Out-of-plane optical anisotropy in organic layers

A spectroscopic ellipsometry study

Corentin Guyot (*) **& Michel Voué**

Université de Mons – Physique des Matériaux et Optique

(*) corentin.guyot@umons.ac.be (+32 65 373390)

Research context and introduction

Introduction and motivation

- **Y-type organic layer stacks** made from fatty acids: simple experimental model to investigate the optical anisotropy of organic material
- Direct link between **optical response** and **structural parameters** considered as latent variables

Sample preparation

- **Multilayer preparation:** Langmuir-Blodgett layers on OTS-derived silicon wafers
- **Sample thickness:** From 2 to 200 layers of Cd^{2+}-behenate in the S-state (Deposition at $\Pi = 30mN/m$ surface pressure, molecular area: 0.194 nm^2, 25 mm/min)

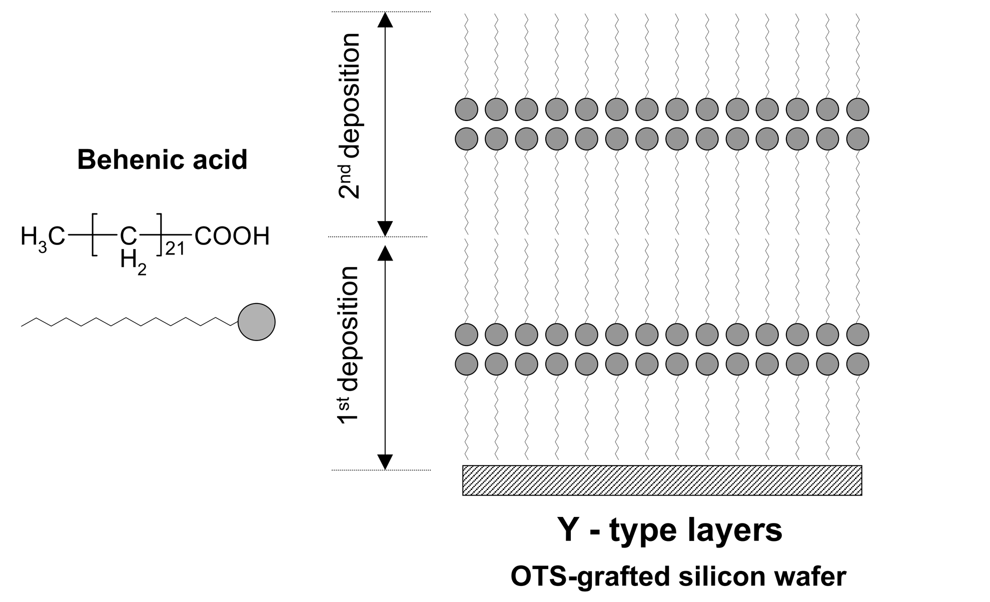

Figure 1: Schematic description of Y-types anisotropic organic multilayers

Optical analysis and modeling

- Determination of sample thickness and refractive index using **spectroscopic ellipsometry (SE)** (SOPRA Gesp5, France)
- Analysis of the SE spectra assuming flat interfaces between layers
- Uniaxial anisotropy of the film taken into account via the formalism proposed by Toussaere and Zyss (1993) considering the optical axis of the film perpendicular to its boundaries (*out-of-plane anisotropy*)
- In-plane birefringence neglected ($\simeq 10^{-2}$)
- Optical model with 5 parameters : thickness (1) and Cauchy law parameters (4) assuming non absorbing materials

$$n_o(\lambda) = A_o + \frac{B_o}{\lambda^2} \quad \text{and} \quad n_e(\lambda) = A_e + \frac{B_e}{\lambda^2}$$

Results and discussion

Surface topography and optical properties

- **Roughness parameters:** R_a = 0.58nm and R_q = 0.84nm (optical profilometry data) (Fig. 2A)
- **Average thickness** for the 20 layers step : 68 nm or 3.4 nm per molecular step (Fig. 2B)

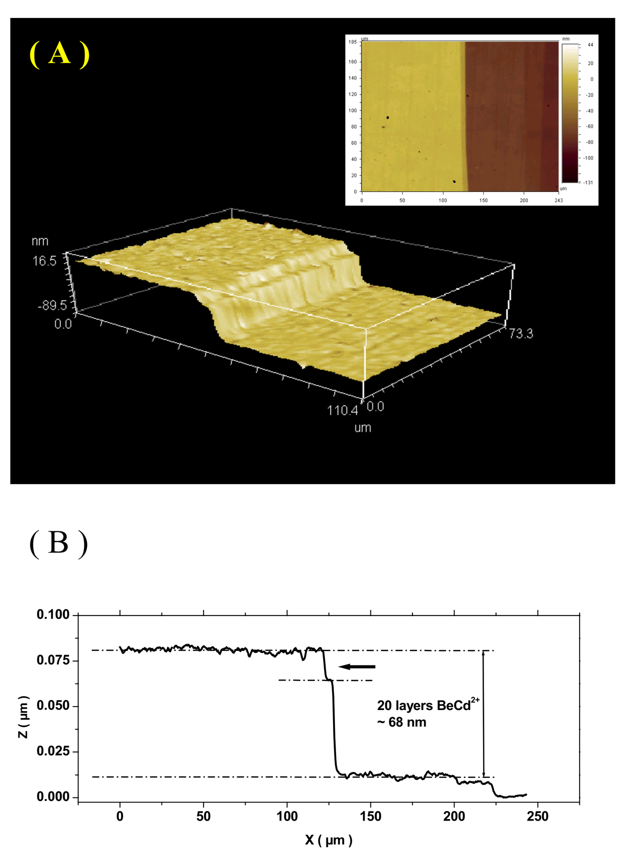

Figure 2: 180-layers samples: (A) Surface topography of a 20-layers step (Magn. 25.4 ×) (B) Thickness profile. Arrow: error in the positioning of the dipper ($\simeq$ 6 μm)

- Excellent agreement between experimental data and optical modeling (Fig. 3 A & B)

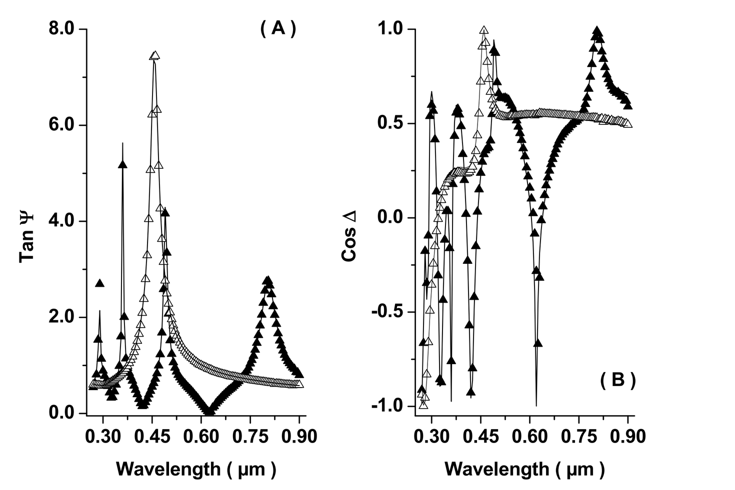

Figure 3: UV-visible ellipsometry of multilayers organic films (speltral range: 270–900nm, AOI: 75 deg.). Symbols: 32 layers film (closed triangles) and 180 layers film (open triangles). Lines: Best-fit results using the uniaxial-Z model without in-plane anisotropy. (A) $\tan\Psi$ spectrum (B) $\cos\Delta$ spectrum

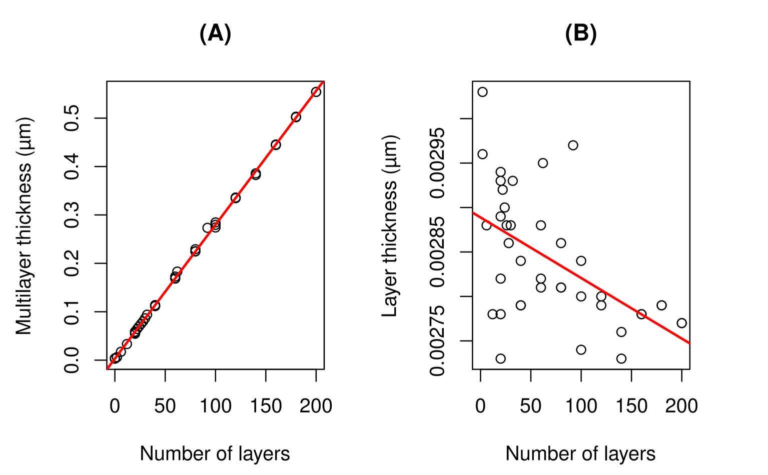

Figure 4: (A) Multilayer variation with the number of layers (B) Evolution of the mean layer thickness: progressive compaction of the layers

- Linear evolution of the global thickness of the coating with the number of layers (Fig. 4 A & B).
- Linear model analysis: 2.766 ± 0.009 nm per molecular layer – Intercept (OTS layer) : 3.0 ± 0.8 nm (Signif. level: 0.999)(Fig. 4A)

- Statistically significant progressive compaction of the layers (Signif. level: 0.999) : decrease of 0.68 ± 0.16 nm per layer (Fig. 4B)
- Very small dispersion of the ordinary and extraordinary refractive index ($B \leq 0.05$)
- Positive birefingence $\Delta n = n_e - n_o$
- No influence of the number of layers for multilayer thickness larger than 100 nm

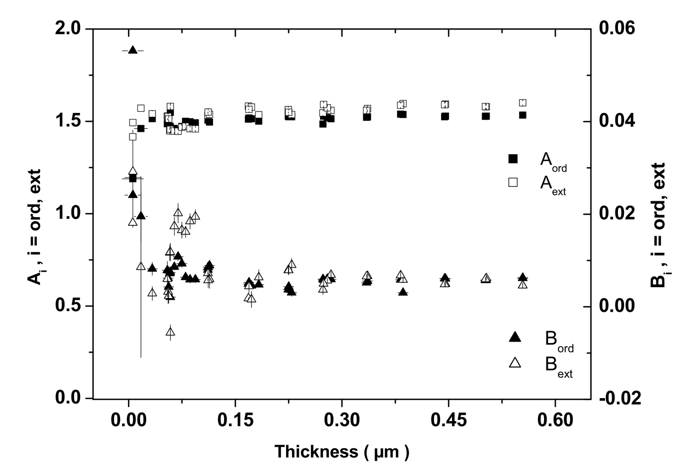

Figure 5: Cauchy parameters A and B of the ordinary and extraordinary refractive index n_o and n_e.

Complex Principal Component Analysis (CPCA)

- Generalization of principal components analysis (PCA) to complex variables (Horel, 1984)
- Multivariate analysis technique used in chemometrics (impedance analysis, ...) (Geladi, 2007) and ellipsometry for gold colloids adsorption (Brouwer, 2004)
- Data transformed to account for both Ψ and Δ values: data matrix is $(N \times 2M)$ with N the number of samples and M the number of wavelengths.

- 50.7% of the variance explained with **2 components** only (Fig. 6).
- Strong linear correlation between the number of layers and the first and second principal components (PCA_1 and PCA_2) ($R^2 = 0.9837$ and $R^2 = 0.9595$)
- Linear regime for $N_{layers} < 40$

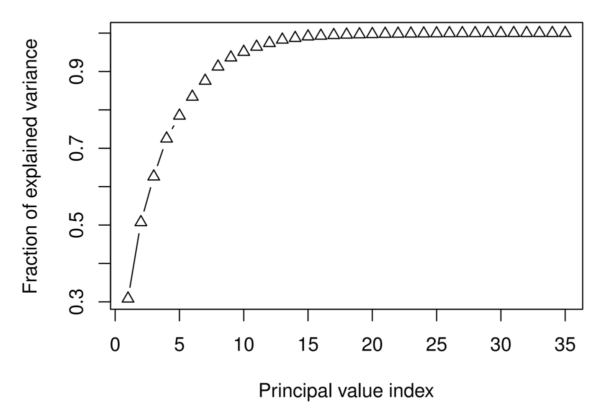

Figure 6: Normalized cumulative sum of the eigenvalue of the PCA analysis: percentage of explained variance

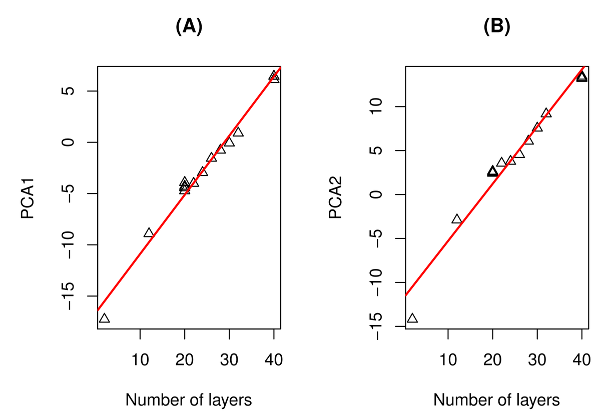

Figure 7: Linear correlation between the number of layers and the principal components. (A) PCA_1 (B) PCA_2

Conclusions

- **Standard SE appropriate to monitor the optical properties of uniaxial-Z materials and in particular of organic multilayers**
- **Multilayers of Cd^{2+}-behenate exhibit a positive birefingence Δn and a small compaction of the layer thickness**
- **CPCA shows linearity between PCA_1 and PCA_2 for $N_{layers} < 40$**
- **More complex behavior for thin multilayers: to be studied in a forthcoming study**

References

1. Horel, J.D. (1984) J. Climate Appl. Meteorology, **23**, 1660.
2. Brouwer, E.A.M. *et al* (2004) J. Phys. Chem. B, **108**, 7748
3. Geladi, P., Nelson, A. & Lindholm-Sethson, B. (2007) Anal. Chim. Acta, **595**, 152.