# Optical behavior of poly-(vinyl)alcohol films embedding silver nanoparticles : a statistical analysis of the film thickness effect

Corentin Guyot and Michel Voué

University of Mons - Materials Physics and Optics Group - Belgium

## Introduction and motivation

### Research context :

- **Optical properties** of metal nanoparticles (NPs) determined by a collective oscillation of the conduction electrons : **surface plasmon polariton resonance (SPPR)**.
- **Ex-situ route for synthesis :** easy control of the shape/size from experimental conditions – Encapsulation step required
- **In-situ route for synthesis :** spontaneous encapsulation in a matrix during synthesis – Less control on the shape/size of the NPs
- **Model system** for silver NPs in a dielectric matrix : poly(vinyl alcohol) (PVA) matrix and chemical reduction of the metal salt during thermal annealing of the film

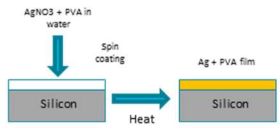
### Motivation :

- **In thin films,** the size of the added NPs controls the roughness of the film

**Open question in the case of *in situ* synthesized NPs !!!**

### Film preparation and characterization :

- **Preparation of Ag-PVA films** with high (> 12.5% w:w) and low doping levels by spin-coating of the doped polymer solution on silicon wafers




- Study of the film topography by **AFM** in **intermittent contact mode**
- Study of the optical properties by **spectroscopic ellipsometry** to simultaneously access to the thickness of the film and to the frequency-dependent dielectric function

$$\epsilon(\omega) = N^2(\omega) = [n(\omega) - ik(\omega)]^2$$

## Optical properties of thick and thin films

**Spectroscopic ellipsometry :** Non-destructive optical analysis technique based on the relative change of polarization of the *p*- and *s*- components of the light at the interface between two media characterized by different optical properties

$$\rho = \frac{r_p}{r_s} = \tan\Psi\, e^{i\Delta} \qquad \alpha = \cos(2\Psi) \qquad \beta = \sin(2\Psi)\cos(\Delta)$$

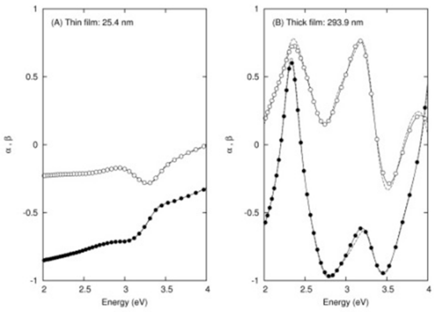
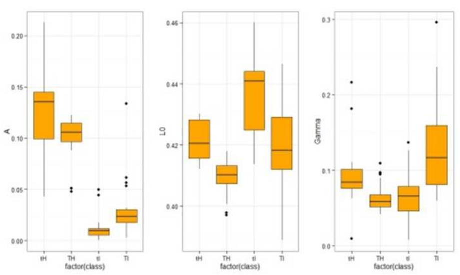



**Figure 1 :** Ellipsometric spectra of Ag -PVA films (Ag/PVA ratio: 25% w: w): A, thin films (thickness: 25.4 nm); B, thick film (thickness: 293.9 nm). Experimental data: $\alpha$ (filled circles) and $\beta$ (open circles). Dashed lines: optimized results from the optical model.

**Lorentzian + Cauchy**

### Significant difference in the refractive index of thin and thick films at constant doping level




**3 parameters to describe the Lorentzian resonance : A, L0, Gamma**

**Figure 2 :** Boxplots of the optical parameters of the resonance peaks. (tH : thin-high, TH : thick-high, tl :thin-low, Tl : thick-low)

### Multivariate statistical analysis of the resonance peak parameters

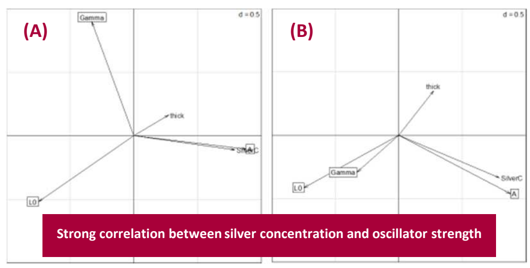



**Figure 3 :** PCA of the resonance parameters (boxed labels) – Silver concentration and thickness as supplementary variables. (A) First factorial plane (PC1-PC2) - (B) Second factorial plane (PC1-PC3)

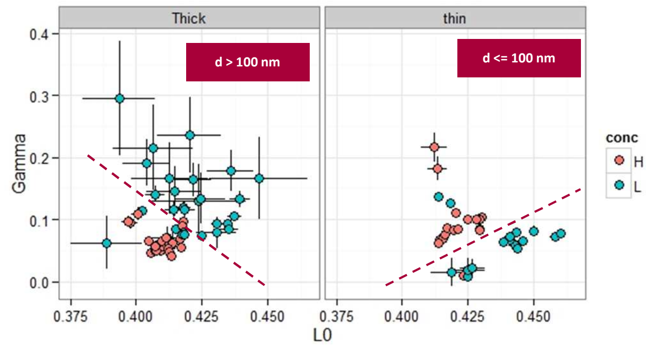



**Figure 4 :** Influence of the thickness of the film on the resonance parameters

## Conclusion and acknowledgements

- In situ synthesis of silver NPs by thermal annealing of a polymer film containing metal salt
- Simultaneous determination of thickness and optical properties : SPPR localized at ~ 3 eV
- Different behavior between thin and thick films (2D ⟶ 3D)
- NPs size determined by the film thickness in the *in situ* synthesis case
- Need to systematically investigate the « topography/film optical response » correlation

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