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Ellipsometry and x-ray reflectometry characterization of self-assembly process of polystyrenesulfonate and polyallylamine

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Abstract: Self-assembly of polyelectrolytes-polystyrenesulfonate (PSS) and polyallylamine (PAH) with added salts of MnCl and NaBr was studied by x-ray reflectometry and ellipsometry technique. The thickness of PSS-PAH bilayer was measured to be 5.1 ± 0.2 nm according to reflectometry and 6.1 ± 0.7 nm according to ellipsometry. The discrepancy in data is attributed to the difference in the interaction of the interfaces with x-rays and visible light. The films are found to be rather homogeneous and the deposition process regular. The refraction indices of the deposited films were found to be $\mathbf{n}_0 = 1.50 \pm 0.05$, $\mathbf{k}_0 = 0.07 \pm 0.05$, $\mathbf{n}_e = 1.53 \pm 0.05$ $\mathbf{k}_e = 0$, optical axis being perpendicular to the surface. The values of refractivity characterize the whole film (up to seven bilayers) and do not vary with increasing thickness.

Key words: Thin films – self-assembly – polyelectrolyte – ellipsometry – optical anisotropy

1. Introduction

Ultra-thin organic films are currently gaining interest in many areas. One of the promising techniques for obtaining such films is self-assembly of polyelectrolytes. It consists in alternating adsorption of anionic and cationic bipolar amphiphiles and/or electrolytes [1, 2]. This approach has the advantage that electrostatic attraction between opposite charges is the driving force for the molecular build-up. In contrast to chemosorption techniques [3] that require a reaction yield of 100% or lateral cross linking in order to maintain a constant surface functional density after each deposition step, no covalent bonds need to be formed. Additionally, an advantage over the classic Langmuir–Blodgett technique [4] is that adsorption processes are independent on surface size and topology. Moreover, self-assembly is applied for the deposition of water soluble substances; this is very important for many biological macromolecules, such as proteins, DNA, etc. [5].

The principle of the multilayer assembly is shown in Fig. 1 and is described as follows. A solid substrate with positively charged surface is immersed in the solution containing the anionic polyelectrolyte, and a layer of polyanion is adsorbed (step A). Since the adsorption is carried out at relatively high concentration of polyelectrolyte, a number of ionic groups remains exposed to the solution, and thus the surface charge is effectively reversed. After rinsing in pure water the substrate is immersed in the solution containing the cationic polyelectrolyte. Again the layer is absorbed, but this time the original surface charge is restored (step B). By repeating steps A and B in a cyclic fashion, alternating multilayer assemblies are obtained.

Recently reported was the construction of alternating multilayer films using polystyrenesulfonate (PSS) and polyallylamine (PAH) [6]. It was established that films composed of at least 60 layers can be grown and the thickness of the bilayer was estimated to be 10.5 Å. It was also shown that the thickness of the bilayer and thus the total thickness of the film can be adjusted precisely in large range by changing the ionic strength of the solutions from which the polyions are absorbed [7].

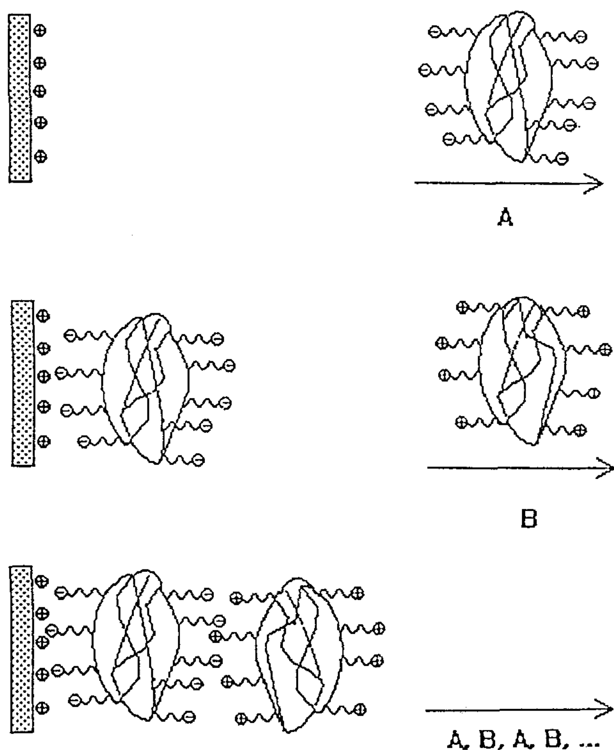

Fig. 1. Scheme of the self-assembly technique. Step A – adsorption of the polyanion, Step B – adsorption of the polycation

It is very interesting to characterize the deposition process and the quality of the film step by step since the procedure of assembling gives such possibility. In the present work we apply optical ellipsometry and x-ray reflectometry for this task. These techniques are known to be powerful tools for studying thin films. From x-ray curves the total thickness of the film is obtained, from ellipsometry data the thickness and refraction index are evaluated. The dependence of the thickness and refraction index of a bilayer on its number gives the possibility of estimating the regularity of the growth and the homogeneity of the entire film.

2. Materials and methods

Polystyrenesulfonate (sodium salt, $M = 100\,000$) (PSS) was obtained from SERVA, polyallylamine (hydrochloride, $M = 50\,000–65000$) (PAH) was obtained from Aldrich. All polyelectrolytes were used without further purification. The ultra pure water used as solvent for the adsorption was obtained by reversed osmosis (Milli-RO 34TS, Millipore) followed by ion-exchange and filtration steps (Milli-Q, Millipore). The resistivity was better than 18 $M\Omega \times cm$.

For the ellipsometric measurements we deposited films onto the silicon substrates, and onto the glass ones for x-ray reflectometry. The substrates were washed in an ultrasonic bath at 60 °C in a solution containing 1% KOH in a mixture of water/ethanol (3 : 1). After cleaning, the substrates were washed in Milli-Q water and immersed in boladication solution for 30 min. After this procedure the substrate is positively charged [1] and used for polyelectrolyte deposition starting with a polyanion.

All electrolytes were absorbed from aqueous solutions containing 0.02 monomol/l polymer (monomol refers to the molar concentration of monomer residues) and 0.01 mol HCl, pH = 2. Salts were added to the solutions of polyions, MnCl for PSS and NaBr for PAH up to 0.5 M and 2 M concentrations, respectively. The adsorption was carried out as follows. The substrates were immersed in 10 ml of polyelectrolyte solution for 20 min at room temperature. After each deposition the samples were rinsed in water and dried in the nitrogen jet.

X-ray reflectometry was performed with AMUR-K small-angle scattering diffractometer in $\theta - 2\theta$ geometry. The copper K_α radiation with wavelength 0.154 nm was used. Data were acquired using a personal computer and a step-width of 0.01 degree (in 2θ) through a counting interval of 5 s. The thickness of the film was evaluated from periods of Kiessig oscillations [8, 9].

Ellipsometric measurements were performed with PCSA (polarizer-compensator-sample-analyser) manual null ellipsometer LEPh-3 (Novosibirsk, Russia) at 633 nm wavelength and angle of incidence of 70°. The measurements were performed after every bilayer deposition. The data were treated according to the two-layer model, in which the lower layer accounts for the imperfections of silicon substrate, and the upper one represents the deposited film. The applicability of such model for the interpretation of the measurements of thin layers deposited onto the silicon substrate was already shown [10]. The optical parameters of the lower layer were determined before deposition according to one-layer model.

3. Results and discussion

X-ray reflectivity curves of the films containing 6–10 bilayers are shown in Fig. 2. The Kiessig oscillations are well pronounced, thus indicating that the films are sufficiently smooth. The thickness of a bilayer can be estimated as 5.1 ± 0.2 nm. This value was obtained from the curves 1, 2 and 3, corresponding to 6, 8 and 10 bilayers, since the peaks for the films with smaller amount of bilayers are not as sharp. As for ellipsometry, the accuracy of thickness determination does not decrease with decreasing thickness so it is possible to monitor the growth from the first bilayer. Corresponding dependence is shown in Fig. 3. The films were supposed to be isotropic and non-absorbent. The refraction index was found to be the same for all the films and equal to 1.50 ± 0.05. (This accuracy is achieved, certainly, for rather thick films having more than four bilayers). The intervals shown do not represent an error in the determination, which is about 1 nm, but rather the difference in thickness of samples. The deposition is rather regular since the least-square line agrees well with the experiment. The thickness of a bilayer is 6.1 ± 0.7 nm. We consider the small deviation of ellipsometric and x-ray reflectometric estimations of the thickness to be due to the roughness and other imperfections of substrate-film and film-air interfaces. In fact, these interfaces are not absolutely sharp, and electromagnetic waves of such different length interact in different manner with them. The surface of polished silicon or glass is too complicated to be accounted for in detail. Besides the roughness, some superficial regions of the material is affected by microcracks, inclusions of the polisher, etc. The silicon surface is covered by silicon oxide as well. Another possible reason for the deviation can be the microstructure of the films. Both ellipsometry and reflectometry treatment were carried out in continuous media approximation, while some salt can be incorporated into the layers, differently affecting the results of the techniques. Anyhow, the deviation is almost within the experimental errors. Obtained figures for the bilayer thickness agree with reported data [7]. A little surprising is the linearity of growth for every deposition starting from the first. Reported earlier x-ray reflectometry data [9] showed that the step of growth achieves its regular, constant value only when the film is thicker than 100 Å, before that the bilayers are thinner. This discrepancy may also arise from the difference between ellipsometry and x-ray reflectometry in the treatment of the interface zone.

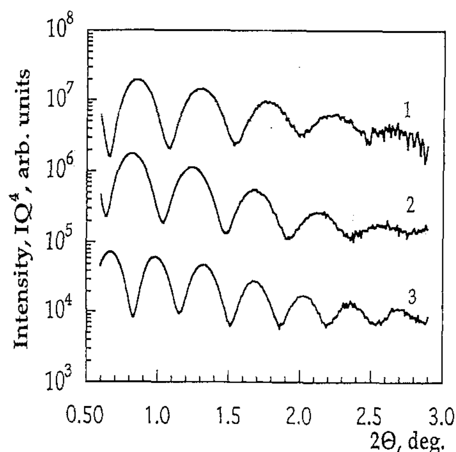

Fig. 2. X-ray reflectivity curves of self-assembled films. Q^{-4} – Fresnel correction, $Q = \frac{4\pi \sin\theta}{\lambda}$, 2θ – scattering angle, λ wavelength, 1 – 6 bilayers, 2 – 8 bilayers, 3 – 10 bilayers

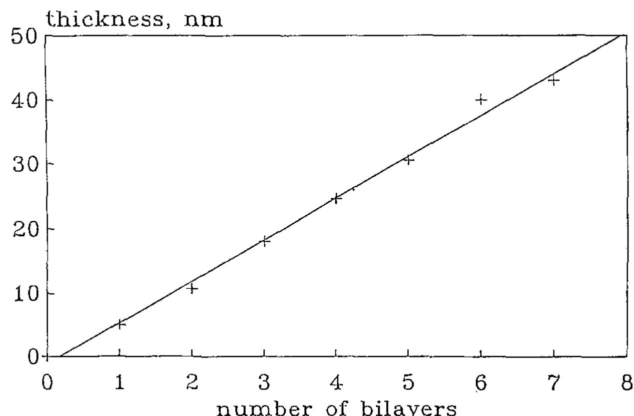

Fig. 3. Dependence of film thickness on the number of bilayers from ellipsometry data. Refraction index of the film was found to be constant for each thickness and equal to 1.50 ± 0.05

The measurement of the films with different thickness allows them to be characterized more completely than just determining the refraction index. As was demonstrated, in this case one can consider the anisotropy and the absorbency of a film [11, 12]. These characteristics can be easily

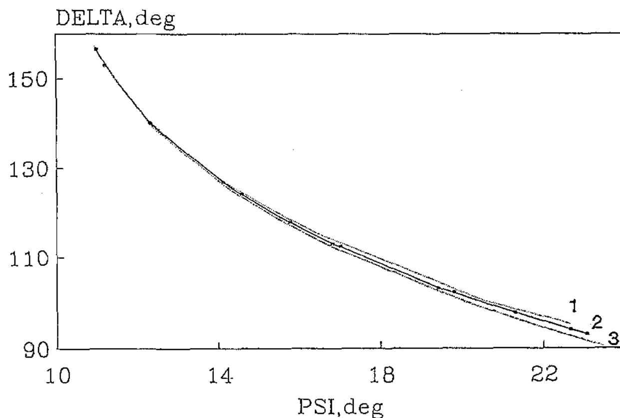

Fig. 4. ψ-δ nomograms for the growing films. Points – experiment, curves-calculation for the parameters of the film: 1 – $\mathbf{n}_0 = 1.453$, $\mathbf{k}_0 = 0.07$, $\mathbf{n}_e = 1.483$; 2 – $\mathbf{n}_0 = 1.503$, $\mathbf{k}_0 = 0.07$, $\mathbf{n}_e = 1.533$, $\mathbf{k}_e = 0.009$; 3 – $\mathbf{n}_0 = 1.553$, $\mathbf{k}_0 = 0.07$, $\mathbf{n}_e = 1.583$

obtained from ψ-δ nomograms. Ellipsometric parameters of the films with different thickness and the same refractivity being plotted one versus another should lie on a curve corresponding to definite optical parameters of the film. This means that both complex ordinary and extraordinary refraction indices of the film can be obtained by fitting the calculated nomogram to the experimental points, i.e., by minimizing the sum:

$$\sum_{i=l}^{l} | R_i^c - R_i^m | ,$$

where $R_i^{c,m}$ is normalized amplitude reflection coefficient:

$$R_i^{c,m} = \left(\frac{r_p}{r_s}\right)_i^{c,m} ,$$

$r_{p,s}$ are amplitude reflection coefficients, p, s indicate the waves parallel and perpendicular to the plane of incidence respectively, c, m stand for calculated and measured values, i indicates different measurements (thicknesses), l is the total number of measurements. R_i^c is a function of five film parameters: ordinary and extraordinary refractivity $\mathbf{n}_0$, $\mathbf{n}_e$, and absorption $\mathbf{k}_0$, $\mathbf{k}_e$, and thickness t_i. For $l > 4$ the problem of finding unknown parameters of the film is over determined. In fact, for $l = 4$ the number of parameters is 8 ($\mathbf{n}_0, \mathbf{k}_0, \mathbf{n}_e, \mathbf{k}_e$, and four thicknesses) and the same is the number of equations which constitute the minimization task, since every measurement gives two equations: one for the real and one for the imaginary part of R_i^m. Each additional measurement gives one more unknown thickness and two more equations. We measured seven bilayers on two samples. Due to statistical deviations, the thicknesses of the same number of bilayers on various samples differ, giving 14 different measurements and thus the minimization problem is sufficiently over determined and has a unique solution. The procedure is similar to that used in [11], but for minimizing the deviation of reflection coefficients instead of ψ and δ parameters. Parameter δ is a discontinuous function of thickness (because 0° and 360° are the same point in fact), thus causing some problems of convergence, while the reflection coefficient is a regular function.

The procedure is demonstrated in Fig. 4. Black quadrates, representing experimental points, are of a size of errors. The best fit curve corresponds to the parameters $\mathbf{n}_0 = 1.503$, $\mathbf{k}_0 = 0.07$, $\mathbf{n}_e = 1.533$, $\mathbf{k}_e = 0.009$. The optical axis is supposed to be perpendicular to the surface. The curves 1 and 3 were obtained with parameters $\mathbf{n}_0$ and $\mathbf{n}_e$ decreased and increased on 0.05 respectively. Since the distance between them covers the corridor of experimental errors, the accuracy of the refractivity indices determination is better than 0.05. Good agreement of the experimental points and curve number 2 proves that the optical indices do not vary with increasing film thickness. Points corresponding to different samples, being of different thickness, lie on the same curve. This is another indication of the regularity of deposition. Rather surprising is the fact that the optical parameters and the thickness of bilayer are constant from even the first one. The film as a whole can be considered as optically isotropic since the small anisotropy, corresponding to the best fit curve is less than experimental errors. This fact is in agreement with our first rough estimation of film refractivity according to isotropic model. As for the absorption, $\mathbf{k}_e$ should be estimated as zero since its obtained value is less than experimental errors, while $\mathbf{k}_0 = 0.07 \pm 0.05$. Thicknesses calculated according to the anisotropy model differ from those indicated in Fig. 3. However, these differences are less than 1%. The mean value for a bilayer obtained through statistical procedure from the series of thicknesses is the same within experimental errors.

4. Conclusions

Self-assembly of polyelectrolytes polystyrene-sulfonate and polyallylamine results in regular growth of the films. The linearity of the growth starts from the very first bilayer. The thickness of the bilayer of PSS/PAH with added salts of MnCl and NaBr is 6.1 $\pm$ 0.7 nm according to ellipsometric measurements and 5.1 $\pm$ 0.2 nm according to the x-ray reflectometry ones. The refraction indices and absorption coefficients were determined to be $\mathbf{n}_0 = 1.50 \pm 0.05$, $\mathbf{k}_0 = 0.07 \pm 0.05$, $\mathbf{n}_e = 1.53 \pm 0.05$, $\mathbf{k}_e = 0$, $\mathbf{k}_0 = 0.07 \pm 0.05$. These parameters do not vary with the thickness of the film, thus proving the homogeneity of the films. No inhomogeneity caused by film-substrate interaction was observed.

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