



SARFUS: Study of layer-by-layer polyelectrolyte deposition

Collaboration: M.Leroy, C. Poleunis, P. Bertrand, A. Delcorte (PCPM-UCL, Louvain-la-Neuve, BELGIUM),

Introduction

In recent years, intensive studies have been carried out on the preparation of multilayer systems by the so-called layer-by-layer method (LbL)¹. This technique based on the successive deposition of very thin layers makes it possible to produce materials with complex properties. In typical processes, two water-soluble polyelectrolytes possessing groups with opposite charges are alternatively deposited by electrostatic attraction on flat surfaces such as glass and silicon substrates. High-quality multilayer films with controlled thicknesses can be obtained by repeating successive cycles of adsorption. This method has been successfully used to produce multilayer films of water soluble polyelectrolytes with various polymeric architecture and functional groups, using suitable commercial polyelectrolytes².

Several surface analysis techniques such as ellipsometry, X-Ray reflectivity, AFM have already been used to characterize such structures. But rapid visualisation techniques are still lacking in order to check quality and homogeneity of the successive layers.

In the present study, we show that SARFUS is a well-adapted and rapid technique to analyse the structure of each layer and in the same time to measure their thicknesses. Compared to AFM, Sarfus allows fast (less than 0.1s s per image) and direct surface analysis (ability to follow polyelectrolyte deposition through microfluidic device, for example). Thanks to large focus (analysis area from few μm^2 to several mm^2), the analysis of the entire surface is rapid and allows validating the quality of the deposited layers. In addition, Sarfus is a non-contact technique and does not alter the outmost surface.

The technique is based on the use of new nonreflecting surfaces for cross-polarized reflected light microscopy. These surfaces (called Surf) generate a contrast enhancement of about twice the magnitude, extending the application fields of optical microscopy toward the nanoworld.

A 3D reconstitution software (Sarfusoft) and certified calibration standard enable the access to the topography of the samples. The technique can also be designed for integration in existing equipment (AFM, RAMAN...) for nano-structures pre-localization.

The present work is focused on the study of the first layers of a multilayer polyelectrolyte (PEI/PSS/PAH/PSS/PAH).

Experimental part

Materials

Standard Surfs (top layer: SiO_2) were pre-treated with piranha solution (50% H_2SO_4 / 50% H_2O_2 ; 20min.) then rinsed with milliQ water (18,2m Ω /cm) and dried under N_2 .

Polyethyleneimine (PEI, Mw= 750,000, Sigma), poly(sodium 4-styrenesulfonate (PSS, Mw=200,000, Aldrich) and poly(allylamine hydrochloride (PAH, Mw=70,000, Sigma) are used as received.

LbL protocol (Figure 1)

Polyelectrolyte films were built by dipping the Surfs in polycation (PAH) and polyanion (PSS) solutions, respectively. As PAH and PSS did not stick well on the surface, a primer layer of PEI was firstly deposited on the substrate by dipping in aqueous solution (5mg/ml). After rinsing with water, successive dipping in aqueous PSS (5mg/ml) and PAH (5mg/ml) solutions were performed. After each poly-ion adsorption, the Surf was rinsed three times in milliQ water.

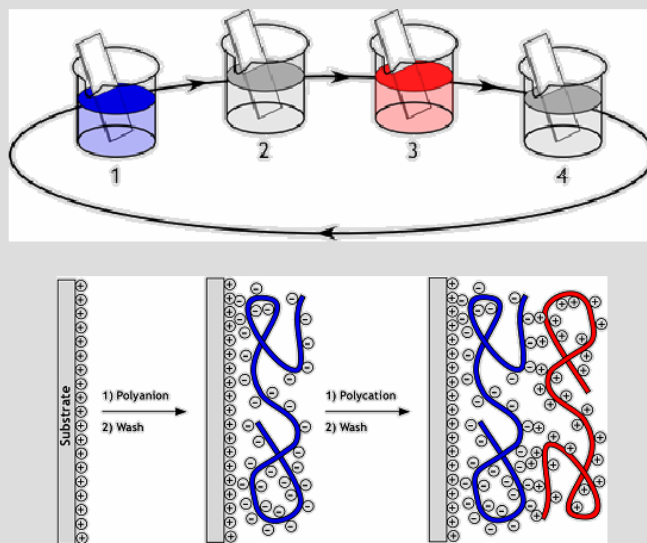


Figure 1: LbL protocol: dipping in 1. polyanion solution, 2. rinsing solution, 3. polycation solution, 4. rinsing solution.

Deposition speed is dependent on physical parameters (pH, ionic force, temperature...) but also on the chemical nature of the components. In our conditions, the adsorption should be complete and homogeneous after a few minutes. The dipping time was fixed to 10 minutes to ensure complete layer deposition.

Sarfus analysis

Optical images were obtained on a LEICA DM4000 optical microscope and collected via a SONY 3CCD camera. The 2D images were treated with Sarfusoft (Nanolane software) and after calibration, 3D images were generated.

It should be noted that the Sarfus analysis of the polyelectrolyte films lasted less than one hour.

AFM analysis

AFM measurements were performed in contact mode on a Nanoscope III (Digital Instruments). Si_3N_4 cantilevers (ThermoMicroscopes, Sunnyvale, CA, US) displayed a curve of 20nm, a length of 320 μm and a width of 22 μm .

1. G.Decher, Science, 227, 27, 1232 (1997)
2. K.Hyde, M.Rusa, J.Winestroza, Nanotechnology, 16, 3422 (2006)

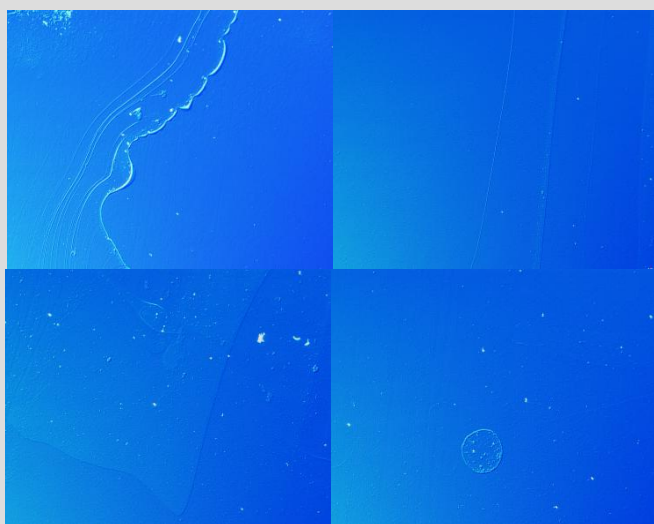


Results and discussion

Quality control of the layers

In this study, two techniques were employed to characterize the topography of the layers: AFM and Sarfus. Because of high signal-to-noise ratio, AFM measurements were only performed on polyelectrolyte films with more than 5 layers (i.e. film thickness higher than 6 nm). For thinner layers, Sarfus was used.

A PEI primer layer was deposited on the pre-treated Standard Surf. This layer appears as a smooth surface with isolated defects. The thickness (with $n=1.6$) of the PEI layer, measured by Sarfus, is about $4.0\text{nm} \pm 1.0$. As shown in figure 2, some topographic features are visible. Their thickness ranges vary from 0.5 to 1nm. Their origin is probably related to local inhomogeneities of the surface hampering, the layer transfer and/or polymer reorganisation in order to minimize surface energy.



Figures 2: Sarfus images of defects on the PEI layer (image scale : $380 \times 300\mu\text{m}^2$).



Figure 3: Microstructuration on a PEI/PSS layer (image scale : $380 \times 300\mu\text{m}^2$).

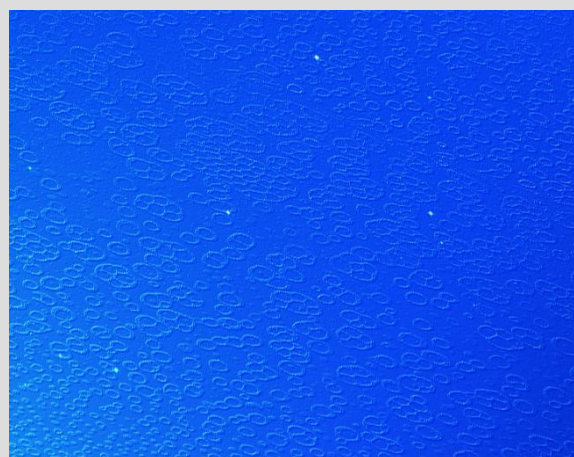


Figure 4: Microstructuration on a PEI/(PSS/PAH)₂ layer (image scale : $380 \times 300\mu\text{m}^2$).

A second negatively charged PSS layer (poly(sodium 4-styrenesulfonate)) is then deposited. Thickness measurement provides a value of $4,9\text{nm} \pm 0,3$. As seen in figure 3, layer microstructuration is observed on a large area of the surface (covering 20 to 50% of the surface). Similar patterns were already observed by Decher et al.³ who described them as small globules (round structures with a diameter ranging from a few to several tens of μm). These microstructures were observed on the whole of polyelectrolyte surfaces studied by Sarfus (from PEI/PSS to PEI/(PSS/PAH)₂, figure 4). Curiously, although several AFM analyses were carried out, none revealed the presence of these microstructures (figure 5). It is possible that during each AFM analysis, the studied zones were apart from these patterned areas.

The origin of this microstructuration is not discussed here but it should be taken into account, for instance, for biological adhesion and proliferation studies, since these behaviours are strongly dependent on the film nature and topography.

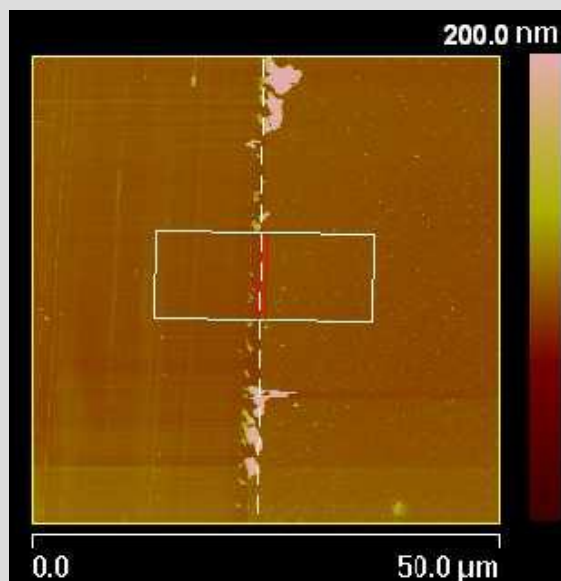


Figure 5: AFM image of PEI/(PSS/PAH)₂ layer. Scratch on left side, polyelectrolyte layer on right side.

3. P.Lavalle; C.Gergely; F.J.G.Cuisinier; G.Decher; P.Schaaf; J.C.Voegel; C. Picart; *Macromolecules*, 35(11), 4458 (2002).



The third deposited layer PAH (poly-allylamine hydrochloride) is positively charged. Due to electrostatic attraction, PAH chains associate with poly-anion chains. In the absence of salts, electrostatic repulsions are expected to prevent multilayer adsorption and limit the deposit only to one single layer. The measured film thickness is about 5.3 nm (figure 6).

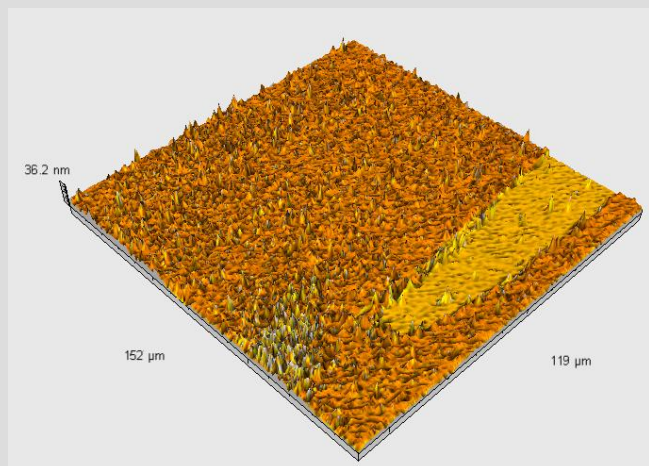


Figure 6: 3D Sarfus image of PEI/PSS/PAH layer.

Thickness measurements of the polyelectrolyte layers

The table underneath summarizes the thickness evolution of the multilayers. The results of AFM analyses performed on the polyelectrolyte films are also indicated. For films thinner than 7 nm, AFM measurements were difficult to interpret due to poor signal-to-noise ratio and baseline deviation. Only one AFM measurement (PEI layer) was validated but for both analyses, the scratch on the PEI layer was not very sharp leading to high uncertainties regarding the corresponding thickness.

Thicker layers were easier to scratch but the presence of microstructures prevented a precise step height measurement.

	Real Thickness (nm)	
	SARFUS*	AFM
1. PEI	4.0±1.0	2.5±1.0
2. PEI/PSS	4.9±0.3	Not valid
3. PEI/PSS/PAH	5.3±0.3	Not valid
4. PEI/PSS/PAH/PSS	5.9±0.3	Not valid
5. PEI/(PSS/PAH) ₂	6.2±0.3	6.9±0.5
6. PEI/(PSS/PAH) ₂ /PSS	Not performed	7.6±0.2
7. PEI/(PSS/PAH) ₃	Not performed	8.1±0.5

*assuming that the optical index of the layers is equal to 1.6

Table 1: polyelectrolyte layer thickness by AFM and Sarfus

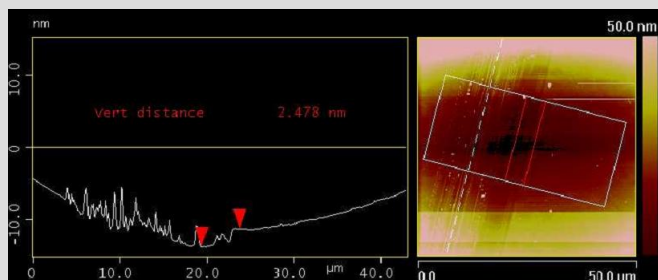


Figure 7: AFM scan on PEI layer.

For the films measured using both techniques (PEI and PEI/(PSS/PAH)₂ layers), a good agreement is obtained. The observed shift might come from the lack of precision of the scratch.

Conclusion

We have demonstrated that Sarfus is a well adapted technique for the measurement and the characterization of nanometric films. Thanks to its rapidity to analyse the whole surface, Sarfus allows an easy detection of defects or specific structures. A quite good correspondence is observed with the AFM measurement, dispersion being probably due to the difficulty of getting a clean scratch of the polyelectrolyte layers.

Contribution/advantages of Sarfus

- Direct and fast analysis of the sample
- Non-invasive/non contact technique
- Ability to analyse soft materials
- Possibility of *in-situ* analysis