

## Polyelectrolyte multilayer films made from polyallylamine and short polyphosphates: Influence of the surface treatment, ionic strength and nature of the electrolyte solution

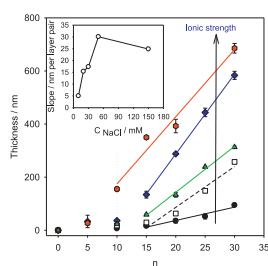
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### HIGHLIGHTS

- ▶ We study the influence of the ionic strength on the deposition of (PAH-PSP)<sub>n</sub> films.
- ▶ We identify two growth regimes as a function of the ionic strength.
- ▶ Ellipsometry is not suited to investigate rough polyelectrolyte multilayers.
- ▶ The composition of the films depends markedly on the supporting electrolyte.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The present article focuses on the influence of the salt concentration as well as on the influence of the nature of the salt on the deposition of (PAH-PSP)<sub>n</sub> films in the case where PSP is made from only 24 monomer units on average. The two main messages of this article are that: (i) for salt concentrations lower than about 0.2 M, the film thickness increases linearly with the number of adsorption cycles after the deposition of a coating with a critical thickness necessary to prime the deposition of the film. In addition, for salt concentrations lower than 0.2 M, there is no effect of the influence of the supporting electrolyte on the film thickness but a marked influence on the film composition as revealed from XPS measurements. (ii) For salt concentrations higher than about 0.2 M, the films are extremely rough, and we demonstrate that the use of a homogeneous and isotropic model is not suited anymore to calculate the film thickness and its refractive index from the measured ellipsometric angles.

Finally we try to rationalize all the data obtained so far on the (PAH-PSP)<sub>n</sub> films on the basis of counterion condensation of Na<sup>+</sup> cations on the PSP chains.

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### 1. Introduction

The functionalization of surfaces with polyelectrolyte multilayer (PEM) films, obtained via the step-by-step adsorption of polycations and polyanions [1] has become a versatile surface functionalization method [2]. This versatility relies on the fact that PEM films can be deposited on planar substrates, on colloidal particles [3] or in the pores of porous materials [4]. The substrates to be

coated with PEM films do not necessarily need to carry charged surface groups because they can be modified either by silanization with silanes carrying charged moieties, self assembled monolayers or activated in a plasma [5] in order to afford the necessary surface charge density. In addition there are different methods to bring the polyelectrolyte solutions in contact with the substrate to be coated: either by alternated dip coating, by alternated spin [6] or spray coating technologies [7]. The same principle of step-by-step adsorption can be applied to species carrying mutually interacting moieties such as polymers carrying hydrogen bond donors and acceptors [8]. This high versatility in the coating technology as well as in the possibility to use polymers and inorganic solids (nanoparticles [9],

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