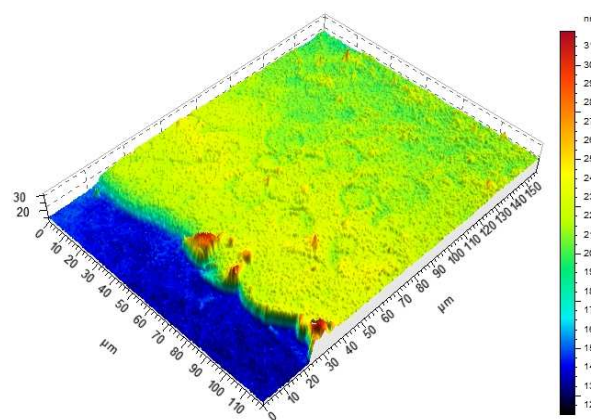
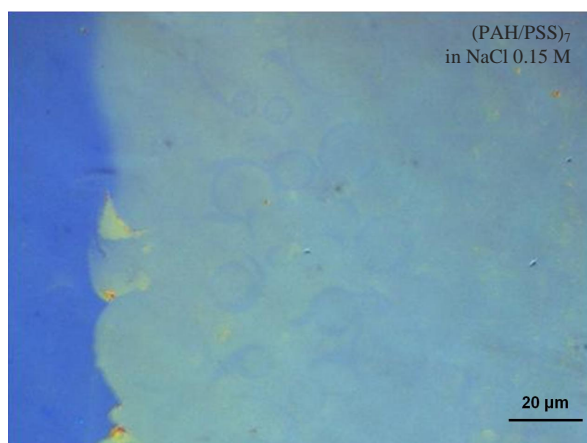


# Visualization and Thickness Measurement of Polyelectrolytes Multilayers in Dry and in Solution

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## Abstract

Different polyelectrolytes multilayers are studied by SARFUS 3D IMM system both in dry and in solution. Thickness measurements of the layers are realized and compared to measurements done with ellipsometry. In this study, we are able to see in real time images of the sample that give us information on the layer homogeneity and structure. SARFUS measurements show as ellipsometry measurements, the layers construction and growth. Moreover, we highlight the swelling behavior of layers by doing measurements in dry and in solution of salt.



## Introduction

Polyelectrolytes multilayers (PEM) are thin films obtained by (LBL) nanofabrication method. This technique based on the successive deposition of very thin layers allows producing nanofilm with complex properties. Two water-soluble polyelectrolytes possessing groups with opposite charges are alternatively deposited by electrostatic attraction on flat surfaces such as glass and silicon substrates. The multilayer buildup process depends on various parameters such as temperature, pH, salt concentration and polyelectrolytes nature and concentration. Applications of polyelectrolytes are wide in biomedical or in sensor domains.

Our aim here is to demonstrate that SARFUS allows studying the multilayer construction both in dry and in solution. We will compare measurements done in dry and in salt solution in order to highlight the swelling behavior of layers.

## Experimental part

### Materials

Sodium chloride (NaCl), poly(allylamine hydrochloride) (PAH, ~ 56,000 g/mol), poly(styrene sodium-sulfonate) (PSS, ~ 70,000 g/mol) were purchased from Sigma-Aldrich. Ultrapure water was obtained by further treatment of water already

purified with a reverse osmosis system with a three-stage Milli-Q system from Millipore. This type 1 (or Milli-Q®) water had a resistivity of 18.2 MΩ/cm or better and a total organic content of 10 ppb or less and was used directly after preparation.

### Instrumentations

#### SARFUS

Visualizations were done with Standard Surfs (top layer: SiO<sub>2</sub>) in dry and Immersion Surfs in solution. Thickness measurements were performed with SARFUS 3D IMM which includes the dry and the immersion version on the same instrument. The refractive index of the sample must be known to estimate the thickness. We used a refractive index of  $n=1.465$  as used for ellipsometry measurements. Ten different thickness measurements were randomly taken on different layer areas.

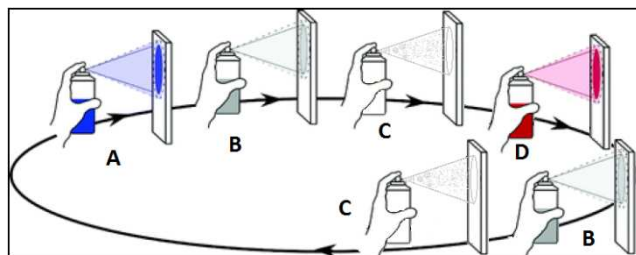
#### Ellipsometry

Measurements of the film thickness were carried out with a PLASMOS SD 2300 ellipsometer operating at the single wavelength of 632.8 nm and a constant angle of 70°. The refractive index of the films was assumed to be constant at  $n = 1.465$ . For each substrate studied, ten different thickness measurements were randomly taken on different film regions over an area of a cm<sup>2</sup> of the film surface.

## Substrate preparation

Surfs were cleaned for 1 h in a mixture of CH<sub>3</sub>OH and HCl (50:50). Subsequent cleaning steps involved immersion in H<sub>2</sub>SO<sub>4</sub> for at least 1h and followed by extensive rinsing in ultrapure water.

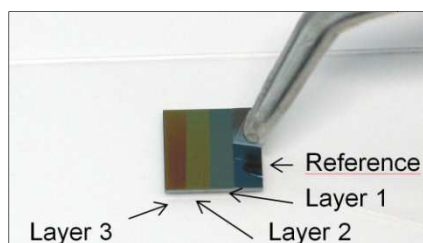
## Sample preparation: Alterneous Spray Coating



**Figure 1: LBL protocol: A. Polycation solution Spraying, B. Rinsing solution, C. Drying step and D. Polyanion solution Spraying.**

Airbrushes model VL from Paasche (USA) were purchased from SEDIP, France. Pressurized gas was supplied by in-house compressed nitrogen lines with overpressure fixed at 2 bars. The solutions were sprayed alterneously on the substrates hold vertically with a vertical or circular movement to improve homogeneity. The liquid flow rates were  $13 \pm 2$  mL/min and  $19 \pm 2$  mL/min for positively and negatively charged components respectively, using a gas pressure of 2 bars. Each spraying steps (Figure 1) lasted 10 seconds and was followed by a 5 seconds rinsing step where Milli-Q Water (pH 5.9) was sprayed with aerosol spray bottles "Air Boy" (ref: 2430), from Roth. The coated substrates were then dried in a stream of compressed at 2 bars.

For simplicity of measurement, each sample is composed of three layers and one area is kept nude as reference (Figure 2).

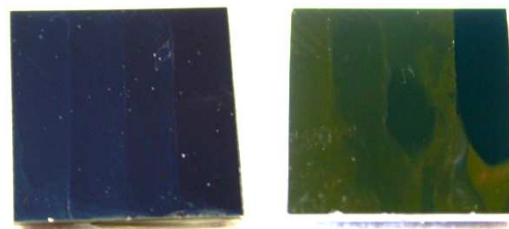


**Figure 2: Surf image with multilayers of polyelectrolytes (35nm/90nm/130nm).**

## Results

### Quality control of layers

Four samples of polyelectrolytes (PAH/PSS) have been done: 2 on Standard Surfs for measurement in dry and 2 on Immersion Surfs for measurement in immersion. Samples have been made under the same experimental conditions. As we can see on two of them Figure 3, the layers of (PAH/PSS) are already visible to the naked eye from the first nanometers of thickness (2-6 nm).

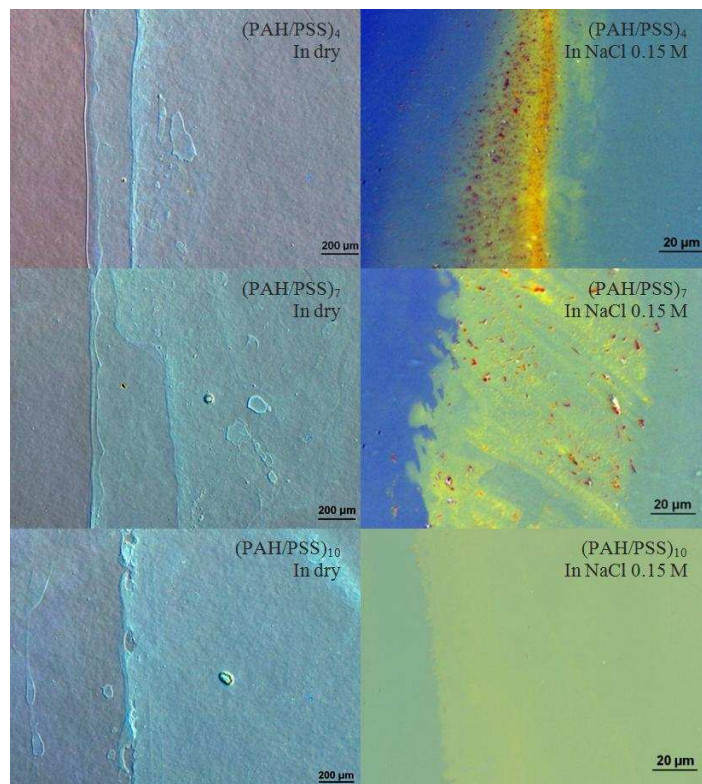


**Figure 3: (PAH/PSS) layers (4, 7 and 10 layer pairs), Left: Standard Surf #1, Right: Immersion Surfs #1.**

The use of Surfs was very useful to immediately check if the spraying has been made in good conditions and to monitor the surface's homogeneity at macroscopic scale during the buildup of the layers. The different layers correspond to different number of layer pairs deposited. Here are deposited 4, 7 and 10 layer pairs of (PAH/PSS). We can observe large defects on the center and on the bottom of the Immersion Surf. The other Immersion Surf #2 showing no defects on it is used for thickness measurements.

### Layers localization

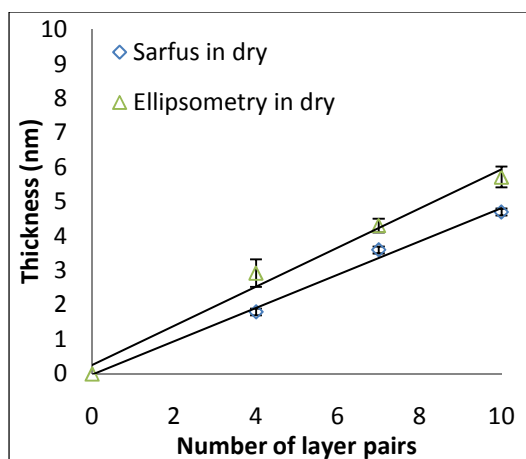
Layers are then observed by SARFUS 3D IMM in dry for the Standard Surf #1 and in a NaCl 0.15 M solution for the Immersion Surf #2. Figure 4 shows real-time images of layers obtained. We can easily localize the different borders between (PAH/PSS) layers and examine quickly layers homogeneity on the surface. We can notice that borders are the main areas of heterogeneity and then as soon as we move away of them defects are nearly non-existent. These defects are not due to the spraying method but just to the vicinity of the adhesive film that allows us to build up several different layers on the same substrate.



**Figure 4: Borders between (PAH/PSS)<sub>n</sub> layers**  
**Left: Standard Surf #1, Right: Immersion Surf #2.**

### Thickness Measurements

After finding homogeneous areas we performed thickness measurements in dry conditions and obtained values graphically represented in Figure 5.



**Figure 5: Evolution of (PAH/PSS)<sub>n</sub> thickness with the number n of layer pairs in dry.**

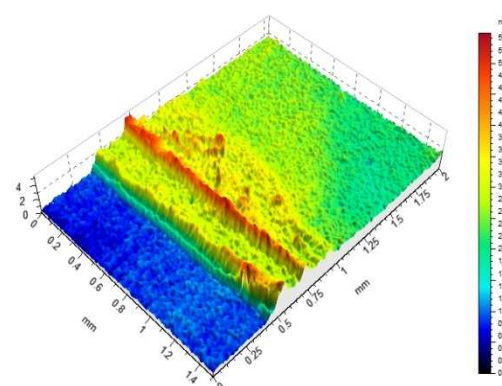
(PAH/PSS) layers are a reference for polyelectrolytes multilayers and are well known to have a linear growth. Measurements done in this study show this behavior with a continuous increase of the film thickness with the number of layer pairs. Moreover, the thickness

measurements by SARFUS are in agreement with values obtained by ellipsometry with a difference about 1 nanometer between values (Table 1).

Number of layer pairs	Ellipsometry Measurements (nm)	Sarfus Measurements (nm)
4	2.9±0.4	1.8±0.1
7	4.3±0.2	3.6±0.1
10	5.7±0.3	4.7±0.1

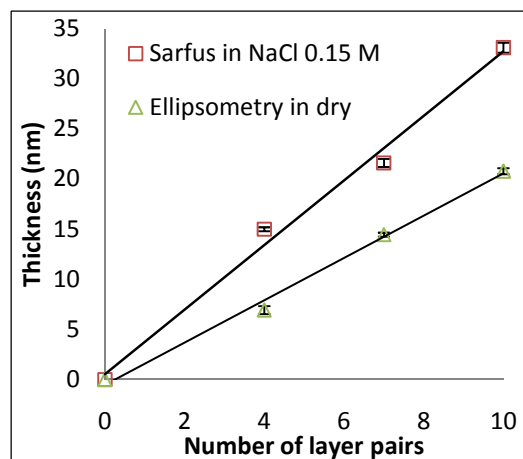
**Table 1: Film thickness data in dry.**

With the SARFUS software, each 2D image could be represented in 3D as shown in Figure 6 and provides us with more information thanks to a topographic view of the sample.



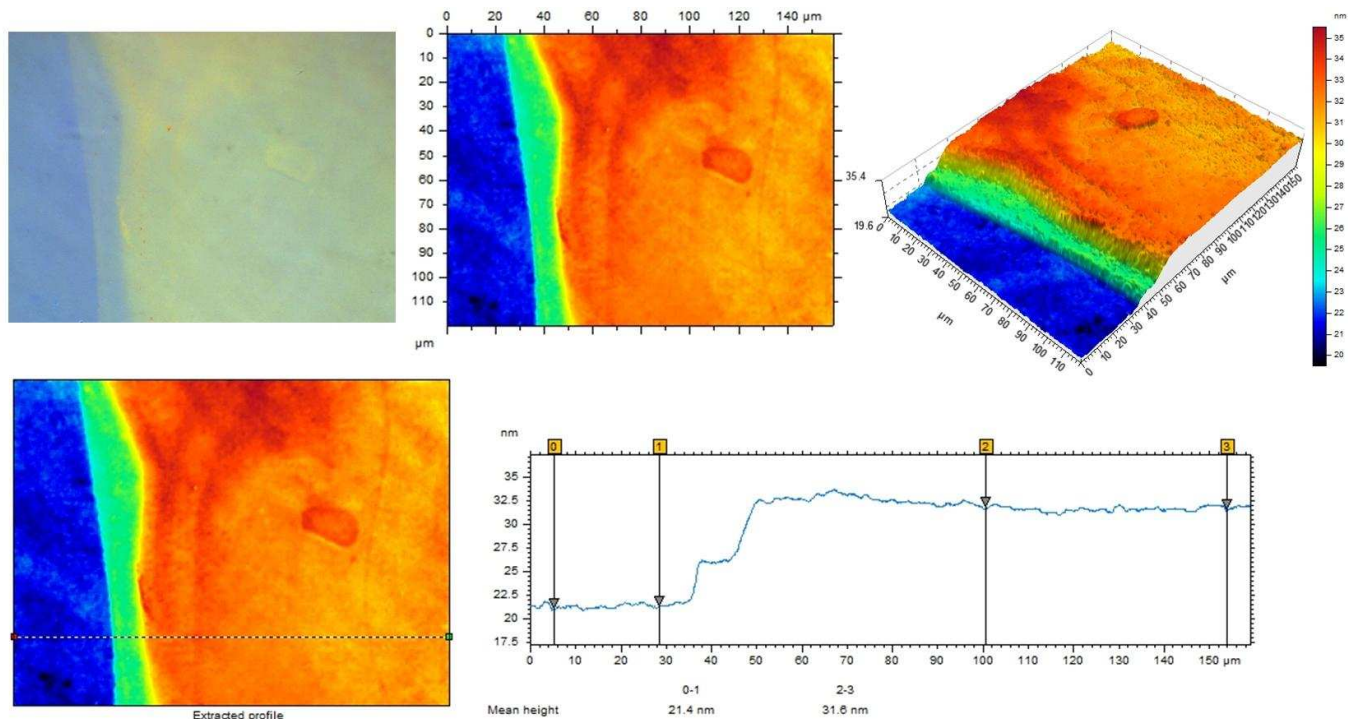
**Figure 6: 3D image of (PAH/PSS)<sub>4</sub> in dry.**

The same measurements done in a salt solution of NaCl 0.15 M were performed on layers of the Immersion Surf #2. We obtained results graphically represented in Figure 7.



**Figure 7: Evolution of (PAH/PSS)<sub>n</sub> thickness with the number n of layer in salt solution.**

Experimental conditions of layer deposition between Standard Surf and Immersion Surf have varied slightly with the time. Consequently, measurements done in the dry state by SARFUS



**Figure 8: (PAH/PSS)<sub>7</sub> and (PAH/PSS)<sub>10</sub> image without treatment, topographic image, 3D image, profile extraction and thickness measurement.**

couldn't be taken into account as reference for the dry values of layers on Immersion Surf. Nevertheless, as demonstrated before, Sarfus and ellipsometry data are very close. As a consequence, we take complementary ellipsometry measurements in dry state as reference in Figure 8 and Table 2.

Number of layer pairs	Ellipsometry Measurements (nm) in dry	Sarfus Measurements (nm) in NaCl 0.15 M
4	6.9±0.05	15±0.2
7	14.4±0.6	21.6±0.4
10	20.8±0.8	33.1±0.5

**Table 2: Film thickness data in solution.**

Thicknesses obtained in immersion are clearly more important than ones made in dry. The ratio between dry and immersion values is about 1.5-2 that confirms the well-known swelling behavior of polyelectrolytes layers.

Figure 8 is an example of layer measurement process with SARFUS 3D IMM. Original image is taken and converted in a topographic image which can be represented in 3D. A profile extraction is done and allows thickness measurement of each layer.

## Conclusion

We have demonstrated that SARFUS 3D IMM can be used to monitor polyelectrolytes construction and growth both in dry and in a salt solution. Here we have only considered the sample in one concentration of salt but we can easily imagine making more experiments to better understand the role of many parameters in polyelectrolytes film buildup. Moreover, we have access in real-time to the image of the sample allowing us checking layer homogeneity more simply and quickly than any other technique is able to do.

We have confirmed that SARFUS thickness measurements are in agreement with others techniques of characterization such as ellipsometry or AFM.

That's why, SARFUS 3D IMM appears as a powerful and must tool in polyelectrolytes domain.

## Advantages of SARFUS

- Work in immersion at ambient conditions
- Fast technique to monitor layer quality
- Large field of view (from 70x70µm to several mm<sup>2</sup>)
- Non-invasive/non contact technique
- No labeling/pretreatment of the sample
- Ability to real-time study
- 3D representation of the sample