Supporting Information
Electrical Detection of Self-Assembled Polyelectrolyte Multilayers by a Thin Film Resistor

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1 Theoretical models for the detection of polyelectrolyte multilayers by the SOI-based thin film resistor

1.1 Model a: Alternating layers with volume charges

We model the polyelectrolyte multilayers sensor system as a series of N alternately positively and negatively charged layers with the volume charge distribution $\rho = \pm\frac{\sigma}{d}$ (Figure 4a, main text). The potential in the silicon/silicon oxide structure is assumed to be linear. It is determined by the capacitance per area of the device $C_{\mathrm{S}} = \frac{\varepsilon_1}{d_1}$ which is given by the effective dielectric constant ε_1 and the thickness d_1. The charge of the silicon oxide surface is given by σ_1. In the PEMs, the Debye-Hückel (DH) equation

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi\left(x\right) - \kappa^2\psi\left(x\right) = -\frac{1}{\varepsilon}\rho\left(x\right)$$

is solved for each single polyelectrolyte layer with $\rho\left(x\right) = \pm\frac{\sigma}{d}$. The screening length inside the PEMs is assumed to be κ^{-1} and the dielectric constant is ε. The diffuse electrical double layer in the electrolyte is described by the dielectric constant for water ε_{w} and the screening length κ_0^{-1} which is

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equal to the effective double layer thickness. The actual distribution of counterions at the charged surface is diffuse and reaches the unperturbed bulk value only at large distances from the surface, which is described by an exponential decay of the potential. However, a diffuse double layer behaves like a parallel plate capacitor in which the separation between the plates is given by the screening length κ_0^{-1}. Thus we can describe the potential within the electrolyte by a plate capacitor with the Debye capacitance per area $C_{\mathrm{D}} = \varepsilon_{\mathrm{w}}\varepsilon_0\kappa_0$. The surface charges σ_0 and σ_L represent the space charges within the seminconductor and the electrical double layer of the electrolyte, respectively. The potential difference between the bulk semiconductor and the bulk electrolyte is U_{tot} and is set by the reference electrode. The potential ψ within the $N + 2$ domains (i), (ii)$_1$, ..., (ii)$_N$, and (iii) is given by

$$
\begin{aligned}
\psi_{(\mathrm{i})}(x) &= A'x + A, \\
\psi_{(\mathrm{ii})_n}(x) &= C_n \exp(-\kappa x) + D_n \exp(\kappa x) + \psi_n(x), \qquad n = 1, \ldots, N \\
\psi_{(\mathrm{iii})}(x) &= B'x + B,
\end{aligned}
$$

where $C_n \exp(-\kappa x) + D_n \exp(\kappa x)$ is the general solution of the homogeneous DH equation and $\psi_n(x)$ is a particular solution of the inhomogeneous DH equation for $\rho(x) = -\frac{\sigma}{d}(-1)^n$. We apply the following boundary conditions

$$
\begin{aligned}
\psi_{(\mathrm{i})}(0) &= 0, & \psi'_{(\mathrm{i})}(0) &= -\frac{\sigma_0}{\varepsilon_1}, \\
\psi_{(\mathrm{iii})}(x_L) &= U_{\mathrm{tot}}, & \psi'_{(\mathrm{iii})}(x_L) &= \frac{\sigma_L}{\varepsilon_{\mathrm{w}}},
\end{aligned}
$$

$$
\begin{aligned}
\psi_{(\mathrm{ii})_1}(x_1) - \psi_{(\mathrm{i})}(x_1) &= 0, & \varepsilon\psi'_{(\mathrm{ii})_1}(x_1) - \varepsilon_1\psi'_{(\mathrm{i})}(x_1) &= -\sigma_1, \\
\psi_{(\mathrm{iii})}(x_{N+1}) - \psi_{(\mathrm{ii})_N}(x_{N+1}) &= 0, & \varepsilon_{\mathrm{w}}\psi'_{(\mathrm{iii})}(x_{N+1}) - \varepsilon\psi'_{(\mathrm{ii})_N}(x_{N+1}) &= 0, \\
\psi_{(\mathrm{ii})_n}(x_n) - \psi_{(\mathrm{ii})_{n-1}}(x_n) &= 0, & \varepsilon\psi'_{(\mathrm{ii})_n}(x_n) - \varepsilon\psi'_{(\mathrm{ii})_{n-1}}(x_n) &= 0, \qquad n = 2, \ldots, N
\end{aligned}
$$

with

$$
\begin{aligned}
x_n &= d_1 + (n-1)d, \qquad n = 1, \ldots, N+1, \\
x_L &= d_1 + Nd + \kappa_0^{-1}.
\end{aligned}
$$

These conditions allow us to calculate the potential $\psi_{\mathrm{S}} = \psi(x_1)$ which determines the sheet resistance of the device. If we define the Debye capacitance per area $C_{\mathrm{P}} = \varepsilon\varepsilon_0\kappa$ within the polyelectrolyte medium we can write ψ_{S} as

$$\psi_{\mathrm{S}}(N) = \frac{(\sigma_1 + \sigma_{\mathrm{eff}})\left[\frac{1}{C_{\mathrm{P}}}\sinh\left(\kappa Nd\right) + \frac{1}{C_{\mathrm{D}}}\cosh\left(\kappa Nd\right)\right] + \left(U_{\mathrm{tot}} - \frac{1}{C_{\mathrm{D}}}(-1)^N\sigma_{\mathrm{eff}}\right)}{(C_{\mathrm{S}}/C_{\mathrm{P}} + C_{\mathrm{P}}/C_{\mathrm{D}})\sinh\left(\kappa Nd\right) + (1 + C_{\mathrm{S}}/C_{\mathrm{D}})\cosh\left(\kappa Nd\right)}$$

with the effective polyelectrolyte surface charge

$$\sigma_{\mathrm{eff}} = \frac{1}{\kappa d}\left[\frac{1 - \exp\left(-\kappa d\right)}{1 + \exp\left(-\kappa d\right)}\right]\sigma.$$

1.2 Model b: Charges overlapping within the PEMs

The polyelectrolyte multilayers are modeled as overlapping and charges are assumed to be completely neutralized within the PEMs. Thus the only uncompensated charges occur at the sensor surface and the PEMs/electrolyte interface (Figure 4b, main text). In this case the potential within the three domains is given by

$$\begin{aligned}
\psi_{\mathrm{(i)}}\left(x\right) &= A'x + A, \\
\psi_{\mathrm{(ii)}}\left(x\right) &= C\exp\left(-\kappa x\right) + D\exp\left(\kappa x\right), \\
\psi_{\mathrm{(iii)}}\left(x\right) &= B'x + B.
\end{aligned}$$

We apply the following boundary conditions

$$\begin{aligned}
\psi_{\mathrm{(i)}}\left(0\right) &= 0, & \psi'_{\mathrm{(i)}}\left(0\right) &= -\frac{\sigma_0}{\varepsilon_1}, \\
\psi_{\mathrm{(iii)}}\left(x_L\right) &= U_{\mathrm{tot}}, & \psi'_{\mathrm{(iii)}}\left(x_L\right) &= \frac{\sigma_L}{\varepsilon_{\mathrm{w}}},
\end{aligned}$$

$$\begin{aligned}
\psi_{\mathrm{(ii)}}\left(x_1\right) - \psi_{\mathrm{(i)}}\left(x_1\right) &= 0, & \varepsilon\psi'_{\mathrm{(ii)}}\left(x_1\right) - \varepsilon_1\psi'_{\mathrm{(i)}}\left(x_1\right) &= -\left(\sigma_1 + \frac{\sigma}{2}\right), \\
\psi_{\mathrm{(iii)}}\left(x_2\right) - \psi_{\mathrm{(ii)}}\left(x_2\right) &= 0, & \varepsilon_{\mathrm{w}}\psi'_{\mathrm{(iii)}}\left(x_2\right) - \varepsilon\psi'_{\mathrm{(ii)}}\left(x_2\right) &= (-1)^N\frac{\sigma}{2},
\end{aligned}$$

with

$$
\begin{aligned}
x_1 &= d_1, \\
x_2 &= d_1 + Nd, \\
x_L &= d_1 + Nd + \kappa_0^{-1}.
\end{aligned}
$$

These conditions allow us to calculate the potential $\psi_{\mathrm{S}} = \psi(x_1)$ and we can write ψ_{S} according to

$$
\psi_{\mathrm{S}}(N) = \frac{\left(\sigma_1 + \frac{\sigma}{2}\right)\left[\frac{1}{C_{\mathrm{P}}}\sinh\left(\kappa Nd\right) + \frac{1}{C_{\mathrm{D}}}\cosh\left(\kappa Nd\right)\right] + \left(U_{\mathrm{tot}} - \frac{1}{C_{\mathrm{D}}}(-1)^N\frac{\sigma}{2}\right)}{(C_{\mathrm{S}}/C_{\mathrm{P}} + C_{\mathrm{P}}/C_{\mathrm{D}})\sinh\left(\kappa Nd\right) + (1 + C_{\mathrm{S}}/C_{\mathrm{D}})\cosh\left(\kappa Nd\right)}.
$$

This is the same result which was obtained for model a if σ_{eff} in that model is replaced by $\frac{\sigma}{2}$. The two models represent limiting cases of the charge distribution. Thus in our models the charge distribution within the PEMs is not crucial for the values obtained for κ^{-1} and ε, respectively. For $\kappa d \ll 1$ and even numbers of N the potential difference $\Delta\psi_{\mathrm{S}} = \psi_{\mathrm{S}}(N-1) - \psi_{\mathrm{S}}(N)$ simplifies to eq 1 (main text). The potential ψ_{S} can now be calculated within the present model as a function of the number N of layers deposited as shown in Figure 1.

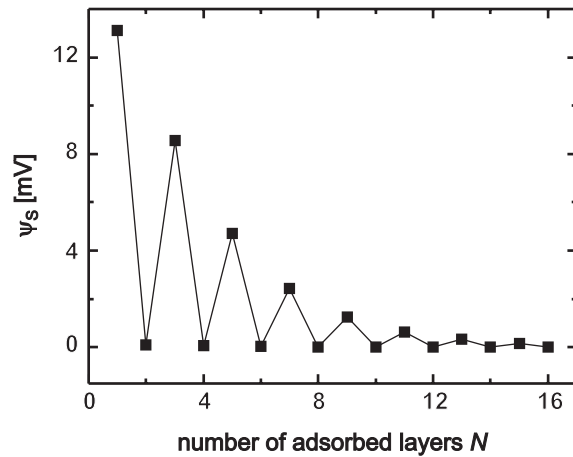Figure 1: The potential ψ_{S} was calculated within the model for the deposition from a salt concentration of 500 mM and plotted as a function of the number of adsorbed layers N. The solid lines are a guide to the eye. For the calculation the following parameters were assumed: $C_{\mathrm{S}} = 2 \times 10^{-3}\ \frac{\mathrm{F}}{\mathrm{m}^2}$, $d = 2.2$ nm, $\kappa^{-1} = 6.5$ nm, $\varepsilon = 21$, $\sigma_1 = -1.25 \times 10^{-2}\ \frac{\mathrm{C}}{\mathrm{m}^2}$ and $\sigma = 2.5 \times 10^{-2}\ \frac{\mathrm{C}}{\mathrm{m}^2}$. In the calculation the voltage between the bulk semiconductor and the bulk electrolyte was set to 7 mV.

2 Ion-partitioning between PEMs and the bulk solution

One can calculate the concentration of ions inside the PEMs from the thermodynamic equilibrium condition with the bulk solution by minimizing the total free energy density (that is free energy per unit volume) of the PEMs/bulk electrolyte system as follows.

The total free energy density consists of the free energy density of the electrical double layer outside the PEMs, $\mathcal{F}_0$, and the free energy density of the PEMs medium $\mathcal{F}_\mathrm{P}$. Within the Debye-Hückel description, the former contribution may be written as $\mathcal{F}_0 = \mathcal{F}_0^{\mathrm{MF}} + \mathcal{F}_0^{\mathrm{corr}} + \mathcal{F}_0^{\mathrm{self}}$ (in units of kT) comprising the mean-field electrostatic free energy density of the double-layer, $\mathcal{F}_0^{\mathrm{MF}}$, the Debye-Hückel correlation (or excess) free energy density, $\mathcal{F}_0^{\mathrm{corr}}$, and the self-energy density of the ions, $\mathcal{F}_0^{\mathrm{self}}$. Note that $\mathcal{F}_0^{\mathrm{corr}}$ takes into account the fact that each ion in the electrolyte is surrounded mostly by oppositely charged ions, which amounts to the standard correlation free energy expression $\mathcal{F}_0^{\mathrm{corr}} = -\kappa_0^3/12\pi$, where $\kappa_0 = (8\pi\ell_\mathrm{B}^0 c_0)^{1/2}$ is the bulk inverse screening length with $\ell_\mathrm{B}^0 = e^2/(4\pi\varepsilon_\mathrm{w}\varepsilon_0 kT)$ being the bulk Bjerrum length.[1] It follows that within the DH approximation, the mean-field free energy $\mathcal{F}_0^{\mathrm{MF}}$ is dominated by the entropy of the ions, which is well-approximated by that of an ideal gas of particles, i.e. $\mathcal{F}_0^{\mathrm{MF}} \simeq 2(c_0 \ln c_0 - c_0)$ assuming the bulk 1-1 electrolyte concentration of c_0. Finally the self-energy contribution of ions reads $\mathcal{F}_0^{\mathrm{self}} = 2c_0\ell_\mathrm{B}^0/2a$ (in units of kT).

Similar expressions may be written for the PEMs medium using the inverse screening length $\kappa = (8\pi\ell_\mathrm{B}c)^{1/2}$, the Bjerrum length $\ell_\mathrm{B} = e^2/(4\pi\varepsilon\varepsilon_0 kT)$ and the ionic concentration c. In this case, the mean-field free energy is again approximated by that of an ideal gas since the net charge within the PEMs is assumed to be zero. One thus has $\mathcal{F}_\mathrm{P}(c) = 2(c \ln c - c) - \kappa_0^3/(12\pi) + 2c\ell_\mathrm{B}/2a$.

Thermodynamic equilibrium is imposed by minimizing $\mathcal{F}_\mathrm{P}(c) + \mathcal{F}_0(c_0)$ with respect to the ion concentration c inside the PEMs, assuming that $c + c_0$ is constant, which is equivalent to setting equal chemical potentials for the two media. One thus finds the ion-partitioning law $c = c_0 \exp(-\Delta\mu/kT)$, where

$$\Delta\mu = \frac{\ell_\mathrm{B}}{2}\left(\frac{1}{a} - \frac{1}{\kappa^{-1}}\right) - \frac{\ell_\mathrm{B}^0}{2}\left(\frac{1}{a} - \frac{1}{\kappa_0^{-1}}\right).$$

The terms proportional to $1/a$ (with a being the mean ion radius) are due to the self-energy (Born energy) difference of the ions in the two media, whereas the terms proportional to the Debye screening

length come from the DH correlation free energy difference. Since κ^{-1} and κ_0^{-1} are typically much larger than a, one can neglect this latter contribution. In fact, an explicit estimate of the dielectric constant of the PEMs, ε, including the DH correlation free energy shows slightly larger values (up to a few percents) as compared with the results reported in the text (obtained based only on the Born energy). The difference is however within the experimental error bars.

References

[1] Resibois, P. M. V. *Electrolyte Theory*; Harper & Row: New York, 1968.