Gold nanoparticles growing in a polymer matrix: what can we learn from imaging ellipsometry?

Corentin Guyot[1], Olivier Deparis[2] and Michel Voué[1]

(1) Materials Physics and Optics Unit – UMONS Research Institute for Materials Science and Engineering – UMONS – Belgium

(2) University of Namur, Physics Department, Namur, Belgium

UMONS Université de Mons

materials

UMONS RESEARCH INSTITUTE FOR MATERIALS SCIENCE AND ENGINEERING

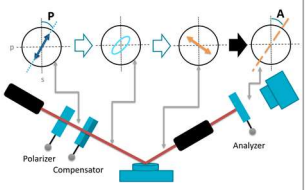
Introduction and research context

Research context and motivation :

- **Optical properties** of metal nanoparticles (NPs) **determined by a collective oscillation of the conduction electrons : Localized Surface Plasmon Resonance (LSPR)**
- **Model system : $HAuCl_4$ mixed with poly(vinyl alcohol) (PVA) and chemical reduction of the metal salt by thermal annealing of the spin-coated film to obtain Au^0 NPs in PVA matrix ($\lambda_{Au} \approx 540\ nm$)**
- ***In situ* route for synthesis : spontaneous encapsulation in a matrix during synthesis but less control on the shape/size of the NPs**
- **Advantages : High concentration of NPs in the film and *in situ* synthesis is simpler and faster than the conventional bottom up approach**

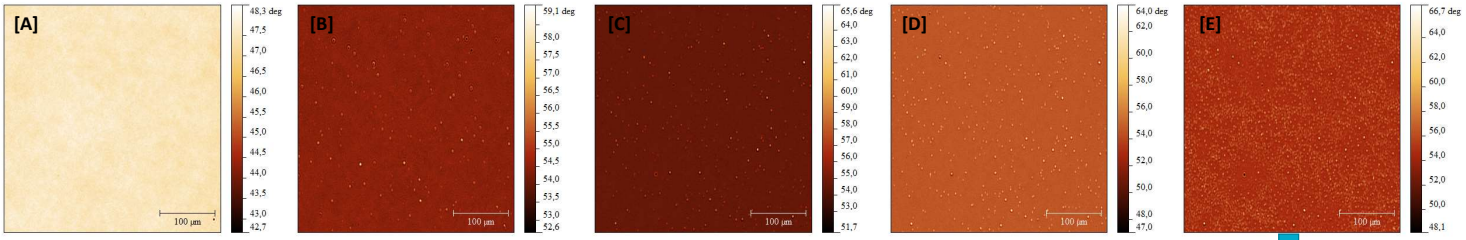
Optical characterization :

- **Imaging ellipsometry (IE) measurements were carried out using an EP3 single wavelength ellipsometer operating at $\lambda = 658\ nm$ (Accurion GmbH, Goettingen, Germany). Ellipsometric angles (Δ and Ψ) images were recorded at an angle of incidence (AOI) $\theta_i = 42°$**



Experimental results

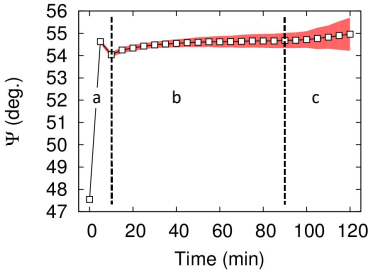
Time variation of the Ψ map during the annealing ($\lambda = 658\ nm$)

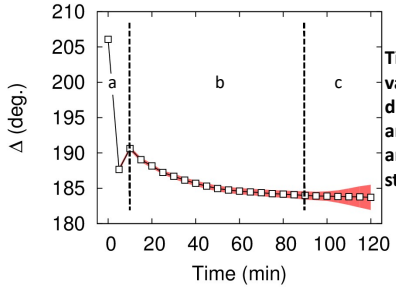


Imaging ellipsometry (IE) maps (Ψ) of Au-PVA film [A] before annealing (T = 22°C), after [B] 30 min, [C] 60 min, [D] 90 min, [E] 120 min annealing at T = 135°C : [A] sample clearly homogeneous, [D] spots (diffraction patterns from NPs) and depletion zones can be observed

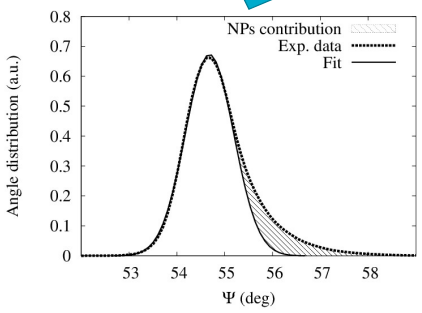
Statistical distribution of the Ψ angles

Monitoring the ellipsometric angles during the annealing: different mechanisms during the dynamics



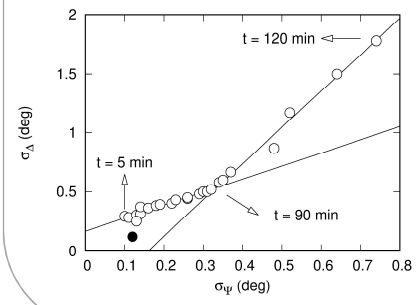


Time evolution of the mean values of ellipsometric angles during the annealing. Left: Ψ angle and right: Δ angle. Red area corresponds to the standard deviations.

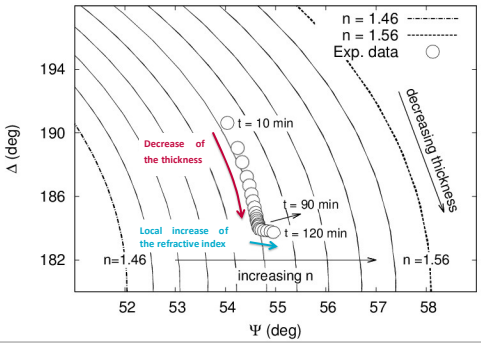


Statistical distribution of the Ψ angles after annealing (t = 120 min).
Dashed line: experimental data; solid line: gaussian fit using the most left part of the data; Shaded area: contribution of the Au NPs.

- **a: relaxation of the mechanical constraint of the film induced by the spin coating**
- **b: slow variation of the ellipsometer angles -> slow variation of the film thickness**
- **c: large increase of the standard deviation after 90 min**



Variation of the standard deviation of the Δ versus the standard deviation of the Ψ. Filled circle corresponds to t = 0 min.
Large increase of the standard deviation of both angles Ψ and Δ after 90 min



Iso-angle of incidence Ψ − Δ curves ($\lambda = 658\ nm$) and $\theta_i = 42°$ for n varying from $n = 1.46$ to $n = 1.56$ and varying film thickness ($k = 0$ in agreement with M-G calculations).
Two different regimes appear
1: decreasing of the thickness
2: local increase of the refractive index

Conclusions and acknowledgements

- **Fast and easy way to produce plasmonic nanocomposites**
- **IE is enough sensitive to detect local information on the optical properties**
- **Variation of the film thickness at constant refractive index followed by an increase of the refractive index due to the growth of the Au-NPs**

This work is financially supported by the National Fund for Scientific Research of Belgium (FRFC project n°1926111)

Faculté des Sciences

Université de Mons | corentin.guyot@umons.ac.be | Materials Physics and Optics Unit