Formation and Dielectric Properties of Polyelectrolyte Multilayers Studied by a Silicon-on-Insulator Based Thin Film Resistor

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The formation of polyelectrolyte multilayers (PEMs) is investigated using a silicon-on-insulator based thin film resistor which is sensitive to variations of the surface potential. The buildup of the PEMs at the silicon oxide surface of the device can be observed in real time as defined potential shifts. The influence of polymer charge density is studied using the strong polyanion poly(styrene sulfonate), PSS, combined with the statistical copolymer poly(diallyl-dimethyl-ammoniumchloride-*stat*-*N*-methyl-*N*-vinylacetamide), P(DADMAC-*stat*-NMVA), at various degrees of charge (DC). The multilayer formation stops after a few deposition steps for a DC below 75%. We show that the threshold of surface charge compensation corresponds to the threshold of multilayer formation. However, no reversion of the preceding surface charge was observed. Screening of polyelectrolyte charges by mobile ions within the polymer film leads to a decrease of the potential shifts with the number of layers deposited. This decrease is much slower for PEMs consisting of P(DADMAC-*stat*-NMVA) and PSS as compared to PEMs consisting of poly(allylamine-hydrochloride), PAH, and PSS. From this, significant differences in the dielectric constants of the polyelectrolyte films and in the concentration of mobile ions within the films can be derived.

Introduction

Polyelectrolyte multilayers (PEMs) formed by the sequential deposition of polcations and polyanions from solution have been investigated intensively since they have first been proposed.[1] The method is very attractive due to its simplicity and its broad range of potential applications in divers fields such as sensor devices, functional and stimuli responsive coatings for biomedical applications, and encapsulation devices. However, for using multilayers as functional materials for complex devices, it is important to understand the internal structure and the formation process.[2] In many earlier papers, the charge inversion after each deposition step is discussed as a precondition for multilayer formation, and it was assumed that electrostatic interactions are its main driving forces.[3,4] This opinion was supported by the fact that normally, after each deposition step, the zeta potential changes its sign, resulting in a kind of zigzag curve.[5] The surface potential itself is not accessible, but the zeta potential can be determined by electrokinetic measurements. Further on, the importance of electrostatic interactions was underlined by studies of the effect of polymer charge density. There, the influence of polymer charge was studied using the strong polyanion poly(styrene sulfonate), PSS, combined with the linear statistical copolymer poly(diallyl-dimethyl-ammonium-chloride-*stat*-*N*-methyl-*N*-vinylacetamide), P(DADMAC-*stat*-NMVA), at various degrees of polymer charge (DC). It was found that the multilayer formation stops after a few deposition steps for a DC below 75%.[6−10] Recent zeta potential measurements indicate that, depending on the assembly

solution pH, a change in sign of the zeta potential after each deposition step is not required.[11,12] Beside the balance of electrostatic attraction and repulsion, the gain in entropy due to the release of counterions is one of the driving factors. Moreover, also nonelectrostatic contributions such as hydrogen bonding and hydrophobic interactions play a role in multilayer stabilization.[13−15] In addition, recent theoretical studies have demonstrated that nonelectrostatic short range interactions strongly influence multilayer formation,[16,17] and polymer specific effects on multilayer formation have been observed. Electric measurements and the study of dielectric properties can provide a means of gaining further insight into the progress of multilayer formation.

The adsorption of polyelectrolyte multilayers consisting of poly-L-lysine and DNA or poly(allylamine-hydrochloride), PAH, and PSS has been observed by the use of field-effect devices.[18−20] These devices allow the determination of the surface potential directly at the polyelectrolyte/sensor interface. This is in contrast to elektrokinetic studies, where the potential at a shear plane outside the outer Helmholtz plane is measured with respect to the outer solution bulk value. Therefore, the changes in surface potential measured by a field-effect device are strongly dependent

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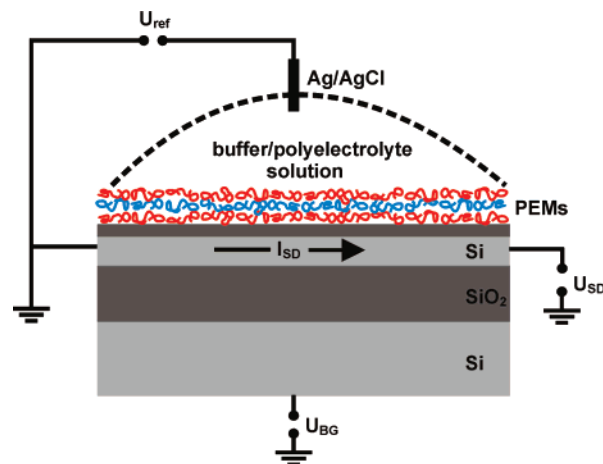
not only on the amount of charge adsorbed to the outermost surface, but also on screening effects within the multilayers inside the polyelectrolyte films, which cannot be determined by zeta potential measurements. A theoretical model has been proposed to relate the response of such a sensor to the properties of the PEMs.[20] The model allows the determination of the dielectric constant and the concentration of mobile ions within the films from the measured change in surface potential and has been successfully applied to multilayers consisting of PAH and PSS.[20,21] It was found that this particular multilayer system exhibits a rather low dielectric constant dependent on the ionic strength of the assembly solution. However, it remains a crucial question how the dielectric properties are affected by the chemical nature of the polymers. Although theoretically multilayers are just described as charged polymers, it could well be that the backbone of the polymer has an important influence on the PEMs properties. Multilayers with different dielectric properties could prove useful for the specific application in the functionalization of biosensing field effect devices. Here, it is desirable to separate the silicon dioxide from the aqueous solution and possibly decrease unspecific adsorptions. However, for such applications, it is mandatory that the intrinsic charge of the analyte is not screened by the underlying polymer cushion.[22]

Here, we employ a previously introduced silicon-on-insulator (SOI) based field effect device[23] for the investigation of the buildup of polyelectrolyte multilayers and their dielectric properties. Field effect devices allow the determination of the surface potential at the sensor/electrolyte interface. The adsorption of charged species such as polyelectrolytes to the sensor surface alters this surface potential and can thus be detected in terms of a sheet resistance change allowing for the detection of PEMs deposition. Only with polyelectrolytes where more than 50% of the segments are charged a multilayer buildup can be achieved. Screening of polyelectrolyte charges by mobile ions within the polymer film leads to a decrease of the sensor signal with the number of layers deposited. Screening effects are much smaller for PEMs consisting of P(DADMAC-*stat*-NMVA) and PSS as compared to PEMs consisting of PAH and PSS, demonstrating the dependency of the multilayer properties on nonelectrostatic properties of the polyelectrolyte such as backbone hydrophobicity.

Experimental Section

The cationic polyelectrolyte P(DADMAC-*stat*-NMVA) (MW = 100 000) was synthesized as described elsewhere.[24−26] All other chemicals including PSS (MW = 70 000) and PAH (MW = 60 000) were purchased from Sigma-Aldrich. Buffers were prepared using ultrapure water (Millipore, France) with a resistivity of >18 MΩ cm. Polyelectrolyte solutions (5 mg/mL) were prepared by direct dissolution in 10 mM Tris buffer at pH 7.5 containing 50 NaCl (κ^{-1} = 1.3 nm). All washing and measurements steps were conducted in the presence of the same buffer solution.

The sensor chips were fabricated from commercially available SOI wafers (ELTRAN, Canon) using standard lithographic methods and wet chemical etching as described in detail elsewhere.[23] The top silicon layer of these wafers was 30 nm thick and slightly doped with boron (10^{16} cm^{-3}). Metal contacts were deposited in an electron

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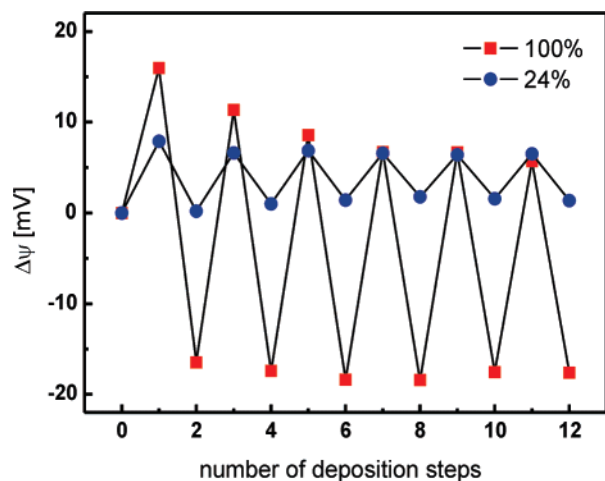(23) Nikolaides, M. G.; Rauschenbach, S.; Luber, S.; Buchholz, K.; Tornow, M.; Abstreiter, G.; Bausch, A. R. *ChemPhysChem* **2003**, *4*, 1104−1106.
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Figure 1. Sketch of the setup and the measurement geometry. Silicon is shown in light gray, silicon oxide in dark gray. From top to bottom: native oxide (1−2 nm), conducting top silicon (30 nm), buried oxide (200 nm), bulk silicon (675 μm). A voltage U_{SD} is applied between the source and the drain contacts and the resulting current I_{SD} is measured yielding the sheet resistance of the device. The carrier concentration in the top silicon layer is tuned by the backgate voltage U_{BG}. The potential of the electrolyte solution is controlled by a Ag/AgCl reference electrode. A microfluidic device allows the rapid exchange of electrolyte solution.

beam evaporation chamber (20 nm Ti, 300 nm Au). After evaporation, the sensor chips were cleaned using acetone and isopropanol. The chips were glued into a chip carrier and the contacts were Au-wire bonded to the carrier. Afterward the chips were encapsulated with a silicone rubber to insulate the contacts from the electrolyte solution. The sheet resistance of the device is measured in a four-point geometry.[27] A flow chamber was mounted on top of the sensor and a Ag/AgCl reference electrode was used to control the potential of the electrolyte solution. In a typical experiment, the sensor is first equilibrated in buffer solution. Before the multilayer deposition, a calibration measurement is performed to relate a change in sheet resistance to a corresponding change in surface potential.[27] The setup and the measurement geometry are shown schematically in Figure 1. For multilayer deposmtion polyelectrolyte solutions were injected into the flow chamber, starting with the positively charged polymer. After obtaining a stable sensor signal, the chamber was rinsed with buffer. As soon as a stable signal was obtained, the next polyelectrolyte solution was injected and the procedure was repeated with the oppositely charged polyelectrolyte. The sheet resistance of the thin film resistor was monitored continuously during the multilayer deposition.

Results and Discussion

Multilayer Formation. The cationic polyelectrolyte P(DAD-MAC-*stat*-NMVA) consists of positively charged diallyldi-methylammonium chloride monomers (DADMAC) and neutral *N*-methyl-*N*-vinylacetamide (NMVA) monomers at total charge densities of 24%, 50%, 75%, and 100%. Multilayer deposition starts with the adsorption of the polycation for 2 min, followed by a rinse with pure buffer solution. When a stable signal is obtained, the PSS solution is injected. After 2 min, the chip is rinsed again with buffer solution and the next polyelectrolyte layer can be adsorbed. During the deposition process, the sheet resistance is monitored continuously. Figure 2 shows the alternating surface potential $\Delta\psi$ as calculated from the measured change in sheet resistance plotted against the number of deposition steps for DCs of 100% and 24%.

The adsorption of the positively charged P(DADMAC-*stat*-NMVA) to the negatively charged silicon oxide sensor surface

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Figure 2. Change in surface potential caused by the adsorption of polyelectrolyte layers plotted against the number of deposition steps. The buildup of multilayers consisting of the fully charged polyelectrolytes PDADMAC (DC 100%) and PSS is shown (squares). Typical errors are in the range of 2 mV. Charged molecules that adsorb to the sensor surface lead to defined potential shifts. For a DC of 24% (circles) small potential oscillations are observed although the layer buildup stops after the fourth monolayer due to a dynamic exchange of polymers at the topmost layer with those in solution.

leads to an increase of the surface potential whereas the subsequent adsorption of the negatively charged PSS decreases the surface potential. For a DC of 100%, polyelectrolyte multilayers are formed, which was confirmed independently by ellipsometric measurements where a continuous increase of the film thickness was found.[9] A slight signal decrease with increasing number of deposition steps is observed. This is caused by the screening of the newly adsorbing charges by mobile ions inside the polyelectrolyte film, which is discussed below. Similarly, multilayer formation is found for a DC of 75%. For a DC of 50% and less, not more than four monolayers can be adsorbed before the multilayer formation and thus the increase in film thickness stops as confirmed independently by ellipsometry.[9] Nevertheless, we observe small potential oscillations of constant amplitude also when the film thickness does not increase anymore as can be seen in Figure 2 for a DC of 24%. We ascribe this to a dynamic exchange of polyelectrolyte molecules.[14] Some polymer of the topmost layer desorbs upon addition of the oppositely charged polyelectrolyte solution, which has previously been demonstrated by fluorescence labeling.[28] The measured potential oscillations correspond to an exchange of surface charge of $\Delta\sigma \approx 3$ mC/m^2 as can be estimated from the Grahame equation.[29]

Charge Compensation. Thus for the buildup of multilayers consisting of P(DADMAC-*stat*-NMVA) and PSS, a minimal charge density of 50% is needed, and in former studies, it was assumed that a charge overcompensation of the substrate charge by the first layer of adsorbing polymer is required for multilayer formation.[9] The SOI based field effect device enables us to verify this important assumption. Here, we take advantage of the fact that changing the ionic strength of the buffer solution on top of a field effect device causes a change in the Debye capacitance of the electrical double layer and thus in the surface potential, which is detected by the measured sheet resistance. The change in surface potential $\Delta\psi_{salt}$ caused by a change of the ionic strength of the buffer solution is a direct measure of the sensor's surface
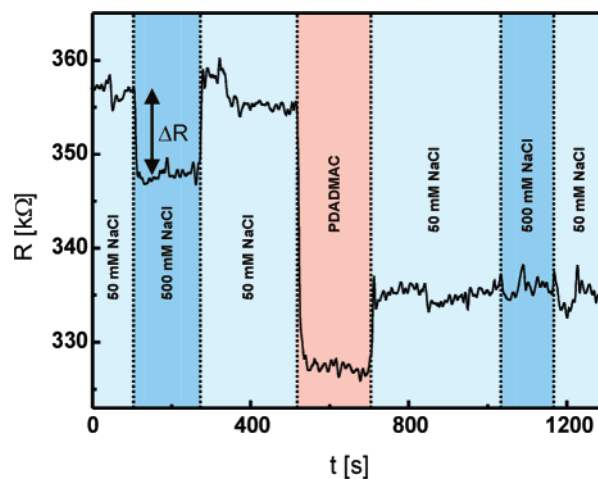
Figure 3. Adsorption of PDADMAC (DC 100%) to a clean sensor surface. The sheet resistance is plotted against time. For the negatively charged silicon oxide surface, a change of the ionic strength of the buffer solution (50–500 mM NaCl and back) causes a change of the surface potential ψ and thus of the sheet resistance R as indicated by the arrow. After the adsorption of PDADMAC, the surface charge is exactly compensated by the polyelectrolyte charge, and therefore no change in sheet resistance is observed upon buffer exchange.

charge: for an uncharged surface, no such change in surface potential occurs. In a first approximation the total surface charge can be directly calculated from the change in surface potential by the Grahame equation,[29] especially as the screening effects in the PEMs are very small. Here, we employed a more exact procedure, where the Grahame equation is combined with the site-binding theory[30] and solved numerically.[31] Figure 3 shows such an experiment where the sheet resistance of the SOI device is plotted against time. First, a 10 mM Tris buffer at pH 7.5 containing 50 mM NaCl is applied to a clean silicon oxide sensor surface. Next, the ionic strength is changed by injecting a 10 mM Tris buffer at the same pH but with a higher concentration of NaCl of 500 mM. As the silicon oxide is negatively charged at pH 7.5, this leads to a lower sheet resistance corresponding to a less negative surface potential. Subsequently, the solution on top of the sensor is replaced again by the buffer containing 50 mM NaCl, and the sheet resistance increases again to the previous level. Now a PDADMAC solution (DC 100%) is injected, and the positively charged polymer binds to the sensor surface increasing the surface potential and thus decreasing the sheet resistance. The sensor is rinsed with the 50 mM NaCl buffer which is then exchanged against the 500 mM NaCl buffer. This exchange now is not accompanied by a change in sheet resistance indicating a sensor surface that is uncharged in total. Therefore, the negative charge of the sensor surface has been exactly compensated by the charge of the PDADMAC layer. Figure 4 shows the changes in surface potential caused by a buffer exchange between 50 and 500 mM NaCl $\Delta\psi_{salt} = \psi_{500mV} - \psi_{50mV}$ and the corresponding total surface charge σ for different polyelectrolytes as the topmost layer. The experiment shown in Figure 3 is represented by the first part of Figure 4a, where the buffer exchange leads to a change in surface potential $\Delta\psi_{salt}$ of 9 mV for the bare sensor surface and 0 mV after the deposition of a PDADMAC layer. After the following adsorption of PSS, an even higher $\Delta\psi_{salt}$ of 18 mV is observed. This can be interpreted as follows: The adsorbing positively charged PDADMAC does

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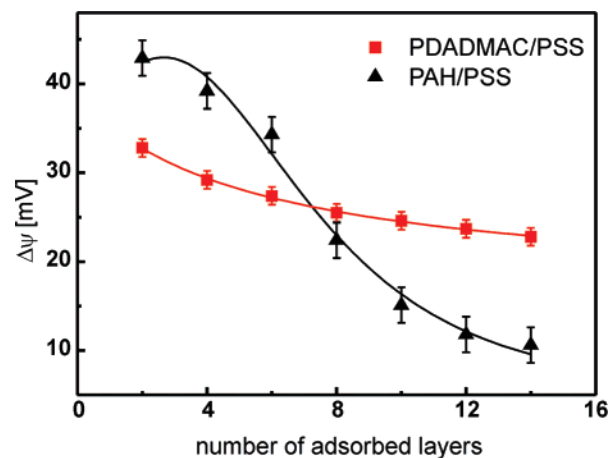
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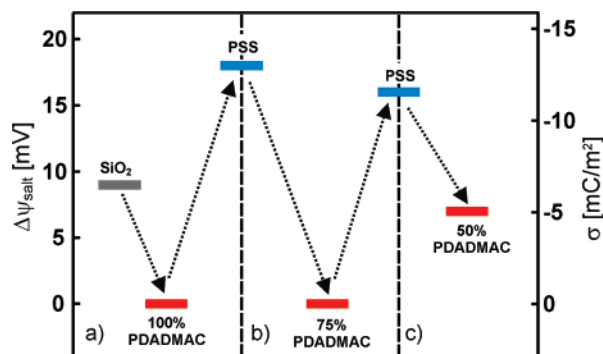
Figure 4. Change in surface potential $\Delta\psi_{salt}$ caused by a buffer exchange between 50 and 500 mM NaCl shown for different polyelectrolytes (left axis, errors in the range of 2 mV). $\Delta\psi_{salt}$ is calculated from the change in sheet resistance ΔR as indicated in Figure 2. On the right axis, the corresponding total surface charge σ is shown as derived from $\Delta\psi_{salt}$. In panel a, the change in surface potential and the total surface charge are given before and after the adsorption of fully charged PDADMAC to the bare sensor surface and after the following adsorption of PSS. In panels b and c, the corresponding values are given before and after the adsorption of P(DADMAC-*stat*-NMVA) to a PSS terminated surface.

not overcompensate, but exactly compensates the negative charge of the silicon oxide surface ($\sigma = -7$ mC/m^2, as derived from $\Delta\psi_{salt} = 9$ mV). Next, the negatively charged PSS is adsorbed on top of the PDADMAC layer. After this deposition step, $\Delta\psi_{salt}$ amounts to 18 mV, indicating that with the PSS about twice the charge density of the original silicon oxide surface ($\sigma = -14$ mC/m^2) has been absorbed. To achieve multilayer buildup, the following layer of positively charged polyelectrolyte should again compensate the previous surface charge to allow for the continuation of the formation process, assuming that each PSS-terminated polyelectrolyte multilayer surface is identical. As shown in Figure 4, panels b and c, this is the case for P(DADMAC-*stat*-NMVA) with a DC of 75% but not for a DC of 50%. For 75%, the charge of a PSS terminated surface is compensated by the adsorption of the positively charged polyelectrolyte ($\Delta\psi_{salt} = 0$), whereas for 50%, no full charge compensation of the previous PSS surface occurs ($\Delta\psi_{salt} = 7$ mV corresponding to a total surface charge of $\sigma = -5$ mC/m^2). Thus, the threshold for charge compensation lies between 50 and 75% in accordance with the threshold observed for the formation of multilayers. The first PDADMAC layer adsorbs at only half of the charge density ($\Delta\sigma = +7$ mC/m^2) that is found for the following layers of PSS and PDADMAC ($\Delta\sigma = \mp14$ mC/m^2). Due to the difference in surface potential of the respective negative surface, it is assumed that the structure of the first PDADMAC layer differs from the latter adsorbed PDADMAC layers. This can be understood in terms of different physical and chemical properties of the underlying silicon oxide surface as compared to the polyelectrolyte layers. The absence of charge reversal in the presented experiments cannot be explained by electrostatic driving forces within a strict mean-field approach. However, when local interactions are taken into account, multilayer formation can be explained even in the case of exact charge compensation. A delicate balance of local electrostatic and nonelectrostatic interactions as well as the gain of entropy by counterion release is thus responsible for the multilayer formation.[17,32−34] A similar reason is given for the formation of multilayers at high ionic strengths (>0.5 M), where the surface charges are more or less screened.[10] The exact values

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Figure 5. Amplitude of the surface potential oscillations caused by the alternate deposition of polyelectrolytes from a buffer solution containing 50 mM NaCl plotted as a function of the number of adsorbed layers. The signal decrease for the PDADMAC/PSS films (squares) is much less pronounced as for the PAH/PSS films (triangles). Error bars are determined from the peak to peak noise of the measurement. Values for the screening length inside the polyelectrolyte films are obtained from a fit (solid curves).

of the charge densities adsorbing in each step as well as the minimum DC required for the multilayer formation will certainly depend on the system under investigation, as for different polyelectrolytes, a different threshold has been observed.[35]

Screening Effects. The influence of the polyelectrolyte backbone on multilayer properties is studied using two different, fully charged polycations in combination with PSS. We compare the buildup of PDADMAC/PSS layers with the buildup of layers consisting of PAH/PSS. Figure 5 shows the change of the potential at the sensor/polyelectrolyte interface $\Delta\psi$ between adjacent depositions of positively and negatively charged polyelectrolytes from a buffer solution containing 50 mM NaCl as a function of the number of adsorbed layers.

These values represent the amplitude of the oscillating surface potential as depicted in Figure 2. As the adsorption of the outermost polyelectrolyte layer is detected at the interface between the sensor surface and the innermost layer, the thereby caused potential change is screened within the PEMs. Therefore, a signal decrease with increasing number of layers and thus with increasing film thickness is observed for both films, which is attributed to the Debye screening of the multilayer charges by mobile ions within the polymer film. In contrast, the buildup of PDADMAC/PSS and PAH/PSS multilayers on polystyrene particles observed by zeta-potential measurements does not result in a decrease of the measured zeta-potentials with increasing number of layers[5] as the potential is measured outside the PEMs. At the same time, for both polyelectrolyte systems, almost identical zeta-potentials are measured. However, the use of the SOI-based field-effect sensor results in distinct curves for both polyelectrolyte systems. The observed potential decrease is significantly faster for the PAH/PSS film as compared to the PDADMAC/PSS film. The proposed capacitor model[20] allows the screening length κ^{-1} to be obtained inside the multilayer films from the signal decrease. Assuming a sensor capacitance C_S of 2 μF/cm^2 and a minimum average monolayer thickness of 1 nm for the PDADMAC/PSS film,[10] a κ^{-1} of at least 33 nm can be estimated. On the contrary, for the PAH/PSS layers at the same ionic strength of the buffer solution (50 mM NaCl), a κ^{-1} of 6 nm is obtained. Assuming

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thermodynamic equilibrium between mobile ions in solution and those in the polyelectrolyte layers, the ion partitioning is governed by the change of the Born energy between the two phases.[20] Combining this relation with the κ^{-1} obtained from the fit of the signal decrease, the static dielectric constant ϵ of the PEMs can be determined as well as the concentration of mobile ions within the film. We find that the ϵ of the PDADMAC/PSS films must be smaller than 19, whereas for the PAH/PSS films, a significantly higher ϵ of 30 is obtained. At the same time, the concentration of mobile ions within the PDADMAC/PSS film is less than 0.02 mM and therefore more than a magnitude smaller than the value obtained for PAH/PSS (0.9 mM). Thus, the concentration of mobile ions inside the films is reduced by $1-3$ orders of magnitude as compared to the bulk concentration. The different values for ϵ obtained for the two different polycations can be interpreted in terms of the different chemical structure of the polymer backbone. Measurements of the contact angle of PDADMAC and PAH coated surfaces demonstrated a higher hydrophobicity of PDADMAC[36] corresponding to the lower ϵ found in this paper. Different values for the dielectric constants of PDADMAC/PSS films (120) and PAH/PSS films (50) were derived from pyrene fluorescence measurements probing the local polarity of the films.[37] A possible explanation for the deviations from the values of the present paper could be the irreversible rearrangement of the polyelectrolyte matrix caused by the drying procedure preceding the fluorescence measurements.

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Of course, not only the backbone, but also the charge density affects the hydrophobicity. But it is difficult to compare the charge density of both types of polyelectrolytes, since PAH is a weak polyelectrolyte and thus can change the degree of protonation at the interface with respect to the degree of protonation in solution.

Conclusion

The direct measurement of the potential at the silicon oxide/polyelectrolyte interface by a field-effect sensor allows for the quantitative investigation of PEMs formation and properties. We find that the minimum DC required for multilayer formation correlates with the DC necessary for the compensation of the preceding polyelectrolyte charge. Furthermore, nonelectrostatic factors such as backbone hydrophobicity influence the properties of PEMs considerably. For different polycations, significant differences in the dielectric constants of the polyelectrolyte films and in the concentration of mobile ions have been observed, the origin of which will need to be addressed further. The small screening effects inside of low dielectric multilayers may proof useful for the functionalization of biosensing field effect devices.