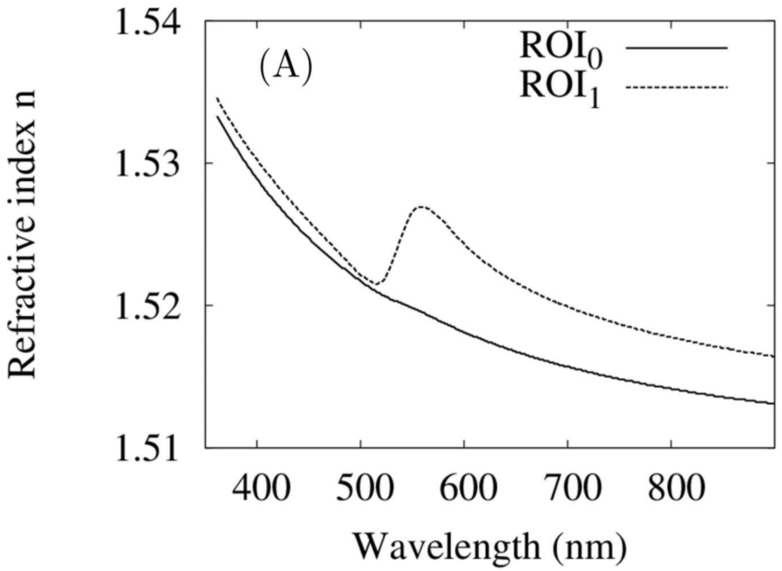
Local optical response at low volume fraction

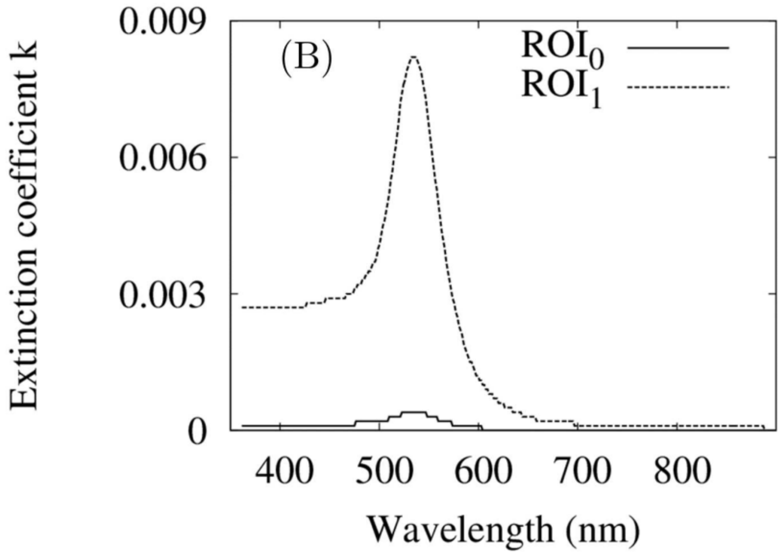


Local spectroscopic optical response of the AuPVA film. Open and close symbols respectively corresponds to ROI_0 and ROI_1.
Plain and dashed lines: best-t data. Insets: details of the ellipsometric spectra in the plasmonic response wavelength range.

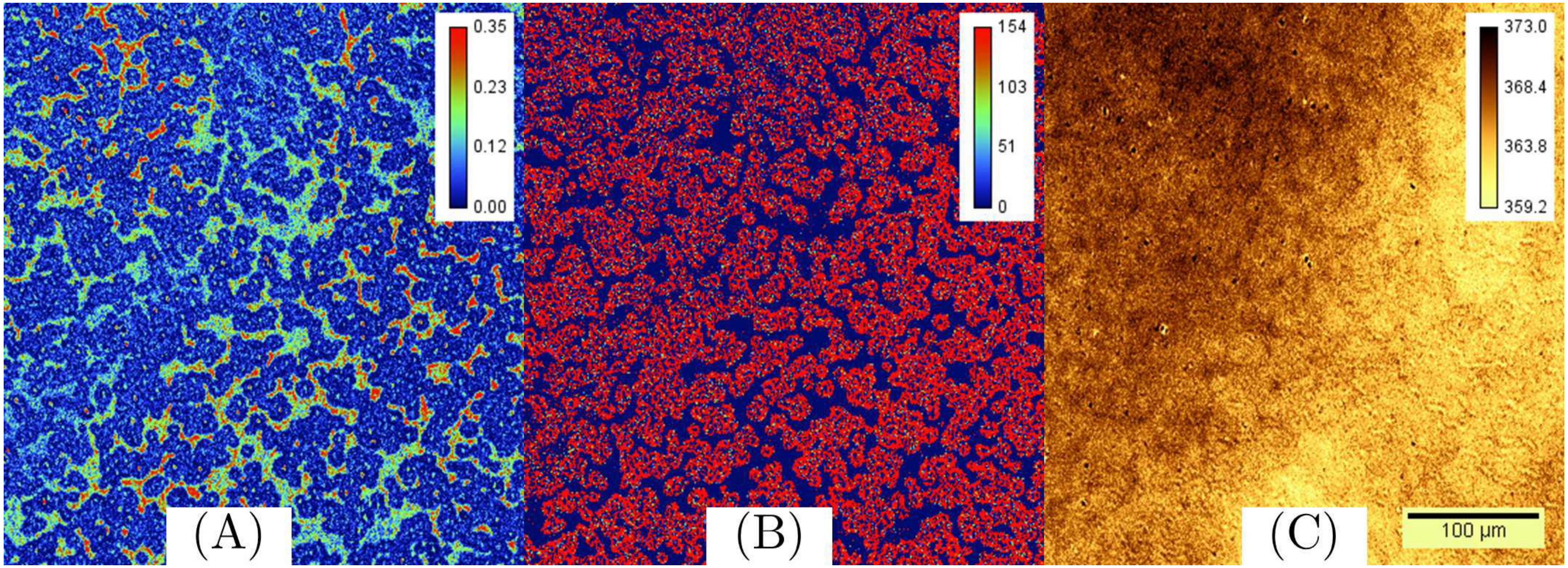
Modeling of the local optical properties using MG-EMA

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



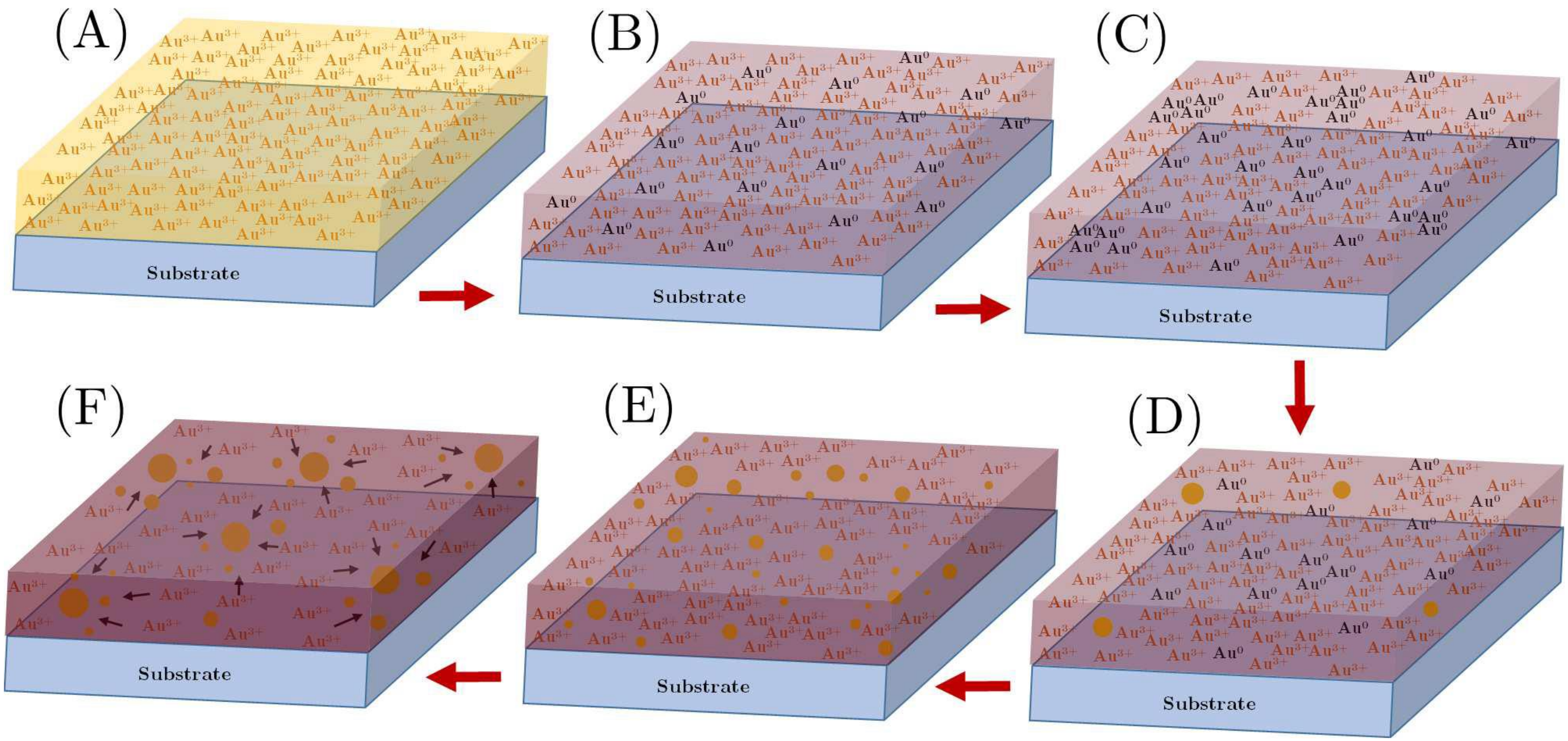


Thickness and volume fraction maps



Results maps for the (A) Gold fraction f_{Au} (%), (B) Relative error $\delta f_{Au}/f_{Au}$ and (C) Film thickness (nm). Images at = 533 nm. Scalebar: 100 m.

Proposed mechanisms for NPs growth



Take-home message …

- SIE : powerful experimental techniques to locally investigate the optical properties
- Experimental evidence for depletion zones in gold-based PNCs

But

- Generation of large sets of data on complex samples with latent variables

Acknowledgements and financial support

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- UMONS – Research Institute for Materials Science and Engineering

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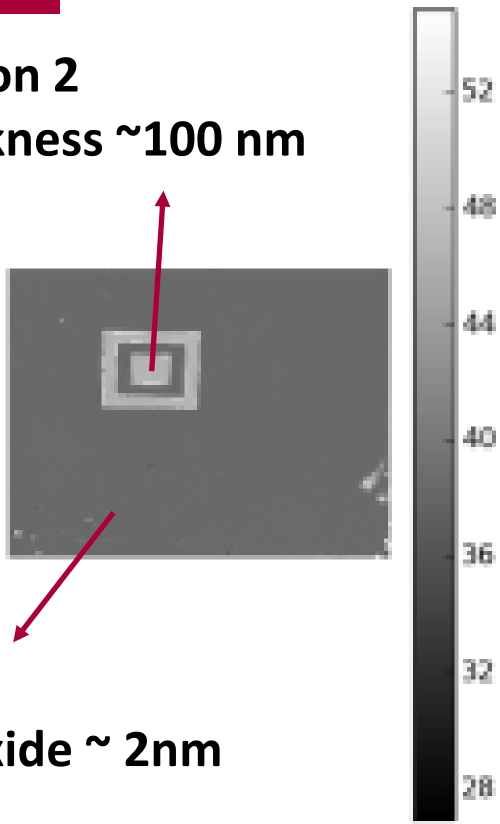
Imaging Ellipsometry

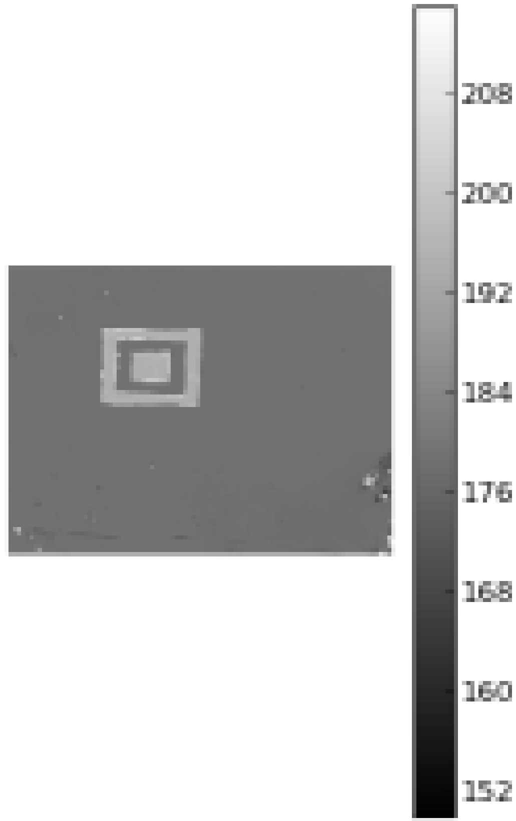
489 nm

Region 2
Thickness ~100 nm



Region 1
Native oxide ~ 2nm

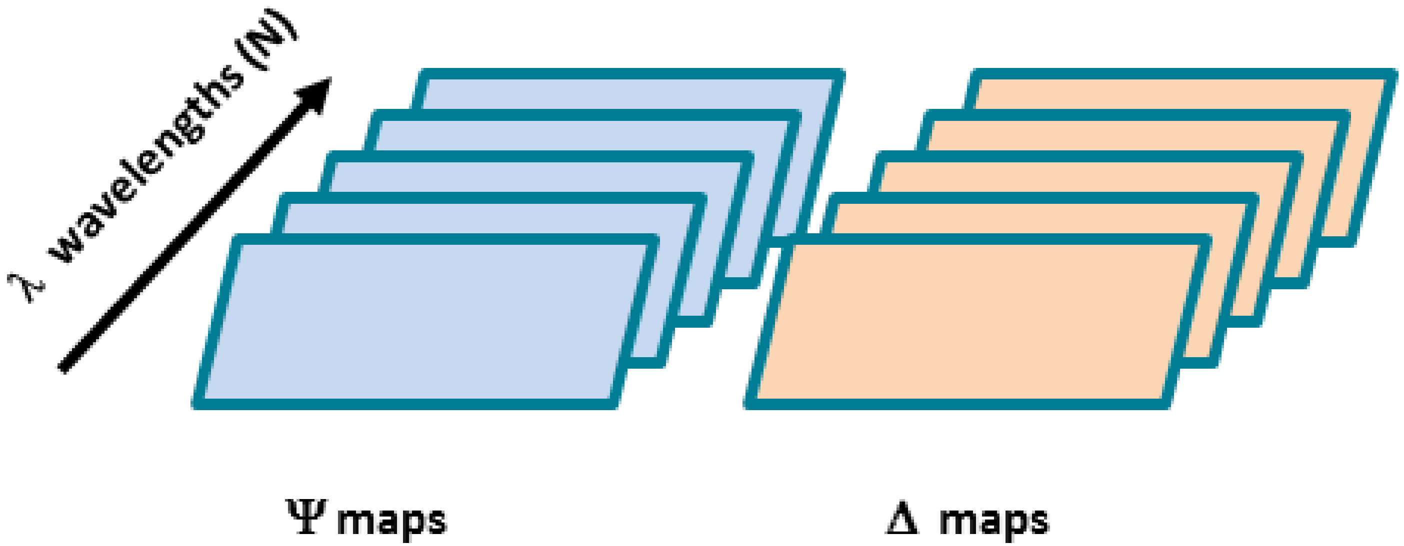
Ψ



Δ

- SiO_2 box on native oxide

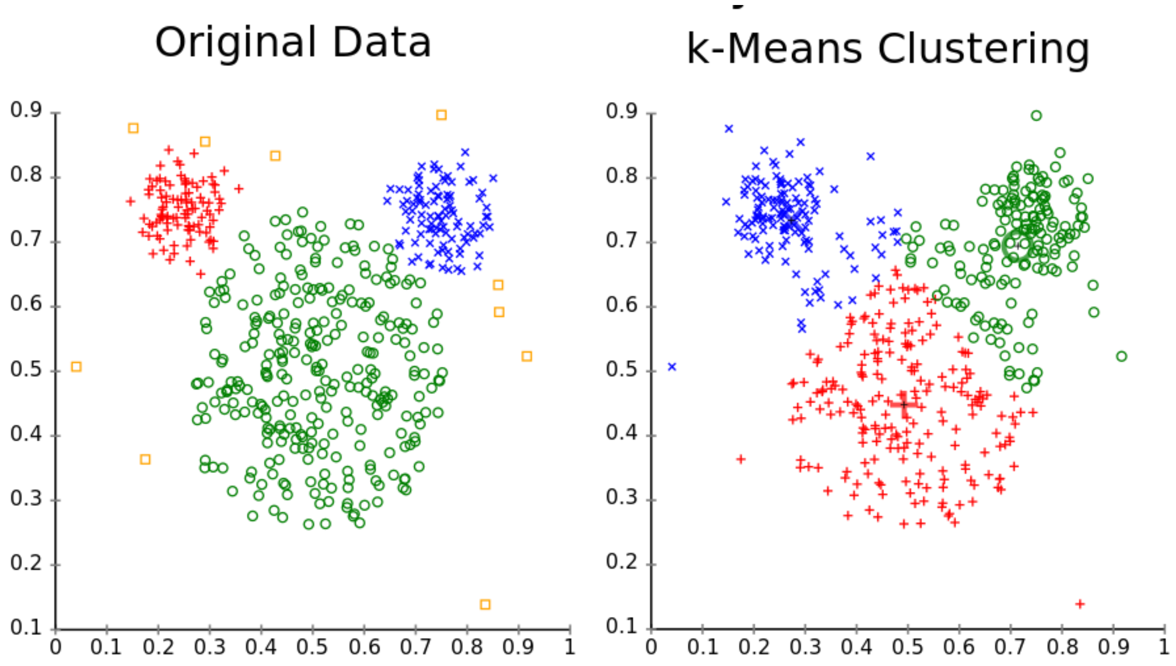
(S)IE data cube



Data cube size : 2N x L x W with N the number of wavelengths, L the length and W the width of the mapped region of interest

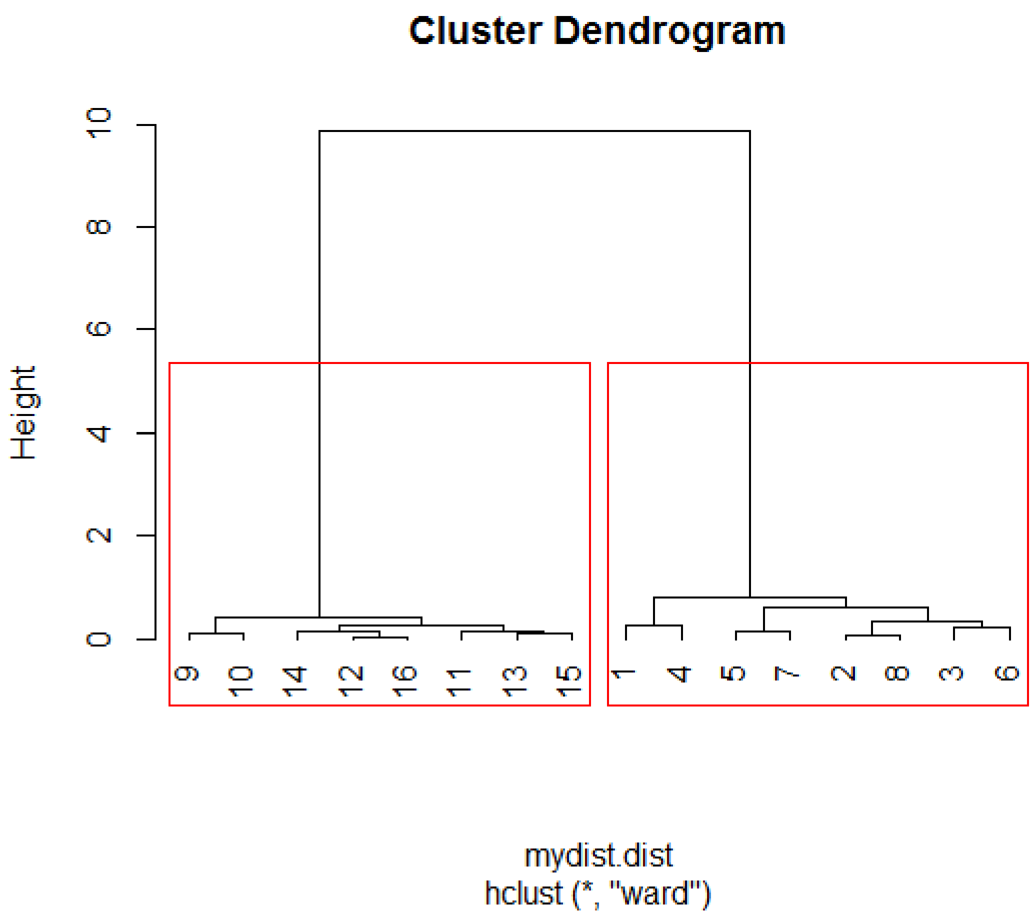
Vector representation : 1 pixel = 1 (super)vector in a 2N-dimensions space

K-means algorithms

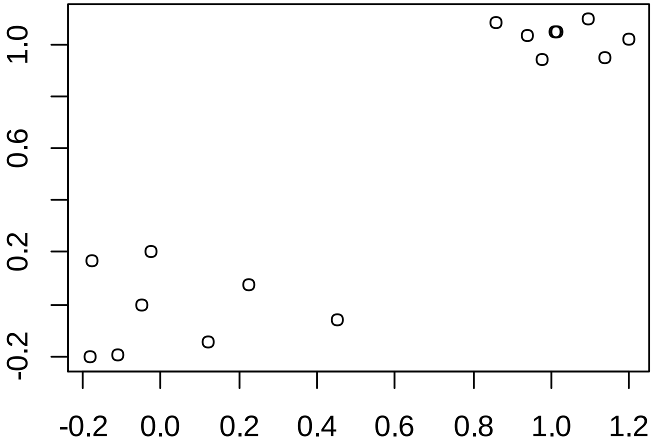


- Iterative method with Random start (local minimum !)
- Element assigned to the nearest cluster
- Number of clusters set at the beginning

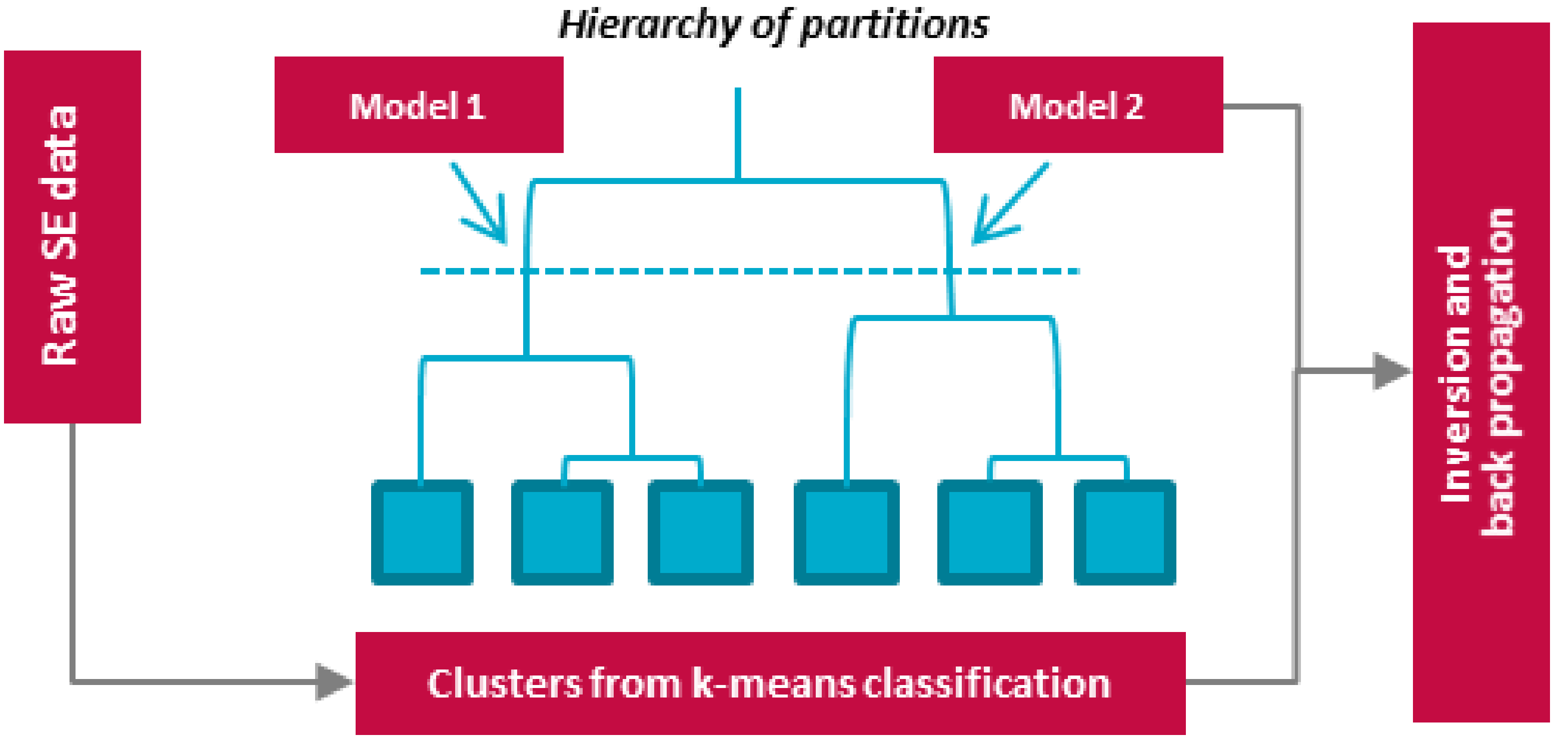
Hierachical clustering



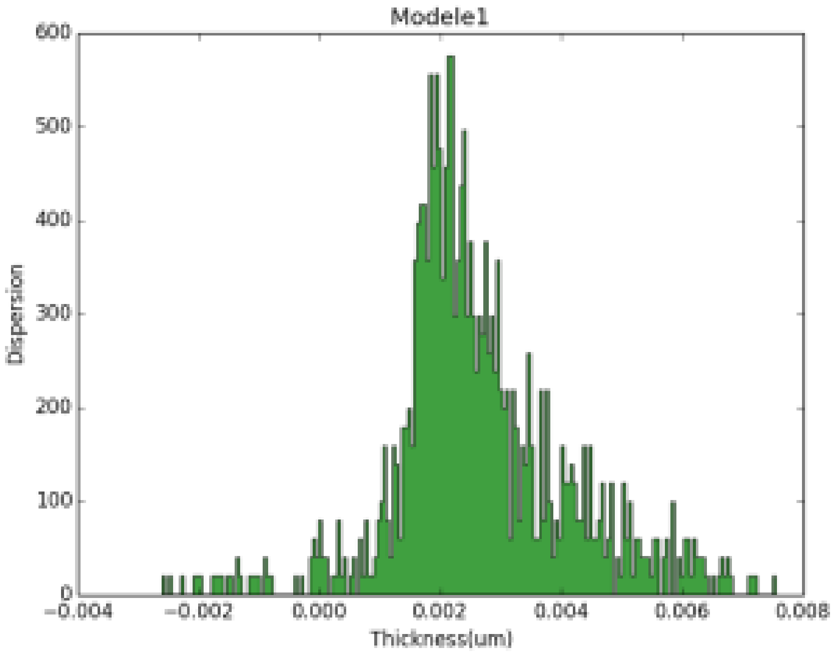
- Distance matrix between elements
- Aggregation of 'nearest' elements (variance criterion)
- Hierachy of partitions
- Dendrogram

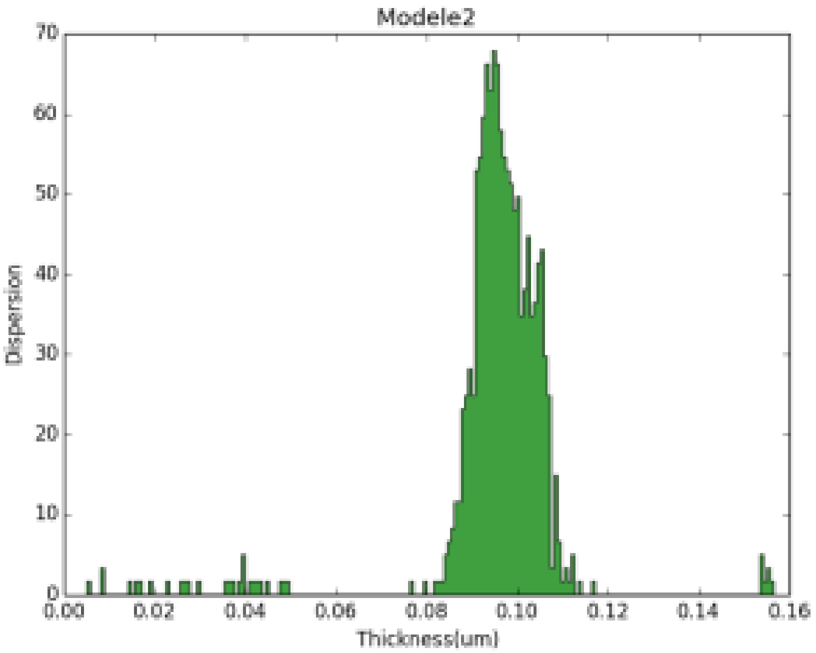


Hybrid clustering method



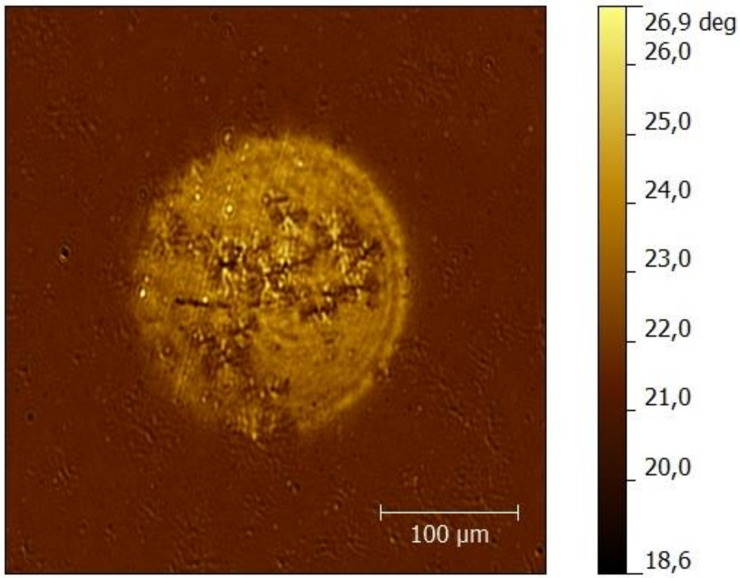
SEI results on SiO_2 box

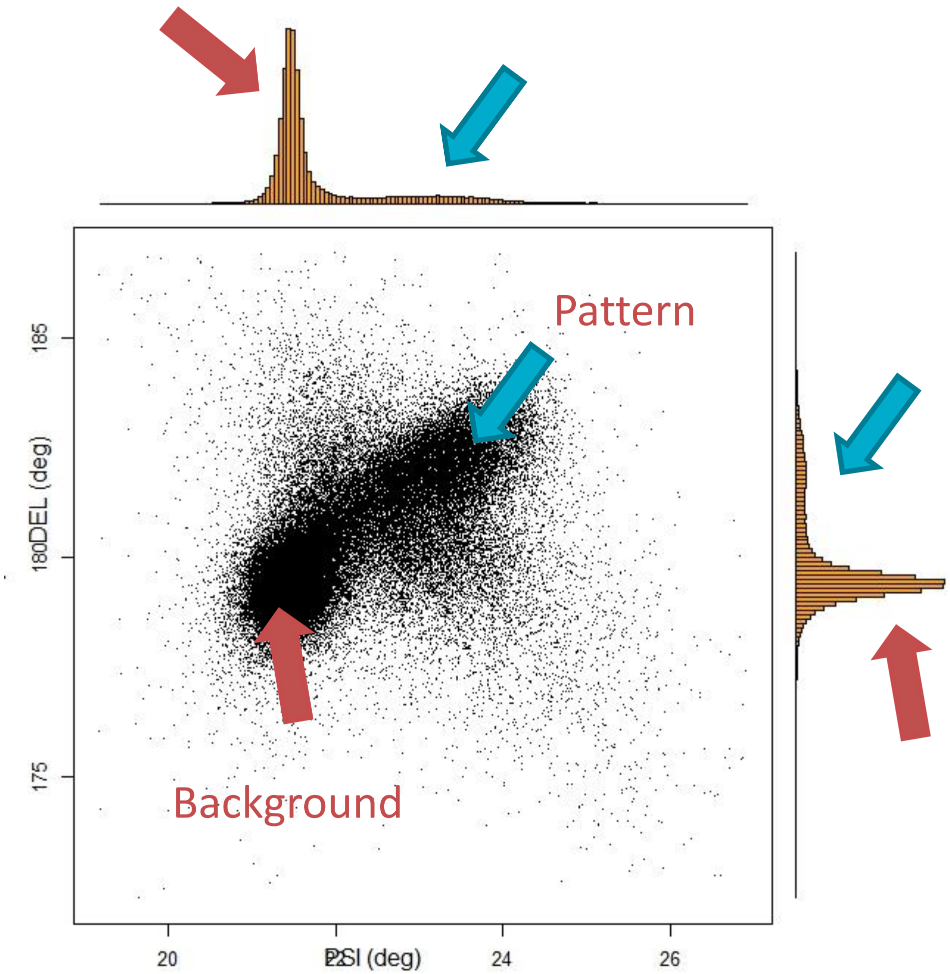




- Inversion of the SIE data and statistics
- Region 1: ~ 2.1 nm
- Region 2: ~ 100 nm

Laser annealing of Ag-doped PVA films





- Two regions (optical models) clearly identified

Take-home message …

- SE and SEI : powerful experimental techniques to locally investigate the optical properties
- Generation of large sets of data on complex samples with latent variables
- Considerable help brought for the data interpretation by multivariate analysis