Step-by-step assembly of self-patterning polyelectrolyte films violating (almost) all rules of layer-by-layer deposition.

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Supporting Information

Experimental details

PSP (M_w = 2930 g/mol, Product No: 04267; CAS: 68915-31-1) (structure done in Scheme 1) and PAH (M_w =56 000 g/mol, CAS: 71550-12-4; cat. no: 28,322-3) were purchased from Sigma-Aldrich. PEI (Lupasol WF, M_w = 2.5 x 10^4 g/mol) was obtained from BASF

(Germany). All the polyelectrolytes were used without further purification. The aqueous solutions were prepared with ultrapure water (resistivity=18.2 MΩ cm, Milli Q-Gradient system).

Characterization of the used polyelectrolytes

Molecular weights of PSP and PAH were checked by end group titration and viscosimetry [1,2].

Molecular weight determination of PSP by end group titration: A Jenway 3040 *pH* meter was used for these end group titration experiments. 0.5 g of PSP was dissolved in 100 mL of water and the *pH* was lowered to about 3 using HCI (1 M), and then, titrated potentiometrically with 0.05 M standard NaOH solution until the *pH* value of 4.5. The volume of added base solution, *A* (mL), consumed until the first end point was determined. The total phosphorus content of the polyphosphate was determined in another sample containing the same amount of PSP after a complete hydrolysis procedure as described in reference [3]. The complete reversion of the polyphosphate to the orthophosphate form was achieved by gently boiling the sample in a HNO_3 (1 M) solution for three hours under reflux. Then, *pH* was lowered to about 3 and the solution was titrated potentiometrically with 0.05M standard NaOH solution until the pH value of 4.5. The titration was continued beyond the second end point at about *pH* 9, and the volume of base, A_h (mL), consumed between two end points was determined.

The fraction of end group was calculated according to :

$$\%P_2O_5(endgoup) = \frac{A}{A_h}100$$

$$\frac{P_2O_5(total)}{P_2O_5(endgroup)} = \frac{n}{2} = \frac{A_h}{A}$$

It came out that the number average degree of polymerization of PSP was of 24 as indicated in Table 1.

Table. 1 : The results of end group titration

Titration Procedure	Added NaOH (V mL)	$\%P_2O_5$
Before Hydrolysis (end group)	5.5	8.33
After Hydrolysis (total)	66.0	99.96
n (degree of polymerization) ≈ 24 Molecular Weighed ≈ 2450 g/mol		

Molecular weight determination of PSP and PAH by viscosimetry: Viscosity measurements of PSP solutions were carried out with an Ostwald type viscosimeter in 0.035 M NaBr solution at 298.5K, and that of PAH were determined in 0.5M NaCl at 298K. The viscosity averaged molecular weights $\overline{M}_V$ of PSP and PAH were found equal to 2930 g/mol and 52000 g/mol by using the Mark-Houwink equation.

Alternated deposition of PSP/PAH and characterization of the deposits.

PSP/PAH deposition at the solid-air interface was carried out by the LBL spray-deposition and the properties of the deposits or of the obtained films were examined by ellipsometry, AFM and by zeta potential measurements.

The used substrates were either silicon wafers for the subsequent characterization by means of ellipsometry and/or AFM and glass slides for the zeta potential measurements. The silicon wafers were purchased from WaferNet, Inc. (San Jose, CA). They were cut in the form of rectangles (4 x 1 cm^2), degreased with acetone and allowed to stand in MeOH:HCl (1:1) solution for 20-30min. This treatment was followed by extensive rinsing with Milli-Q water and blowing-dry with nitrogen. Finally, the wafers were immersed into concentrated H_2SO_4 for at least 4 hours, rinsed extensively with Milli-Q water and blown-dry again with nitrogen. The glass slides, never used before LBL spray coating, were cleaned in a 2 % (v/v) Hellmanex (Hellma GmbH, Germany) solution at 70 °C during half an hour, extensively rinsed with Milli Q water, immersed in a hot (70°C) 0.1 M hydrochloric acid solution, rinsed again with Milli-Q water and blown dry with nitrogen.

The PSP and PAH were solubilized at 10^{-x} monomol/L (with respect to the monomer repeating unit and with x= 5, 4, 3, 2) in a solution having an ionic strength of I=0.15M in NaCl. The *pH* of each solution was adjusted to 6.70 with addition of appropriate amount of 0.1M NaOH. Hence the solutions contained exclusively sodium and chloride ions originating either from the added NaCl or from the polyelectrolyte's counterions.

The chosen pH value of 6.70 was selected on purpose because it corresponds to the average pK_a value of PSP and PAH of which were calculated by equation [1]. This was made in order to keep the degree of dissociation for both polyelectrolytes as identical.

$$K_a \left(\frac{\Lambda^2_o}{\Lambda_c}\right) - K_a \Lambda_0 = \Lambda_c C \qquad [1]$$

where, Λ_c and Λ_o corresponds to equivalent conductivity at a definite concentration and at infinite dilution respectively.

In order to determine the pK_a values of PSP and PAH, they were converted into their acidic ($(HPO_3)_n$) and basic forms (PAHOH) using Amberlite IR-120 (strong acid cation exchanger) and Ion Exchanger III (strong base anion exchanger) respectively. The ion exchange columns were prepared as described in the literature[4]. Then, series of solutions for ($(HPO_3)_n$) and (PAHOH) were prepared at different concentrations and their average K_a values were determined by conductometry. K_a value for acidic form of PSP ($(HPO_3)_n$) and K_b value for basic form of PAH (PAHOH) were found as 6.63×10^{-3} and 1.64×10^{-3} respectively, corresponding to respective average *pKa* values of 2.46 and 9.41.

Alternated deposition of PSP and PAH on substrates was performed by alternatively spraying the polyelectrolyte solutions (at 10^{-x} M in the presence of 0.15 M NaCl and at *pH* 6.7) using "AIR –BOY" (Roth Sochiel E.U.R.L) spray bottles. The solutions were sprayed onto vertically hold silicon substrates from a distance about 15 cm. All $(PSP/PAH)_n$ multilayers were deposited on a single PEI anchoring layer. PEI was dissolved at 2.5 mg/mL in MilliQ water and sprayed on the cleaned silicon wafer for 10s. This step was followed by spray-rinsing 10 sec. with Milli-Q water, and blow-drying with nitrogen. When not specified, the same spraying time of 10 s was always used for each subsequent spraying step, either PSP, PAH or Milli-Q water. The spraying sequence was hence PEI-$(PSP/PAH)_n$.

The average thickness of the PEI-$(PSP/PAH)_n$ deposits was measured at ambient temperature and moisture by means of ellipsometry as a function of the spraying step number. For convenience let us call the number of spraying steps (which would correspond to the number of layers in an ideal LBL architecture), m with $m = 2n+1$. Hence an even value of m corresponds to a deposit in which the last deposited polyelectrolyte is PSP whereas an odd

value of *m* corresponds to a deposit in which the last deposited polyelectrolyte is PAH. The optical measurements were performed by using a PLASMOD SD2300 ellipsometer with He-Ne laser (632.8 nm) illumination at an incidence angle of 45°. The refractive index for the polyelectrolyte multilayers was assumed to be 1.465. Although this procedure could lead to slightly incorrect values with respect to the absolute film thicknesses, it allows for the quick monitoring of the deposition process. For each studied polyelectrolyte deposit, 10 different measurements acquired at regularly spaced locations along the main axis of the wafer were performed to obtain an average thickness as well as to determine the homogeneity of the deposit.

AFM images were obtained on the same deposits as those used for ellipsometry measurements in tapping mode and at room temperature, in air, using a Nanoscope IIIa Multimode AFM (Digital Instrument Inc., Santa Barbara, CA). Tips with a terminal radius of curvature less than 10 nm and silicon cantilevers with a nominal spring constants of 40 N/m (resonance frequency of 300 kHz) were used. Several scans were performed over a given area in order to produce reproducible images to ascertain that there was no sample damage induced by the tip. Height and phase images were scanned simultaneously at a fixed scan rate between 0.5–1 Hz with a resolution of 512x512 pixels^2. The scan sizes varied from 1 x 1μm^2 to 5 x 5 μm^2. The root-mean-squared roughness (RMS) values of roughness were calculated from images corresponding to a fixed area of 5 x 5 μm^2. Images were acquired, stored, and visualized using the Nanoscope software. Grain size analyses of the AFM topographies were carried out using the "ImageJ" software. More than 100 grains were measured for each sample.

Zeta potential measurement of PEI-(PSP-PAH)$_n$ deposits on the surface of glass substrates.

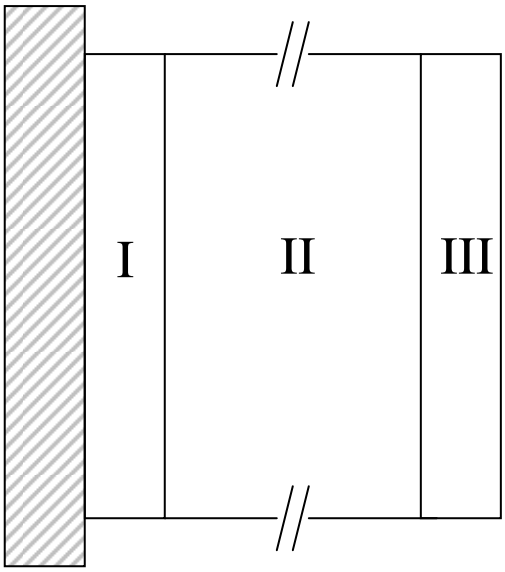
PEI-(PSP-PAH)$_n$ or PEI-(PSP-PAH)$_n$-PSP deposits were sprayed simultaneously on 2 vertically hold glass surfaces in the same manner as for the silicon wafers. The streaming potentials of each particular deposit on glass slides were measured with a ZetaCAD device (CAD Instrumentation, Les Essarts le Roi, and France). The two covered glass slides are mounted parallel to each other in the plexiglass sample holder and are separated by a 500 µm thick poly(tetrafluorethylene) (PTFE) spacer. Great care was taken to avoid any contact of the faces on which the PEI-(PSP-PAH)$_n$ deposits were sprayed with any kind of surface. For all measurements, NaCl with a concentration of 5 mM is circulated between the samples. Notice that we reduced the ionic strength during zeta potential measurement with respect to ionic strength used during the spray deposition (0.15 M) in order to reduce the influence of ionic screening. We make the assumption that this reduction in ionic strength does not influence the structure of the deposit, which is reasonable owing to the fact that a reduction in salt concentration tends to freeze in the mobility of polyelectrolyte chains[5]. The streaming potential is measured 5 times on the same substrate, before and after functionalization with sprayed deposits and the obtained values are averaged. These experiments are aimed to define if the LBL deposition follows the regular charge inversion usually observed during the alterated deposition of polycations and polyanions [6]. The ζ-potential is calculated from the streaming potential using the Smoluchowski relationship[7]:

$$\zeta = \frac{\Delta E}{\Delta P}\frac{\eta}{\epsilon} \qquad [2]$$

where ζ, η, λ and $\epsilon\epsilon_0$ are the ζ-potential, the solution viscosity, the solution conductivity

and the dielectric permittivity of water. $\Delta E/\Delta P$ is the streaming potential, namely the slope of the potential difference versus pressure difference curve. The potential difference ΔE is measured between two Ag/AgCl reference electrodes located on both sides of the measurement cell. The pressure difference ΔP between the two electrolyte compartments is varied with compressed air by increments of 5 kPa between –30 kPa and +30 kPa. Since the viscosity and the dielectric permittivity are temperature dependent, the temperature of the solution is regularly measured *in situ* and its value is used to calculate temperature corrected values of the dielectric permittivity and viscosity. The solution conductivity is also measured *in situ*.

Schemes



Scheme 1 : three zone model describing the build-up of regular layer-by-layer films[6a]. Zone I describes the first few "layers" which are under direct influence of the substrate, zone II corresponds to the "bulk of an ideal multilayer film. In the case of linearly growing films, it could correspond to the region where some ordering with interpenetration across few layers can be found in neutron or X-ray scattering experiments. In the case of exponentially growing films zone II will only be reached when the film thickness is above the maximal distance the polyelectrolytes can diffuse during a given deposition time. Zone III corresponds to the interfacial zone between the film and the solution. In the case of linearly growing films, it is only a few layers thick, in the case of exponentially growing films, it could correspond to the diffusion zone. This model means that exponentially growing films have a zone II only when they undergo the exponential to linear transition during their growth, before that transition the film is made only from a zone I and a zone II.

Additional figures :

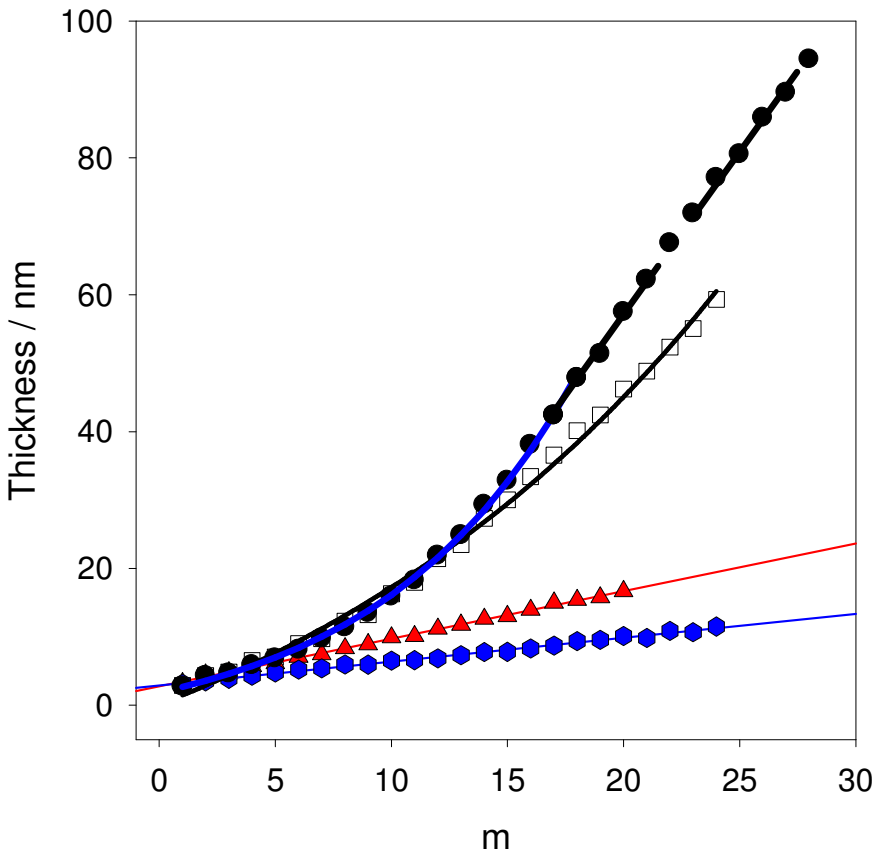


Figure 1-SI: Thickness of PEI-(PSP-PAH)$_n$ deposits obtained by spray deposition (in the presence of 0.15 M NaCl and at *pH* = 6.7) at different concentrations of PSP and PAH (identical for each polyelectrolyte in a given experiment) as a function of $m = 2n + 1$, the number of spraying steps : ⬢ : 10^{-5} M, ▲: 10^{-4} M, □ : 10^{-3} M, ● : 10^{-2} M. The lines correspond to the fit of a linear function to the data obtained at 10^{-5} and 10^{-4} M in polyelectrolyte and to the fit of an exponential function ($d = a + b.exp(-k.m)$) at 10^{-3} in polyelectrolyte. We obtained $k = (0.050 \pm 0.005)$. For the deposition experiment performed at 10^{-2} M in polylectrolyte, the growth curve was fitted with an exponential function (_____) up to $m = 17$ ($k = 0.118 \pm 0.004$) and with a straight line (_ _ _) from $m = 17$ up to $m = 28$ deposition steps.

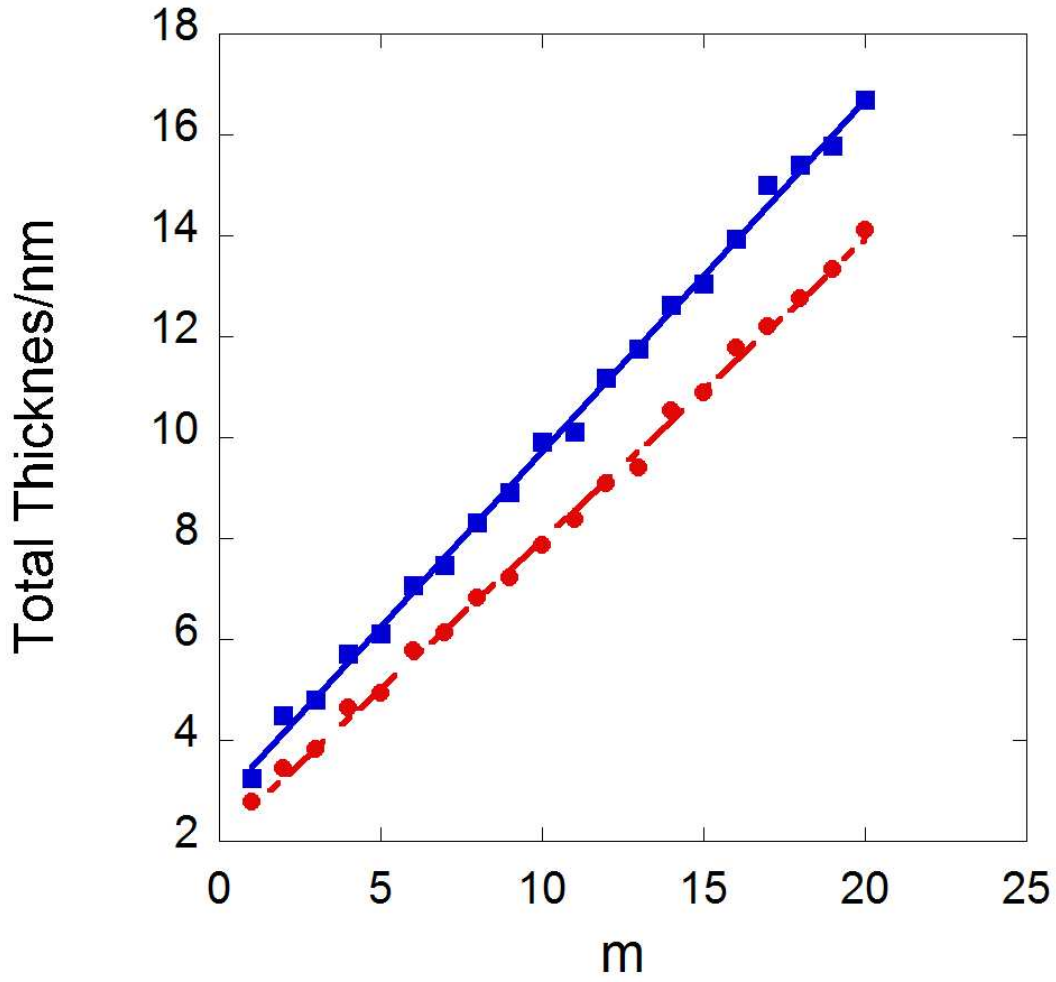


Figure 2-SI: Thickness of PEI-(PSP-PAH)$_{20}$ deposits obtained by spray deposition of PSP and PAH (both at 10^{-4} M in the presence of 0.15 M NaCl at *pH* 6.7), as a function of $m = 2n + 1$, (spraying time per deposition step: ● : 5s, ■ :10s. The lines correspond to the fit of a linear function *(y=ax+b)* where *x*=0.59 nm/deposition step, *b*=2.1 nm and *x*=0.70 nm/deposition step, *b*=2.8 nm were obtained for 5s and 10s spraying time respectively.

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