Real-time UV-Visible reflectometry as a tool to monitor the growth of noble metal nanoparticles in a polymer matrix

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Research context and introduction

Introduction and motivation

- Numerous applications of dielectric matrices embedding metal nanoparticles (NPs)
- "One-pot" synthesis methods
- Details of the NPs growth in films not clearly understood
- Real-time non destructive analysis methods (reflectometry, ellipsometry) important
- Ag-doped poly(vinyl) alcohol films (Ag-PVA) : Model systems for plasmonic nanocomposites
- Influence of the film thickness on the growth mechanism

Reflected amplitude and reflectivity

At **normal incidence**, the reflected **amplitude** for an "ambient/film/substrate" optical stack is given by

$$r_{tot} = \frac{r_{01} + r_{12}\, e^{-2\beta j}}{1 + r_{01}\, r_{12}\, e^{-2\beta j}} \tag{1}$$

with

$$\beta = \frac{2\pi\, d}{\lambda}\, n_1 \quad \text{and} \quad r_{ij} = \frac{n_j - n_i}{n_j + n_i} \tag{2}$$

where λ is the radiation wavelength, $n_j (j = 0, 1, 2)$ is the complex refractive index and d is the thickness of the layer.

The **reflectivity** is given by $R = r_{tot}\, r^*_{tot}$ where '*' denotes the complex conjugate.

Samples

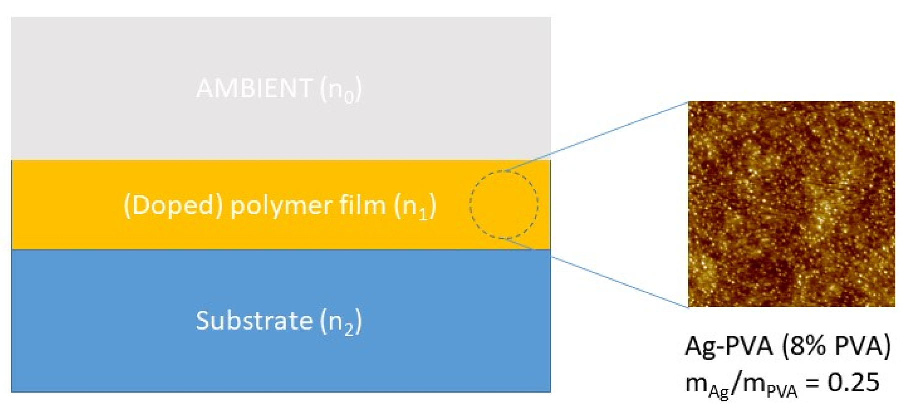

Figure 1: Model system for plasmonic nanocomposites: Ag-doped poly(vinyl) alcohol films (Ag-PVA)

Samples prepared by **spin- coating** of a polymer/metal salt solution to achieve the required thickness at a given metal-to-polymer ratio (25% w:w in this study).

Optical model

- Ambient : Air
- (Doped-)polymer layer : Cauchy law (3 parameters) with classical oscillator (3 parameters)
- Substrate : Crystalline silicon (database)

Main experimental setup

- Thorlabs CCD spectrometer (190nm-1000nm) with bifurcated optical fiber
- Heating stage
- Real-time acquisition of the reflected intensity (typically: every 5 s over 3600 s).

Results and discussion

PVA films

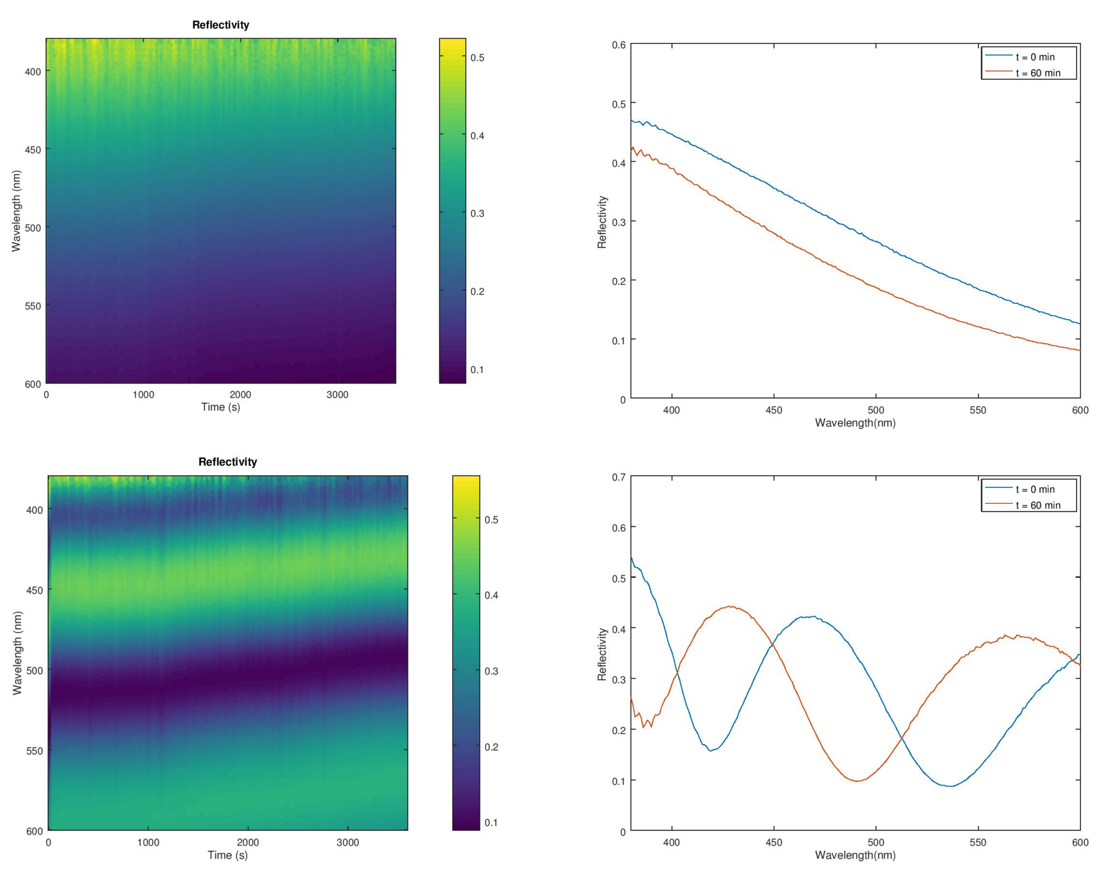

Figure 2: Annealing of the **UNDOPED** polymer film at $\simeq 90^oC$ – Polymer concentration: 2% (top) and 8% (bottom).

Doped PVA films

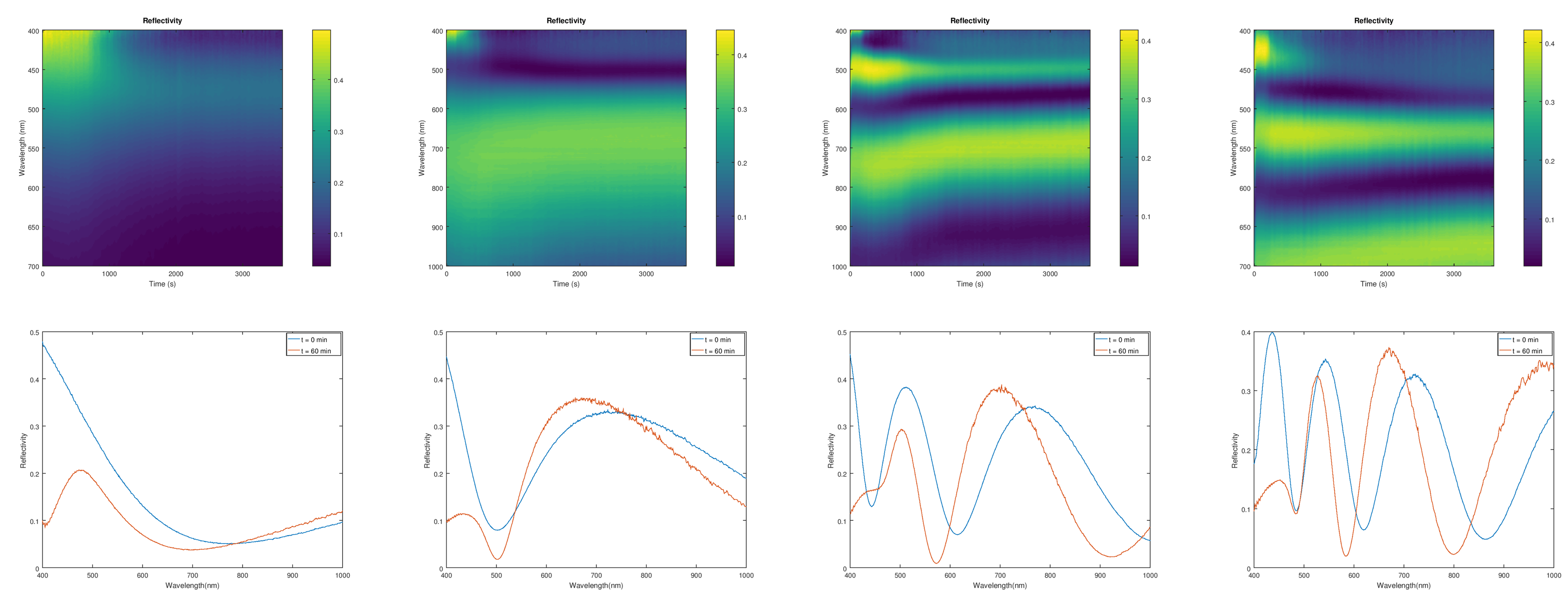

Figure 3: Annealing of the **DOPED** polymer film at $\simeq 90^oC$ - Polymer concentration (from left to right) : 2%, 4%, 6% and 8%

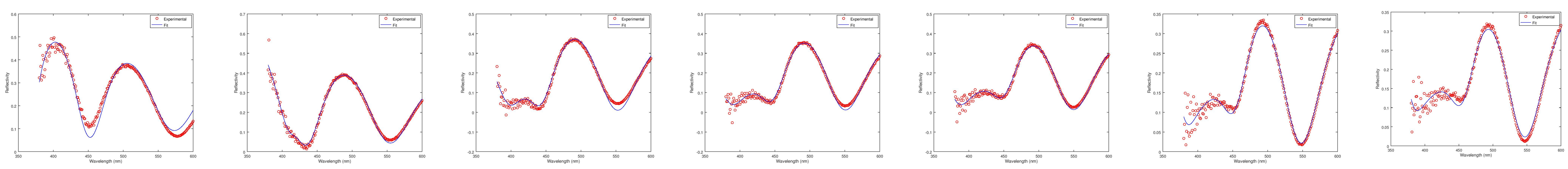

Figure 4: Fitted reflectivity spectra for a 8% AgPVA film – Annealing time: from 0 to 1800 s by 300 s (from left to right)

Conclusions

- **Complex reflectometry spectra**
- **At least, 4 simultaneous mechanisms : residual solvent evaporation, mechanical constraints relaxation, glass transition and nanoparticles growth**
- **For inorganic layers (data not shown) (i.e. SiO_2) : no change in the reflectometry spectrum (low dilatation coefficient and low refractive index temperature coefficients)**
- **For polymer layers (PVA) : initial evaporation of the residual solvent and change of the optical properties at the glass transition evidenced by a (slight) shift of the reflexion peaks**
- **For the doped polymer layers (AgPVA) : same as before but disappearance of some reflexion peaks at $\simeq$ 400-420nm due to the onset of the plasmon resonance**

Perspectives

- **Realtime monitoring of the optical model parameters (partially done)**
- **Comparison of the kinetics as a function of the initial film thickness**
- **More accurate control of the temperature**
- **Optimization of the optical system (more strongly focusing the beam)**
- **Decreasing time laps between the spectra to reach 100 ms**

References

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[3] Nguyen T. K. Thanh, N. Maclean, and S. Mahiddine, *Chem. Rev.* 114 (2014) 7610.

[4] C. Guyot, and M. Voué, Submitted to *J. Appl. Phys*, 2018.