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ORIGINAL CONTRIBUTION

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Poly(dimethylaminoethylmethacrylate) hydrochloride (PDMAEM-HCl) a well behaving polycation for multilayer formation on planar surfaces

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Abstract The polycation preparation of poly(dimethylaminoethylmethacrylate) hydrochloride and the multilayer formation in combination with poly(sodium 4-styrenesulphonate) as polyanion studies onto different substrates, as followed by streaming potential measurements, in situ surface plasmon resonance spectroscopy, and multi-wavelength ellipsometry, are reported. Furthermore, we studied the resulting multilayer buildup of dry surfaces by UV-Vis spectroscopy, X-ray photoelectron spectroscopy, and atomic force microscopy measurements. Thereby, the layer built up at the solid/liquid-interface could be followed and quantified at the molecular level.

Keywords Polyelectrolyte adsorption · Multilayers · Self-assembly · Surface modification · Surface functionalization

Introduction

Self-assembled layered polymer films are materials obtained by sequential adsorption of two or more polymers onto a substrate. The technique introduced by Decher [1] is based on the alternating dipping of the substrate into solutions of polyelectrolytes of opposite charge. The method is called ‘‘electrostatic self-assembly’’ (ESA) [2] because the primary forces for layer formation are the electrostatic interactions between polyelectrolytes and the substrate. However, secondary shorter range forces also play a role in determining such important parameters like film thickness, film morphology, surface properties, and in some cases, can even determine whether stable multilayers form at all [3]. Because of the versatility and simplicity of the technique, there has been a fast growth of publications in this area [3, 4]. The proposed applications for the so prepared novel materials range from biosensors [5], light emitting diodes [6], non-linear optical devices [7], and perm selective gas membranes [8] to controlled release micro-capsules [9] and bioactive surfaces for implants and tissue engineering [10]. Although the number of polyelectrolytes tested for ESA is vast [4], most of the publications in this area use a reduced number of commercially available materials like: poly(allylamine) hydrochloride (PAH), poly(ethyleneimine), and poly(diallyldimethylammonium chloride) as polycations and poly(sodium 4-styrenesulphonate) (PSS), poly(potassium vinylsulphate) (PVS) and poly(acrylic acid) as polyanions. With this communication, we want to bring attention to an alternative easy to prepare polycation: poly(dimethylaminoethyl methacrylate) hydrochloride (PDMAEM-HCl, Fig. 1) as a well-behaving material for multilayer formation. The precursor polymer PDMAEM is a weak polyelectrolyte that has already been studied for multilayer formation by the group of Cohen-Stuart [11–13]. From these studies, it resulted that its ability for multilayer formation depended strongly on the pH and the ionic strength of the polyelectrolyte solution; moreover, the whole multilayer assembly was destroyed at ionic strengths around 1 mol l^{-1} if PDMAEM built the outer layer [11, 13]. Under the best conditions, up to eight double layers were constructed onto titan dioxide [12] and up to six double layers were constructed onto silicone dioxide surfaces [13]. Quaternized derivatives of PDMAEM were prepared and used for multilayer formation by the Laschewsky group [14–16]. These include poly(chinoline methacrylate) (PCM), which is a bromo methylated PDMAEM and also a copolymer of the former, containing some amounts on bromo decylated analog units. Laschewsky reported that PCM is a good polycation for multilayer formation, showing linear growth up to 25 double layers onto silicon wafers when a rigid clay platelet was used as a polyanion [16].

In their surface analytical studies employing secondary ion mass spectrometry and X-ray photoelectron spectroscopy (XPS), Laschewsky et al. [17] showed the stepwise covering of a freshly cleaned silicon substrate by its successive dipping in the oppositely charged PCM and PSS polyelectrolyte solutions. With increasing layer number, all the atomic percentages tend slowly to the stoichiometric values of the PCM/PSS layers. The results indicate that one polyelectrolyte double layer is not enough to fully cover the substrate.

In the case of more conventional polyanions like PSS and PVS, a good behavior was reported only up to four double layers onto poly(ethylene terephthalate) [14], but the growth was non-linear when non-polar surfaces like polypropylene were used [14, 15]. In this latter case, the already mentioned quaternized copolymer was a better alternative [14].

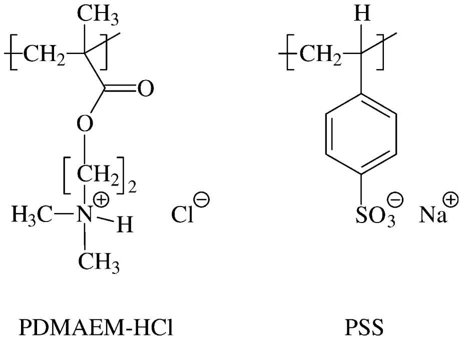

Fig. 1 Structure of the polyelectrolyte molecules employed for multilayer formation on inorganic substrates

The goal of this work is the study of PDMAEM-HCl as a polycation capable of multilayer formation in combination with PSS as a polyanion. Here, we report the polycation preparation and the multilayer formation studies onto different substrates, as followed by streaming potential measurements, in situ surface plasmon resonance spectroscopy (SPR) and multi-wavelength ellipsometry. Furthermore, we studied the resulting multilayer buildup by UV-Vis spectroscopy, XPS, and atomic force microscopy measurements (AFM).

Experimental

Polyelectrolytes

In this study, we used PSS with a molecular weight of 70,000 g mol^{-1} as polyanion (Aldrich). The polycation PDMAEM-HCl (Fig. 1) was prepared employing the following synthetic procedure: First, PDMAEM was synthesized by free radical polymerization of dimethylaminoethyl methacrylate (Aldrich) in tetrahydrofuran (THF, 6 g in 40 ml) under argon at 60 °C for 72 h using 1 mol% of azobisisobutyronitrile as the initiator. The polymer was dissolved in THF and precipitated in petroleum ether three times for purification. The polymer was dried in a vacuum oven at 40 °C for 2 days. After this, the polymer PDMAEM was dissolved in THF and under stirring and cooling (ice bath), gaseous HCl was bubbled through the solution. Gaseous HCl was produced by the dropwise addition of concentrated sulfuric acid to dry NaCl and was conducted directly to the polymer solution. The PDMAEM-HCl product precipitates directly from the solution, nevertheless the bubbling of HCl was continued in excess to allow complete conversion. After filtration, the product was washed with large amounts of THF and ether. Finally, the polymer was dried in the vacuum oven at 40 °C for 2 days.

Multilayer deposition

The buildup of the multilayers was carried out at room temperature in recipients containing the polyelectrolyte solutions (1 g l^{-1} polyelectrolyte/solution). NaCl was added to the polyelectrolyte solutions to yield ionic strengths of 0.01 mol l^{-1}, and 1 mol l^{-1}, but also solutions without added salt were tested. The pH of the polycation solution was adjusted to pH = 4.5–5.0 by adding HCl while the pH of the polyanion solution was not adjusted. Several samples were immersed at the same time for 20 min. After every deposited layer, the samples were rinsed three times with bi-distilled water. The substrates were chosen according to the requirements of the analytical methods: quartz sheets for the use of UV/Vis spectroscopy, glass sheets for streaming potential, silicon wafers for XPS, and ellipsometric studies and gold-coated glass surfaces for SPR spectroscopy.

Electrokinetic measurements

Electrokinetic measurements for the polyelectrolyte layers were carried out by means of an Electrokinetic Analyzer device (Anton Paar GmbH, Austria). The values of zeta-potential (ζ) were calculated according to the Smoluchowski equation:

$$\varsigma = \frac{\eta}{\varepsilon_0 \varepsilon_r} \cdot \frac{\Delta U}{\Delta P} \cdot \kappa \qquad (1)$$

Where ΔU is streaming potential measured between two Ag/AgCl electrodes located at the opposite ends of the substrates, η, ϵ_r, κ are the dynamic viscosity, relative permittivity, and conductivity of the flowing electrolyte solution (0.001 mol l^{-1} KCl), respectively, ε_0 is the permittivity of vacuum, and Δp is the applied pressure (150 mbar). Solutions of KOH and HCl (0.1 mol l^{-1}) were used to vary the pH value of the streaming electrolyte solution in the range of 9≥pH≥2.

Surface plasmon resonance spectroscopy

Surface plasmon resonance data for the layers were obtained by means of the equipment consisting of a He–Ne laser with $\lambda_{\text{laser}} = 632.8$ nm (Uniphase, USA), a semi-cylinder made of SF10 glass, a liquid flow cell with a volume of 2.5 ml and a E10 V large area silicon photodiode detector with an integral pre-amplifier (Linus GmbH, Germany). The laser emitted polarized light (polarization ratio was 500:1) with power of 3 mW onto a semi-cylinder whose plane face was coupled, via index matching fluid, to the substrate examined (quartz slide covered by the gold layer and then by the polyelectrolyte layers). The liquid flow cell was attached to the other side of the substrate and sealed with a rubber *O*-ring. The light was reflected onto the gold layer to excite surface plasmons. The intensity of the reflected light was measured by the photodiode. Both the semi-cylinder and the detector were mounted in an in-house $\theta/2\theta$ goniometer in such a way that the laser beam was incident on the detector at any angle of incidence. The goniometer and the photodiode were interfaced (MotionMaster 3000, Newport Corp., USA) to a personal computer. An in-house 32-bit software package was used for goniometer control, data acquisition, curve modelling, and curve fitting. For scans over a certain range of incidence angles, a step width of 0.1° was used. The curves obtained were fitted according to Fresnel equations for a four-layer model (glass/metal/dielectric/surrounding medium). The average thickness of the layer of the cationic polyelectrolyte adsorbed onto the substrates was evaluated by means of surface plasmon resonance. In this case, the substrate was deposited onto the SF10 glass slide covered by the thin gold layer. At first, the angular dependence of reflectivity was obtained for the original film that was brought in contact with water continuously circulated at the speed of 10 ml min^{-1} through the liquid flow cell by a peristaltic pump. Then, the pure water was changed for the solution of the polycation in this solution. All measurements were made at room temperature.

Ellipsometry

For spectroscopic ellipsometry, a rotating analyzer type variable-angle multi-wavelength ellipsometer (M-44, J.A. Woolam Co., Lincoln, NE, USA) was applied. Our modified M-44 type was equipped with an automatic computer controlled goniometer and horizontally mounted sample stage. The angle of incidence can be set continuously in the range of 20°–90° under stepper motor control, with setting repeatability better than 0.01°. The light source was a stabilized 75-Watt Xenon short arc lamp, radiation below 400 nm was filtered off by a WG 360 Schott glass filter before reaching the polarizer (Glan Taylor, calcite) via optical quartz glass fiber. After reflection from the sample, the light was dispersed onto an array of silicon detectors which permits to perform measurements at 44 wavelengths between 428 nm and 763 nm simultaneously.

The average refractive index, *n*, and the thickness, *d*, assuming a uniform adsorbed layer, were calculated from the experimental values of Δ and Ψ, where Δ is the relative phase difference and Ψ is the azimuth angle of the amplitude ratio for light polarized parallel and normal to the plane of incidence, respectively.

Every sample was measured at three angles of incidence (65°, 70°, 75°).

UV-Vis spectroscopy

Absorbance spectra of the dried films after each deposition cycle were measured by means of a Lambda 800 UV/VIS spectrometer (Perkin Elmer Ltd., USA). Multilayers were dried at room temperature in air atmosphere, and then analyzed by means of the spectroscopic methods.

X-ray photoelectron spectroscopy

All XPS studies were carried out using an AXIS ULTRA spectrometer (KRATOS ANALYTICAL, Manchester, England). The spectrometer was equipped with a monochromatic Al Kα ($h\nu = 1486.6$ eV) X-ray source of 300 W at 15 kV. The kinetic energy of the photoelectrons was determined with an hemispheric analyzer with a constant pass energy of 160 eV for wide scan spectra. During all measurements, electrostatic charging of the sample was over-compensated by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount which was necessary to set the C 1-s peak for saturated hydrocarbons to 285.00 eV [18].

The elemental compositions were quantified from the peak areas using experimentally determined sensitivity factors and taking the spectrometer transmission function.

Angle-resolved spectra were recorded for three different take-off angles ($\theta = 0°$, 60°, and 75°). The take-off angle was defined as the angle between the sample surface normal and the optical axis of the photoelectron spectrometer.

During all measurements, the base pressure in the analysis chamber was better then 10^{-9} mbar.

Atomic force microscopy

The AFM experiments were carried out with a NanoScope IIIa—Dimension 3100 system (Veeco, Santa Barbara, USA) in the tapping mode. The used tips for the experiments were silicon probes from NanoSensors (Darmstadt, Germany).

Results and discussion

Polycation

The preparation of the polycation PDMAEM-HCl was straightforward and was obtained with almost quantitative yields. The zeta potential of the pure polycation PDMAEM-HCl in KCl as a function of pH showed an isoelectric point at pH = 7.2 and a maximum of positive charge at pH values between 4.5 and 5.0. Therefore, we decided to adjust the pH of the polycation solution for the multilayer formation to a pH between 4.5 and 5.0 to maximize the number of positive charge carriers.

Overview of the adsorption process

As already mentioned, the adsorption of polyelectrolytes depends on the effective charge density of the polyelectrolyte molecules and the surface charge density of the substrate, furthermore on the hydrophobic part of the polyelectrolytes and on electrolyte concentration (ionic strength) [22, 23]. Figure 2 shows the streaming potential results on glass plates to which one monolayer of PDMAEM-HCl was adsorbed under different bath conditions. The charge distribution differs between the bulk phase of a liquid and the phase boundary between a solid and a liquid, as charges accumulate at this phase boundary. They originate from the dissociation of ionogenic groups at the solid surface, as well as from the adsorption of ions from the bulk phase. Thus, the formation of what is known as electrochemical double layer or Stern layer. Using the values obtained by measuring the streaming potential between two electrodes, the zeta potential values were calculated. The dependence of the zeta potential on the pH of the solution is caused by the presence of acidic or basic groups at the interface of the solution. Thus, a negative zeta potential results from the adsorption of negatively charged ions, and in the course of pre-adsorbed OH^- ions' dissociation, reactions of Brønsted acidic groups may be initiated. If the dissociation reaction is the potential determining process, the concentration of the charged groups can be obtained from the pH value at which the sign of the surface charge is changed (isoelectric point, $pH_{IEP} = pH|_{\zeta 0}$). Figure 2 shows that the negative charge of the glass plates was diminished by the adsorption of one layer of polycation, nevertheless a net positive charge of the glass surface was achieved only when an acid (pH = 1) was added to the aqueous electrolyte solution. Another important result is that the variation of the ionic

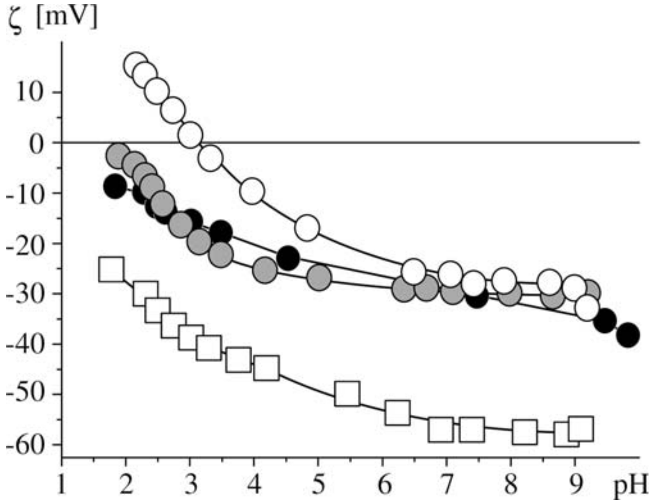

Fig. 2 The zeta potential of one PDMAEM-HCl layer adsorbed onto glass as a function of pH. *open square* bare glass, *filled circle* glass with one PDMAEM-HCl layer adsorbed in 0.01 mol l^{-1} NaCl, *gray circle* glass with one PDMAEM-HCl layer adsorbed in 1 mol l^{-1} NaCl, *open circle* glass with one PDMAEM-HCl layer adsorbed in pH 1

strength in the aqueous electrolyte solution (0.01–1.0 mol l^{-1}) did not influence the charge of the glass substrate after adsorption of one layer of PDMAEM-HCl.

Characterization of wet surfaces

Many studies on multilayer formation are followed by characterizing the resulting surfaces in the dry state by techniques like UV-Vis spectroscopy, XPS, and Microscopy. However, the formation of multilayers takes place in a wet state and the layers formed are more likely to be soft and gel-like as a result of the water entrapped inside. Therefore, after drying, the structure of the multilayers may change in an unpredictable way. Our approach is to study both the multilayer formation in the wet state by in situ SPR and ellipsometry, while the dried surfaces are studied by UV-Vis spectroscopy, XPS, and AFM. In this way, we may get conclusions about the multilayer formations and their changes after drying.

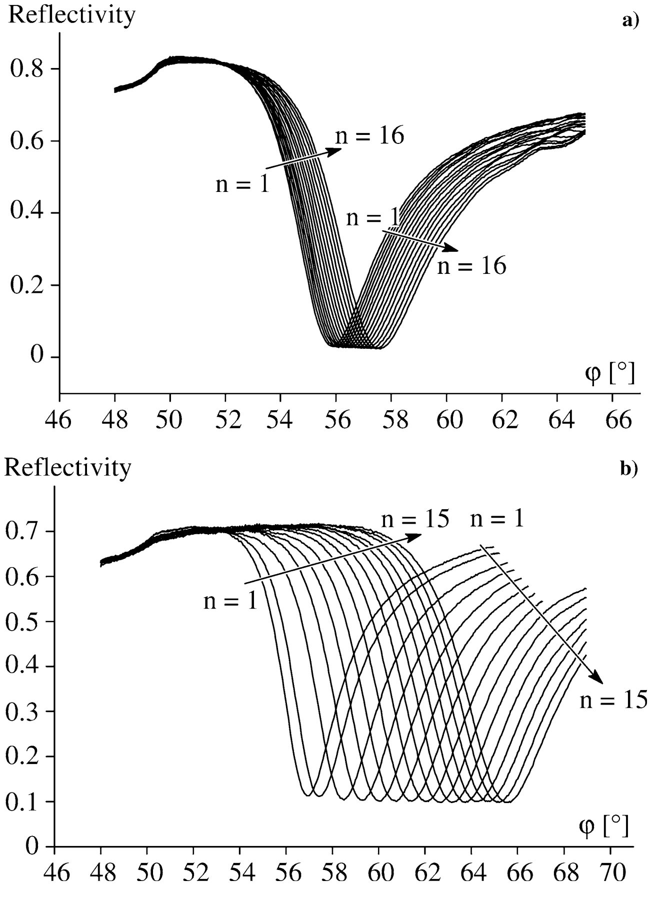

Fig. 3 SPR curves for the formation of PDMAEM-HCl/PSS double layers as a function of ionic strength, **a** 0.01 mol l^{-1} NaCl, **b** 1.0 mol l^{-1} NaCl (n = number of the deposited polyelectrolyte double layers, ϕ = angle of incidence)

The process of polymer deposition from the solution was studied by SPR on a layer-by-layer adsorption basis. The resonance angle shift was measured at the solid–liquid interface. Figure 3 presents the reflectivity depending on the internal angle for the several multilayers built in a solution of 0.01 mol l^{-1} and 1.0 mol l^{-1} of NaCl. As can be seen, the minima of reflectivity, the so-called SPR angle, is shifted depending on the number of double layers. Clearly, it can be seen that the minimum of reflectivity shifts towards higher SPR angles after the substrates get into contact with the solution of the cationic and anionic polyelectrolytes. This shift is correlated with the adsorption of macromolecules onto the substrate. Multilayers built with a low salt concentration reflect low SPR angles, and therefore low film thickness. The calculated thickness grows linear with an increase of 2.2 nm per double layer for the multilayers built in a solution of 1.0 mol l^{-1} NaCl.

The charge densities at the gold surface which is necessary for the SPR-measurements are relatively small, so that only a little polymer is adsorbed. On the other side, using a high salt concentration, the shifts in SPR angles are much higher; therefore, the film thickness also increases proportionally. The fact that the adsorption of polyelectrolyte may increase with increasing salt concentration is not new and was already reported for other systems [19, 20]. The surprise here is that PDMAEM, which is quarternized with HCl (PDMAEM-HCl), is not only able to withstand the high ionic strength concentration, it is also deposited onto the substrate and builds in a regular fashion up to 15 double

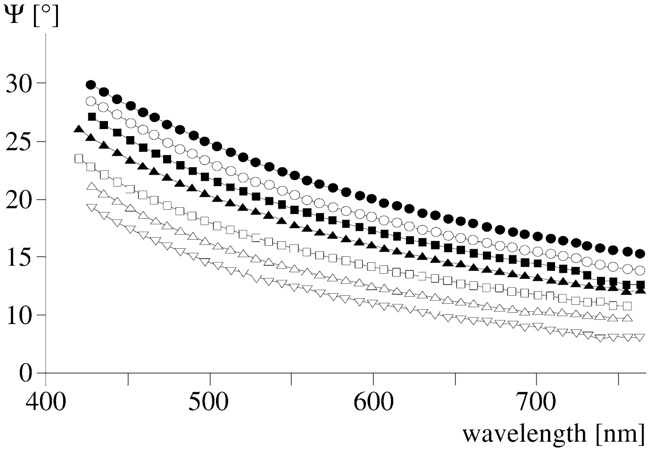

Fig. 4 Results from multi-wavelength ellipsometry for the formation of PDMAEM-HCl/PSS multilayers: *inverted triangle* substrate without a polyelectrolyte double layer, *open triangle* 2 double layers, *open square* 3 double layers, *filled triangle* 4 double layers, *filled square* 5 double layers, *open circle* 6 double layers, and *filled circle* 7 double layers (electrolyte 1.0 mol l^{-1} NaCl)

layers without trouble. This seems to contradict results reported earlier by other authors [11]. The multilayer buildup at high ionic strength conditions was confirmed by multi-wavelength ellipsometry, as can be seen in Fig. 4. For clarity, only seven double layers are plotted. The layering process is clearly regular also onto the silicon wafer surface used at 1.0 mol l^{-1} NaCl conditions.

On the assumption that the value of the refractive index of the adsorbed polymeric layer is 1.5, which is the typical value for organic compounds, the average thickness of the different layers built up on the systems of PDMAEM-HCl with PSS, in the two different concentrations of NaCl (0.01 mol l^{-1} and 1.0 mol l^{-1}) were evaluated from the SPR measurements, while from ellipsometry measurements also the layer thickness was calculated for the system prepared at a high salt concentration. The layer thickness for seven double layers is 80 nm with an increase of about 10 nm per double layer in 1.0 mol l^{-1} NaCl.

Characterization of dry surfaces

Former AFM studies' phase contrast images showed that polyelectrolyte layers formed in pure water are very smooth with uniform softness but in the presence of the added electrolyte, particles appear on the surface. We expected this behavior in our systems, and indeed, the first results showed the difference on the roughness of the samples with the number of multilayers. Figure 5 shows AFM images of the PDMAEM-HCl/PSS multilayers on silicon wafer in NaCl for 1, 3, 7, and 9 double layers. The roughness increased linearly with the number of double layers.

Information on the resulting multilayered structure by the interaction between PDMAEM-HCl and PSS was obtained by UV-Vis Spectroscopy after drying. The absorbance spectra of multilayers depending on the layer number, prepared from 1.0 mol l^{-1} NaCl solutions showed an increase in the absorption bands at $\lambda_{ads} < 225$ nm (absorbance of aromatic rings of PSS) clearly (not shown here). The increase in the intensity of the absorption bands is a consequence of adsorption of more layers of PSS onto the quartz glass substrate. Figure 6 shows the variation of the absorbance at 225 nm, depending on the number of multilayers, for the systems of PDMAEM/PSS in water and in solutions of NaCl 0.01 mol l^{-1} and 1 mol l^{-1}. It can be seen that the results for the salt-free and the aqueous 0.01 mol l^{-1} NaCl solutions are similar, and only a small increase of the absorption appears. For the 1 mol l^{-1} solution, the increase in the absorption is higher and shows almost a linear correlation with the number of multilayers. Without added electrolyte, only small amounts of polyelectrolyte were adsorbed on the negatively charged substrate surfaces in a rather flat conformation. The addition of 1:1-electrolyte changes the conformation of the polyelectrolyte to a more coiled conformation and

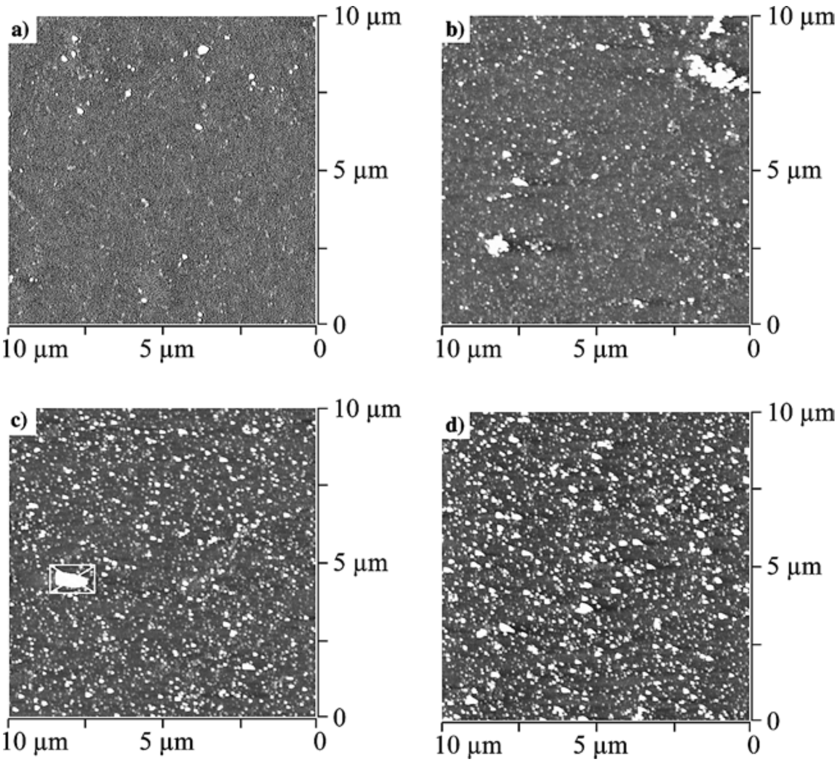

Fig. 5 AFM images of the PDMAEM-HCl/PSS multilayer surfaces (electrolyte 0.01 mol l^{-1} NaCl) **a** 1 double layer, **b** 3 double layers, **c** 7 double layers, and **d** 9 double layers

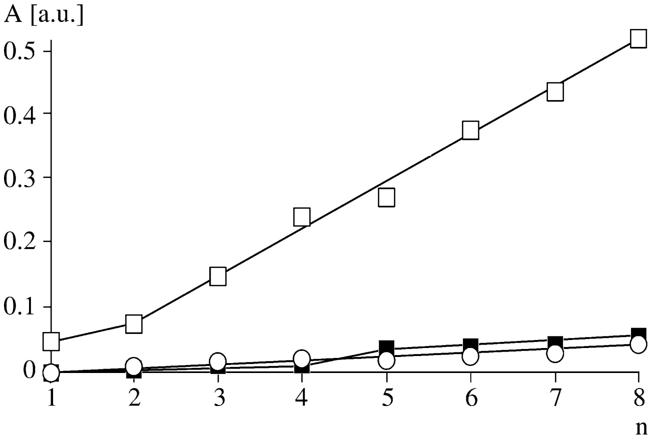

Fig. 6 Influence of the ionic strength on the multilayer formation as followed by absorbance change at $\lambda_{ads} = 225$ nm, *open circle* adsorption from salt-free solution, *filled square* adsorption from 0.01 mol l^{-1} NaCl solution, *open square* adsorption from 0.1 mol l^{-1} NaCl solution, n = number of deposited PDMAEM-HCl/PSS double layers, A absorbance

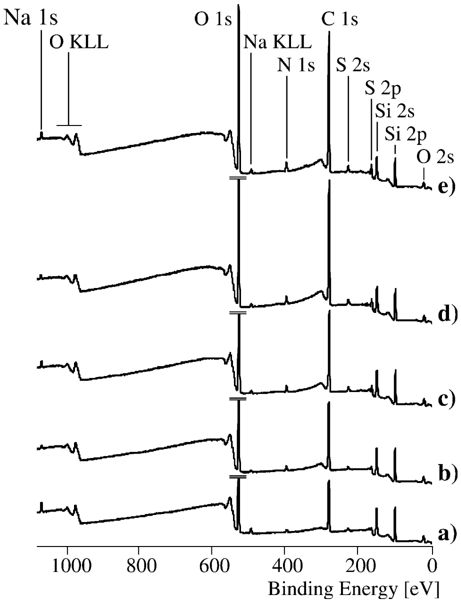

Fig. 7 Wide-scan photoelectron spectra of PDMAEM-HCl/PSS double layers deposited on thermally oxidized silicon wafer surfaces, **a** 4 double layers, **b** 6 double layers, **c** 8 double layers, **d** 8 double layers, and **e** 10 double layers. All spectra were recorded at a take-off angle of 0°, for comparison all spectra were normalized by setting the O 1-s peak on the same peak area

reduces the polymer–polymer interactions. Hence, more polymer chains can find a free site on the surface and the amount of adsorbed polyelectrolyte molecules is increased.

With an information depth (ID) of ca. 10 nm in maximum, XPS can be considered as an extremely surface-sensitive technique able to study thin films on solid surfaces. The surface sensitivity of the method can be enhanced by varying the take-off angle θ according to $ID = ID_{max}\cos(\theta)$. The knowledge of the relationship between the spectral intensity $I(X)$ of an element X and the information depth allows us to determine the thickness d of a coating layer and quantify its homogeneity [21]. To characterize a surface layer concerning its thickness and homogeneity, two requirements must be fulfilled. The layer as well as the substrate must contain an element or a functional group which is typical for its origin and can be considered as a label for information from the substrate or the coating layer. Second, the layer thickness must be thinner as the information depth or in other words, the XPS spectrum must contain the label of the coating layer as well as the substrate. Equation 1 shows the simple overlayer model which can be used to calculate the layer thickness of a homogeneous thin film (containing the label element X) covering a substrate (containing the label element Y) [19]:

$$\frac{I(X)}{I(Y)} = \frac{I_0(X).(1 - \exp[-d/\lambda(X).\cos\theta])}{I_0(Y).\exp[-d/\lambda(X).\cos\theta]} \qquad (1)$$

Where I_0 is the intensity of a finite thick sample of the layer and substrate material, and λ is the inelastic mean free path of electrons. According to Seah's approximation [20], the values for λ are: $\lambda(N) = 1.12$ nm and $\lambda(S2\ s) = 1.24$ nm. The values for I_0(X) were determined from PSS and PDMAEM-HCl samples measured in substance, and I_0(Y) were determined from a thermally oxidized silicon wafer with an oxide layer much more thicker as the information depth. Those pre-treated silicon wafers were also used as substrate material to prepare the polyelectrolyte multilayers.

Figure 7 shows a series of XPS wide scan spectra. As can be seen from the spectra of the polymers PSS and PDMAEM-HCl (Figure 8), the N 1-s and the S 2-s peaks can be considered as typical label atoms of the polyelectrolyte layers, while the Si 2-p peaks specifically indicate the substrate material.

As expected, each double layer deposited on the silicon wafer increases the amount of the polyelectrolyte double label atoms (in Fig. 9, expressed as the ratio ([N] + [S]):[Si]). However, the slope is not constant because with each additionally deposited double layer, the photoelectrons appearing from Si (substrate label) have an increased probability for inelastic scattering in this additional polyelectrolyte layer, which contributes a lot to the spectral intensity.

Figure 10 also shows that the buildup of ten double layers has an overall thickness clearly smaller than the information depth of the method. This result is in contrast to the layer thickness values determined by means of ellipsometry and SPR and cannot be explained by the different substrate materials used for different analytical

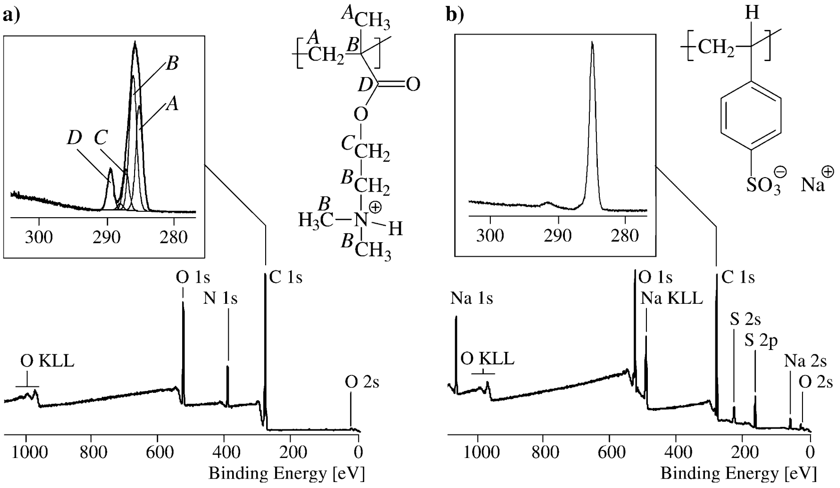

Fig. 8 Wide-scan and high-resolution C 1-s photoelectron spectra of bare PDMAEM-HCl (**a**) and PSS (**b**). The assignation of the fitted component peaks is given by the *italic-style letters*

methods. Under ultra high vacuum conditions, the water which is contained in the polyelectrolyte layers and stabilizes their conformation is mainly removed. Hence, in the case of XPS the polyelectrolyte double layers have another conformation as in the wet state. However, it is expected that the removal of water results in an 1-D process which has a disastrous effect only on the layer thickness, but not on the distribution of the polyelectrolyte molecules in the other 2-D. This means that in the case of XPS, we studied multilayer buildups with lateral polyelectrolyte distributions like in their wet states but they are compressed in the height of the deposited layers.

The dependence of the elemental ratio [N]:[S] on the number of the deposited double layers is shown in Fig. 9. The constant slope of the functions indicates that the number of the potential charge carriers in each polyelectrolyte single layer is not completely compensated by the oppositely charged polyelectrolyte single layer. With each deposited double layer, the nitrogen content appearing from PDMAEM-HCl increases compared with the amount of sulfur, which corresponds with the number of the PSS charge carriers ($–SO_3^-$).

Employing Eq. 1, it is possible to calculate the overall layer thickness of the polyelectrolyte layers depending on their deposited number *n*. However, Fadley's overlayer model [19] requires a homogeneous layer which must at first be closed over the whole substrate. The homogeneity of the polyelectrolyte layer can be evaluated by recording angle-resolved XPS spectra. It is easy to understand that the tilting of the sample under the analyzer of the spectrometer, which changes the take-off angle, cannot have an influence of the layer thickness of the polyelectrolytes nor their homogeneity. Hence, for a closed and homogeneous layer, the parameter *d* calculated from Eq. 1 must be independent of the adjusted

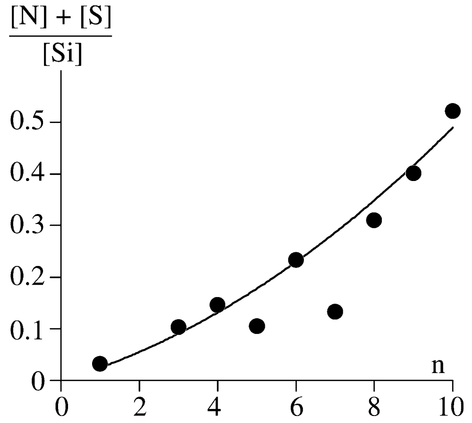

Fig. 9 Evolution of the multilayer buildup on silicon wafer surfaces indicated by the elemental ratios ([N] + [S]):[Si]), where [N] and [S] label the polyelectrolyte molecules, while [Si] represents the substrate. All values were determined from wide-scan XPS spectra recorded at a take-off angle of 0°

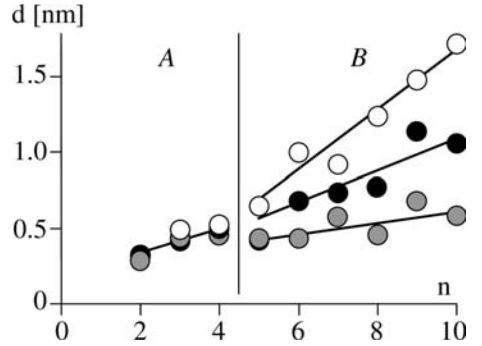

Fig. 10 Apparent overall layer thicknesses *d* calculated according to Fadley's overlayer model [18] depending on the number *n* of PDMAEM-HCl/PSS double layers deposited on silicon wafer surfaces, *open circle* take-off angle $\theta = 0°$, *filled circle* take-off angle $\theta = 60°$, *gray circle* take-off angle $\theta = 75°$. The meaning of the *italic-style letters* is explained in the text

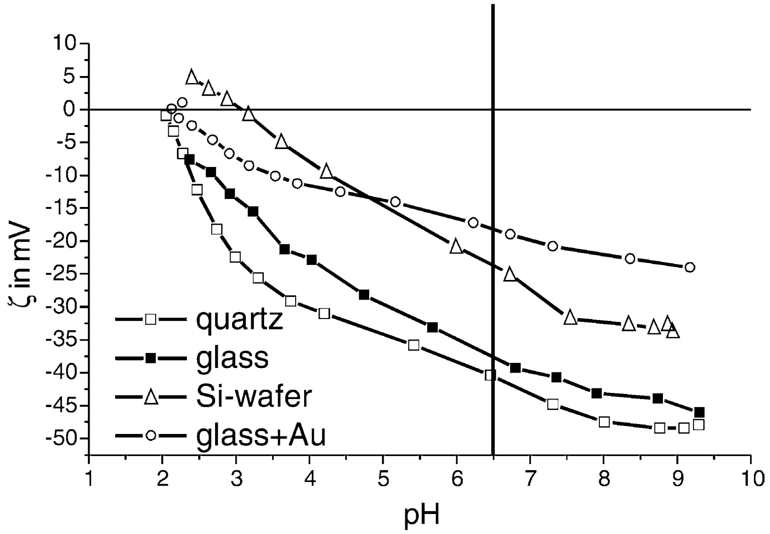

Fig. 11 Dependence of zeta potential on pH for silicon wafer *open triangle*, glass modified with a thin gold layer *open circle*, glass *filled square* and quartz glass *open square*

take-off angles θ. In the other case, it must be concluded that the buildup of the polyelectrolyte double layers does not fully coat the silicon wafer surface. In that case, a two-parameter model where the degree of coverage is included as a free parameter must be applied [21].

For the first deposited polyelectrolyte double layers, we found, depending on the adjusted take-off angle, small deviations for the calculated d values (Fig. 10, section A). From this result, we can conclude that only a few of double layers are necessary to fully cover the silicon wafer surface. If the number of adsorption steps is increased ($n > 7$), a significant dependence of the d values on the take-off angle was observed (Fig. 10, section B). It indicates that the double layer buildup on pre-adsorbed polyelectrolyte layers is more and more disturbed by non-flat adsorbed polyelectrolyte segments. But this conclusion is not in conflict with the observation of the closed polyelectrolyte layers near the silicon wafer surface. Obviously, each of the deposited polyelectrolyte double layer contributes to the increase in the polyelectrolyte layer (Fig. 10). This finding is in good agreement with measurements of the layer thickness in the wet state mentioned above.

Effect of the substrate

An important parameter to analyze is the charge density of the substrate used. The analytical techniques used to characterize the PEL layers required different substrates: quartz for UV spectroscopy, glass covered with a thin gold layer for SPR and silicon wafer for ellipsometry, XPS, and AFM. The charge densities were characterized by the zeta potential, which was measured over a certain range of pH values. The dependence of the zeta potential on pH for silicon wafer, glass modified with a thin gold layer, and quartz glass is shown in Fig. 11. There were big differences in the dependence of the kind of substrate. The charge density at pH 6.5 decreased in the following range: quartz glass, Si-Wafer, and glass coated with Au. Suitable substrate materials must carry a minimal surface charge. That means the adsorption and also the adsorption amount and the layer thickness should be the highest for quartz glass and the lowest for glass coated with Au. So the result of determined thickness is in agreement with the surface charge densities of the used substrate.

Conclusions

Results of the characterization of various PDMAEM and PSS multilayers by a variety of surface analytical tools were given. The adsorption of these multilayers was investigated by SPR, ellipsometry, and zetapotential on wet surfaces and XPS, AFM, and UV spectroscopy on dry surfaces. All theses methods ensure a high sensitivity required for the small amounts of adsorbed material. Essential parameters for the regular adsorption of subsequent polymer layers by electrostatic interactions are the charge of polyelectrolyte and of the outermost surface region, the surface of the substrate, and the pH and ionic strength. Significant differences of polyelectrolyte adsorption were observed depending on the kind of substrate. So, the adsorbed amount per double layer was dependent on the substrate and investigation on wet or dry surfaces.

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