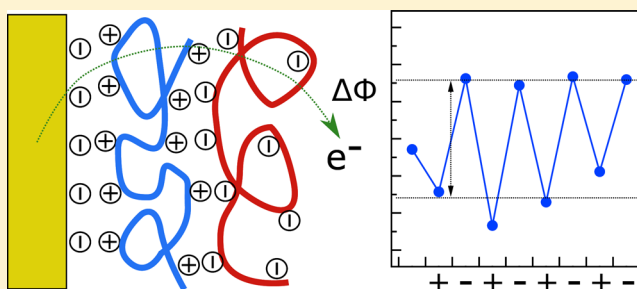


# Simplified Approach to Work Function Modulation in Polyelectrolyte Multilayers

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**ABSTRACT:** The layer-by-layer (LbL) method is based on sequential deposition of polycations and polyanions. Many of the properties of polyelectrolyte thin films deposited via this method depend on the nature of the topmost layer. Thus, these properties show odd–even oscillations during multilayer growth as the topmost layer alternates from polycations to polyanions. The work function of a (semi)conductive substrate modified with an LbL polyelectrolyte multilayer also displays an oscillatory behavior independent of film thickness. The topmost layer modulates the work function of a substrate buried well below the film. In agreement with previous observations, in this work, we show that the work function of a gold substrate changes periodically with the number of adsorbed layers, as different combinations of polycations and polyanions are deposited using the LbL method. For the first time, we rationalize this behavior in terms of formation of a dipole layer between the excess charge at the topmost layer and the charge of the metal substrate, and we put forward a semiquantitative model based on a continuum description of the electrostatics of the system that reproduces the experimental observations.



## INTRODUCTION

The layer-by-layer (LbL) method<sup>1,2</sup> is arguably among the most versatile and successful tools for thin-film deposition. There exist hundreds of works that explore the applications of thin multilayer films prepared using LbL deposition. The deposition process comprises the sequential adsorption of polyelectrolytes of alternating charge. In a first step, the substrate to be modified is immersed in a solution of an oppositely charged polyelectrolyte (e.g., a negatively charged substrate is immersed in a solution of a polycation). The polyelectrolyte adsorbs on the substrate surface, reverting its original charge. The substrate is then rinsed and immersed in a solution of an oppositely charged polyelectrolyte (in our example, a solution of a polyanion), which also adsorbs and inverts the surface charge. The film is grown by sequentially exposing the substrate to the polycation and polyanion solutions until the desired number of layers is achieved. The polyelectrolyte chains adsorbed in each adsorption step constitute a layer, and the neighboring layers are highly interpenetrated.<sup>2</sup> The inner structure of LbL films is generally described in terms of a three-zone model.<sup>3</sup> Zone I in the model comprises the first few polyelectrolyte layers, which are located closest to the substrate. Zone III spans the last few layers (including, but not limited to, the topmost layer), which are located at the film/polyelectrolyte interface and have an excess of charge given by the topmost layer charge. Zone II comprises the layers between zone I and zone III, and it is typically free of mobile ions because polycation and polyanion charges are stoichiometrically compensated (intrinsic compensation).<sup>4</sup>

Despite the outstanding technological appeal of LbL films and the existence of qualitative structural models, several fundamental aspects related to the formation and inner structure of LbL films remain unclear. For example, many properties of the film, such as water content<sup>5,6</sup> and mobility,<sup>7</sup> thermal behavior,<sup>8</sup> electrochemical charge transport,<sup>9,10</sup> and electrocatalytic properties,<sup>11</sup> depend on the charge of the polyelectrolyte at the topmost layer, and therefore, these properties exhibit odd–even oscillations during the multilayer buildup. Note that these properties are “bulk” properties (i.e., they depend on the structures of zones I to III, not just the interfaces), and therefore, for very thick films, they are not expected to change appreciably when the composition of the topmost layer (zone III) is changed. In practice, however, these odd–even effects are not attenuated by the number of layers in the film, even for films much thicker than the lengthscale of interpenetration between neighboring layers.<sup>2</sup> Furthermore, the charge of the topmost layer can strongly affect the properties of the polyelectrolytes located near the substrate/film interface (zone I): Xie and Granick assembled multilayers of a strong polycation and a strong polyanion on top of a layer of a weak polycarboxylic acid and showed that the degree of ionization of the carboxylic groups in the polycarboxylic acid oscillated between 30% and 80%, depending on the charge of the topmost adsorbed layer.<sup>12</sup> The set of results described above suggests the presence of long-range mechanisms by which the

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nature of the topmost layer can affect the properties of the whole film.

In organic electronics, one of the most important properties of organic thin films is their capacity to control the work function of the underlying conductive substrate. Work function control aligns the transport levels of the conductor and the organic semiconductor, improving carrier injection or extraction, with great importance in the performance of organic electronic devices.<sup>13</sup> The work function change of semiconducting or conducting substrates due to LbL polyelectrolyte films is controlled by the topmost layer, and it exhibits odd–even oscillations independent of the number of deposited layers.<sup>14–18</sup> This is accounted for qualitatively in terms of the alternate reversal of a surface dipole upon sequential deposition of polyelectrolyte layers. In the present investigation, the modulation of a gold substrate work function is followed as a function of the number of deposited layers in LbL polyelectrolyte films grown using four different combinations of polycations and polyanions. Furthermore, a mechanism for the formations of a surface dipole and a model that accounts for the observed phenomenon are put forward. The novelty of our work is the introduction of the first semiquantitative model for the oscillations of the work function with the number of adsorbed layers. Our model explains the fact that the oscillations are not dampened by film thickness, the effect of ionic strength, and the potential of the substrate on the oscillations.

## EXPERIMENTAL SECTION

**Materials.** All solutions were prepared using ultrapure type I water. The following chemicals were used without further purification: poly(diallyldimethylammonium chloride) (PDDA, Aldrich); poly(allylamine hydrochloride) (PAH, Aldrich); poly(acrylic acid) (PAA, Aldrich); poly(sodium vinyl sulfonate) (PVS, Aldrich); sodium 3-mercaptopropane-sulfonate, (MPS, Aldrich); and 2-mercapto ethylamine hydrochloride (MEA, Aldrich). The chemicals employed in electrolyte solutions, NaOH, HCl, and NaCl, were of analytical grade and used as received. The concentration of the polyelectrolyte solutions was 20 mM, and the pH was 8.5 for PAH and 3 for PAA.

**Sample Preparation.** Au substrates were prepared by coating silicon (100) surfaces with a 15 nm titanium and 30 nm palladium adhesion layer and a 90 nm gold layer thermally evaporated using an Edwards Auto 306 vacuum coating system. The Au substrates were cleaned by exposure to UV–ozone for 20 min (PSD Pro Series UV Ozone System, Novascan) followed by ethanol rinsing.<sup>19</sup> The polyelectrolyte film was grown as follows. In the first step, the Au surface was functionalized with a self-assembled monolayer (SAM) of sulfonate groups by immersing the clean Au substrate into an MPS solution for 2 h. This was followed by copious rinsing with ultrapure water and drying using N<sub>2</sub>. After the MPS SAM formation, the first polycation layer was deposited on the Au/MPS substrate by immersing in the PDDA or PAH solution for 15 min, followed by substantial rinsing with ultrapure water. The next and subsequent layers were deposited onto the modified surface by alternate immersion in a solution of the respective polyanion (PVS or PAA) or polycation (PDDA or PAH) for 15 min and rinsing with Milli-Q water until the desired number of layers was achieved. Before work function measurements, the samples were dried under an N<sub>2</sub> gas flow.

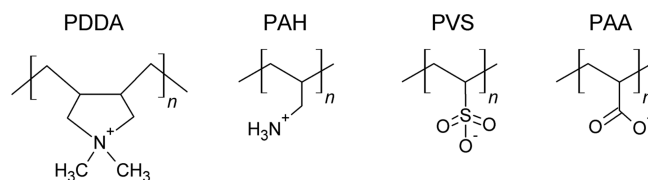
**Work Function Measurements.** Absolute work function values were obtained from the secondary electron cutoff in the ultraviolet photoelectron spectroscopy (UPS) spectra as discussed below. UPS measurements were performed using an ultrahigh vacuum chamber (UHV; base pressure < 5 × 10<sup>−10</sup> mbar) with a SPECS UHV spectrometer system equipped with a hemispherical electron energy analyzer having a mean radius of 150 mm and a nine channeltron detector. UPS spectra were acquired with normal detection at a

constant pass energy of 2 eV using a He I radiation source (21.2 eV). The samples were biased at −10 V to resolve the secondary electron cutoff in the UPS spectra. Furthermore, the work function changes were measured using a single-point ambient Kelvin Probe (KPSP KP Technology) under an N<sub>2</sub> atmosphere at room temperature using a 2 mm diameter vibrating tip. Tips were cleaned with UV–ozone for 20 min before use. The work function was reported as an average value of 50 measurements in three different sample positions with an error bar given by one standard deviation of the measured values.

## RESULTS AND DISCUSSION

Scheme 1 shows the molecular structures corresponding to the four polyelectrolyte molecules employed in this work: two

**Scheme 1. Molecular Structures of the Polycations and Polyanions Employed in This Work<sup>a</sup>**

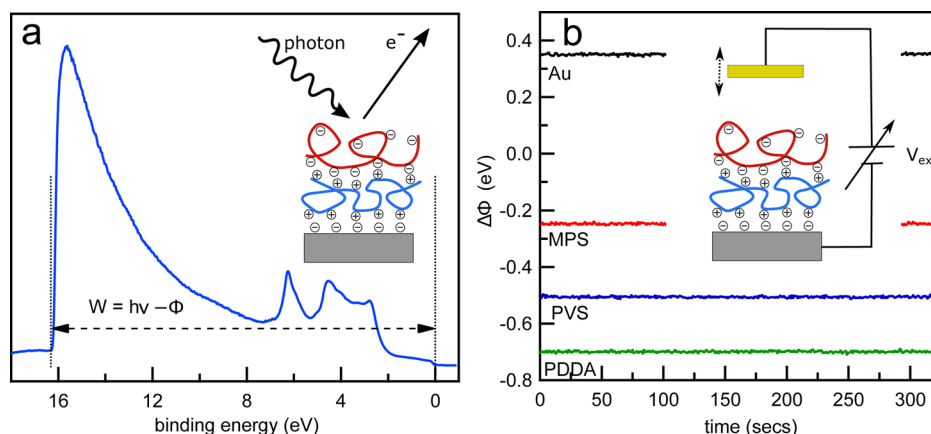


<sup>a</sup>Note that in solution, these polymers are charged and counterions are present, balancing charges to ensure electroneutrality.

polycations, PDDA and PAH and two polyanions, PVS and PAA. PDDA and PVS are strong polyelectrolytes, whereas PAH and PAA are weak polyelectrolytes. The effect of the polyelectrolyte multilayer on the work function of the underlying metal substrate was followed as a function of the number of deposited layers for the four possible combinations: PDDA/PVS (strong/strong), PDDA/PAA (strong/weak), PAH/PVS (weak/strong), and PAH/PAA (weak/weak).

Work function changes are usually determined using UPS or the KP method. In the first case, the absolute value of the work function can be determined from the secondary electron cutoff in the UP spectrum.<sup>20</sup> The UP spectrum of clean Au substrate in Figure 1a shows the Fermi edge, a broad 6s band followed by several peaks corresponding to the 5d bands and a secondary electron tail that cuts off at approximately 16.2 eV. The absolute work function  $\Phi$  can be determined from the width  $W$  of the UP spectrum using the following relation  $\Phi = 21.1 \text{ eV} - W$ . This yields a value of approximately 5 eV for the initial Au substrate, in good agreement with previously reported values for polycrystalline gold.<sup>21</sup>

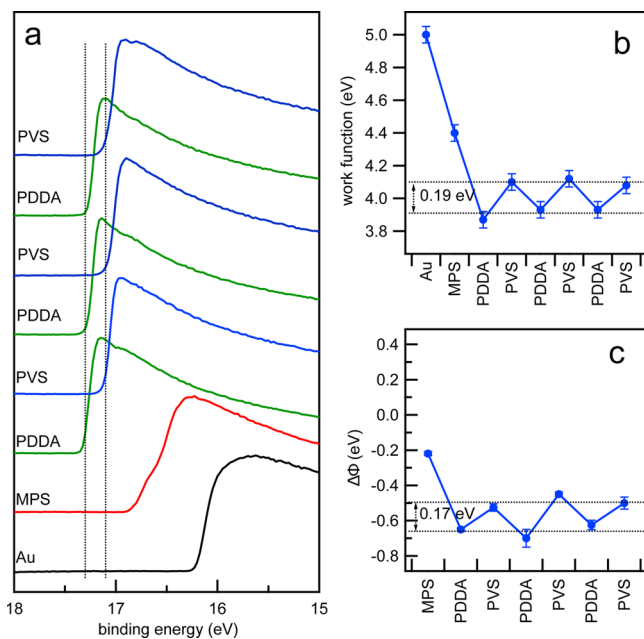
Conversely, the KP method is an indirect noncontact technique to determine work function differences between a conductive sample and a reference electrode or tip. The basic principle behind the KP method is illustrated in the inset of Figure 1b. When the sample is placed in electrical contact with the tip, the two Fermi levels equalize and a contact potential difference develops, forming a parallel-plate capacitor.<sup>22</sup> The tip position is vibrated periodically above the sample, generating an alternate current. In the simplest case, the work function difference between the sample and the tip is determined by applying an external voltage that cancels the current flow. Here, the more precise off-null detection method was employed.<sup>23</sup> Figure 1b shows the work function change ( $\Delta\Phi$ ) determined using the KP method of: (i) the initial clean Au substrate (Au), (ii) the Au surface modified with MPS (Au/MPS), (iii) the surface after the subsequent deposition of a PDDA layer (Au/MPS/PDDA), and (iv) the surface after the subsequent deposition of a PVS layer (Au/MPS/PDDA/PVS). The



**Figure 1.** (a) UPS spectrum of the bare Au substrate and (b) changes in the work function of modified Au substrates determined using the KP method.

reference tip work function can be determined from the change in work function corresponding to the clean Au substrate  $\Delta\Phi = \Phi_{\text{Au}} - \Phi_{\text{tip}} = 0.35$  eV and the Au substrate absolute work function of 5 eV determined by UPS, yielding a value of  $\Phi_{\text{tip}} = 4.65$  eV.

Figure 2a shows the secondary electron cutoff in the UP spectra, and Figure 2b shows the respective work function

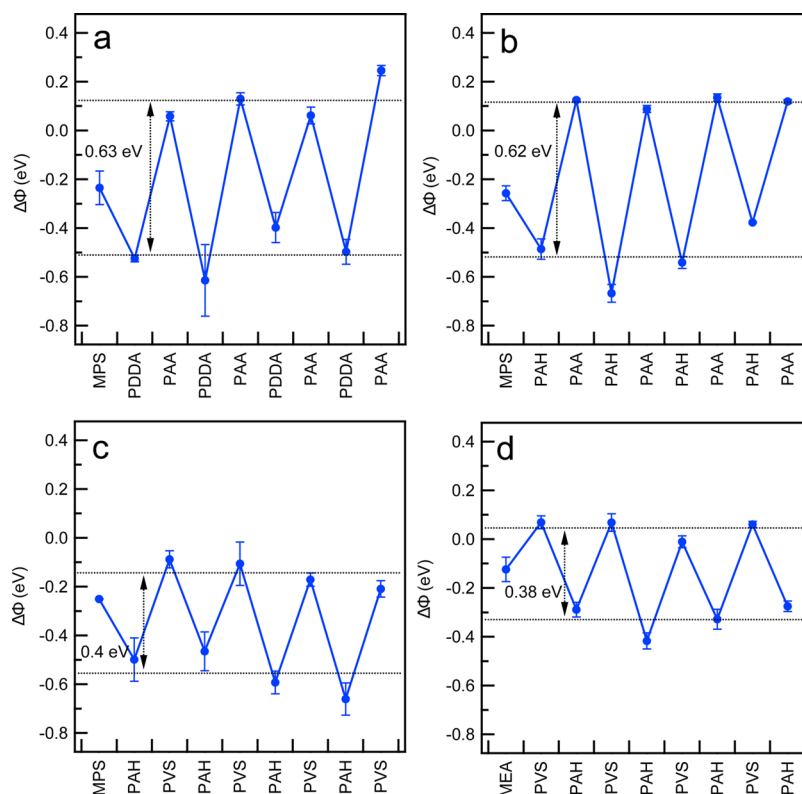


**Figure 2.** (a) UP spectra secondary electron cutoff, (b) absolute work function values, and (c) work function changes determined using the KP method of an Au substrate modified with different successive layers.

values corresponding to the clean Au substrate, Au modified with MPS, and subsequent layers of PDDA and PVS grown on the top. Figure 2c shows the work function change measured using the KP method for the same system, that is, as a function of the deposition of PDDA and PVS layers. Two things should be noticed. First, the MPS SAM lowers the work function of the Au substrate by 0.6 eV. This observation deserves some discussion before getting to the second point: although the quality of the organic film is an important factor determining the magnitude of the work function change, we have observed a

similar work function change for the MPS SAM on Au using different Au substrates and different deposition conditions. Furthermore, our experimental observation is in complete agreement with the measurements of Cho and co-workers, who also observed a work function decrease of about 0.6 eV for the MPS SAM grown over Ag surfaces.<sup>24</sup> Using the very simple electrostatic model presented in Figure 4 below, a SAM layer terminated with negative charges (as the MPS layer) should result in a work function increase which is contrary to the experimental findings. Thus, considering only the intrinsic molecular dipole does not suffice to explain the observed work function decrease. Therefore, we need to consider the dipole formed at the metal–SAM interface (head dipole) and at the SAM–vacuum interface (tail dipole). The sign of the total work-function change induced by the SAM depends on the relative magnitude of the head and tail dipole moments of the SAM. For short chains, there is a strong electrostatic interaction between the two dipoles which depolarizes them decreasing their magnitude. Sushko and Shluger demonstrated that the polarizability of the tail groups of alkylthiol SAMs is the main figure of merit determining the SAM-induced work function change,<sup>25</sup> explaining why short alkanethiols with negative tail groups could result in a decrease in the work function of the underlying metal as we observed here. The second point to be noted in Figure 2c is that the consecutive deposition of PDDA and PVS layers results in a periodic work function oscillation, where the last layer controls the work function value. Indeed, polycations result in lower work function values than polyanions. Finally, the excellent agreement between the absolute (UPS) and relative (KP) measurements should be noted.

Figure 3 shows the effect of the layer-by-layer growth of the rest of the polyelectrolyte combinations on the work function change of the underlying Au substrate as determined with KP. Figure 3a shows  $\Delta\Phi$  for the sequential deposition of PDDA/PAA polyelectrolyte layers, 3b shows  $\Delta\Phi$  for PAH/PAA, and 3c shows  $\Delta\Phi$  for PAH/PVS. The same general trend is observed, in agreement with the data presented in Figure 2, that is, as the polyelectrolyte layers are deposited over the Au/MPS substrate,  $\Delta\Phi$  oscillates with a minimum value for the polycation-terminated film and a maximum for the polyanion-terminated film. This behavior was reproduced for the sequential deposition of up to 14 polyelectrolyte layers. Note that in these cases, the amplitude of the  $\Delta\Phi$  oscillation lies in the 0.4–0.6 eV range, that is, much larger than the amplitude

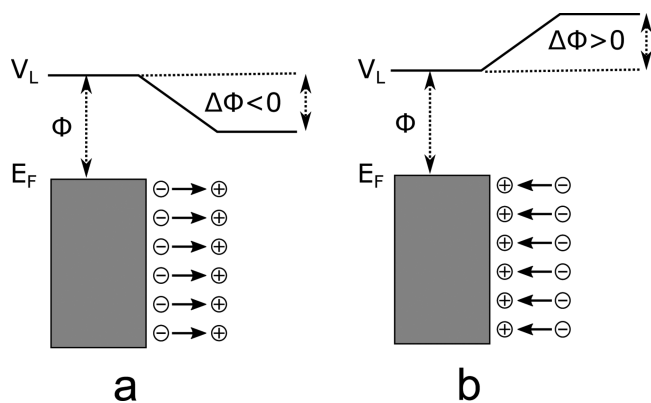


**Figure 3.** Work function change determined with the KP method for the deposition of (a) PDDA/PAA layers, (b) PAH/PAA layers, (c) PAH/PVS layers over Au/MPS substrates, and (d) PVS/PAH layers over MEA/Au substrates.

observed for the PDDA/PVS system of around 0.2 eV observed in Figure 2. This difference is due to the different excess charge densities at the topmost layer of the film, as we explain below with our model. The PDDA/PVS system is expected to have a smaller thickness per layer, and thus, a smaller excess charge density at the topmost region of the film than the other systems. Finally, to rule out the influence of the initial MPS negative SAM on the oscillations of  $\Delta\Phi$  during the assembly of the polyelectrolyte film, a new Au sample was prepared by modifying the bare substrate with MEA, a positive SAM. These data are shown in Figure 3d for the growth of PVS/PAH layers. In agreement with the data shown in Figure 3c,  $\Delta\Phi$  oscillates with an amplitude of around 0.4 eV with a minimum for the polycation and a maximum for the polyanion. Overall, the data presented in Figures 2 and 3 are in agreement with all previous studies that report a periodic behavior in the work function change of polyelectrolyte films grown layer by layer: the work function change is only determined by the nature of the last layer, and the films terminated with polycations give lower work function values than the films terminated with polyanions.<sup>14–18</sup> Although the oscillations arise from the charge at the topmost layer, it is not clear how the surface dipole responsible for the work function modification is formed in the dry film. In other words, it is not clear where the second plane of charge (required to compensate the charge of the topmost layer and form the dipole) is located and why the amplitude of the oscillations does not change with the thickness of the film. These were open questions that we address here for the first time with the model presented below. We propose that the oscillations are the result of the formation of a dipole from the excess charge at the metal substrate and the uncompensated charges at the topmost region of the LbL film. This

organization results from the electrostatic potential profile of the system in solution upon the condensation of the counterions onto the polyelectrolyte during drying.

The work function ( $\Phi$ ) is the energy required to remove one electron from the Fermi level and place it at rest in the vacuum level (a point just outside of the surface where the image-charge forces have declined to zero).<sup>26</sup> The work function is thus composed of the chemical potential ( $\mu$ ) of the electron and the contribution necessary to overcome the electrostatic potential across the surface dipole layer, that is, the surface potential ( $\chi$ ):  $\Phi = \mu - e\chi$ .<sup>27</sup> The first term contributing to the work function is a bulk contribution determined by the attraction for its electrons by the lattice of positive ions as a whole, whereas the second term is a surface contribution determined by the dipole layer formed after the spilling over of electron density from the metal into the vacuum<sup>28</sup> when the surface is clean. This intrinsic surface dipole layer could be modified by adsorbates, modifying the work function because of changes in the electrostatic potential across the surface dipole layer, that is,  $\Delta\Phi = -e\Delta\chi$ . If adsorbed molecules form a 2D dipole layer, the change in surface potential would be equal to the potential across a parallel-plate capacitor, that is,  $\Delta\chi = \sigma \times \delta / (\epsilon_r \epsilon_0)$ , where  $\sigma$  is the charge density ( $Q/A$ ),  $\delta$  is the dipole thickness,  $\epsilon_r$  is the relative dielectric constant of the dipole layer, and  $\epsilon_0$  is the dielectric permittivity of vacuum.<sup>29</sup> This simple electrostatic model shown in Figure 4 indicates that a dipole layer with negative (positive) charges residing at the metal/monolayer interface and positive (negative) charges at the monolayer/vacuum interface causes a work function decrease (increase).<sup>28</sup> Organic adsorbates can form or modify the interfacial dipole layer by many different mechanisms: (i) electron transfer between the molecule and the conductive substrate, (ii)

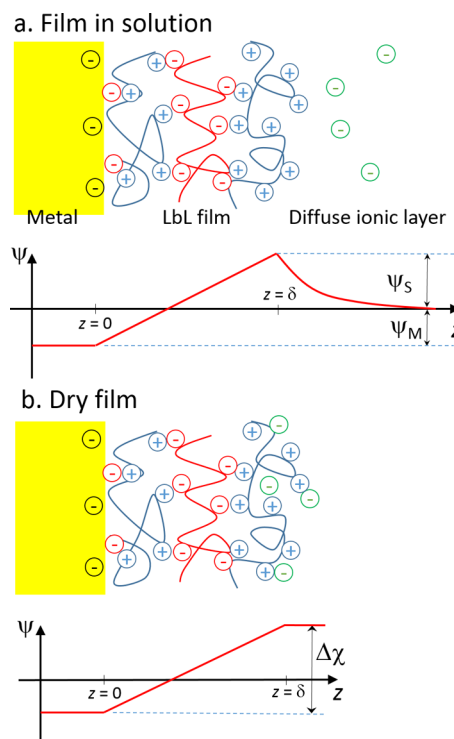


**Figure 4.** Work function change caused by a dipole layer terminated in (a) positive charges and (b) negative charges.

adsorption of molecules with a permanent molecular dipole, (iii) formation of a chemical bond between the molecule and the substrate creating a bond dipole, (iv) formation of an image charge in the metal that could polarize nonpolar molecules or reinforce intrinsic molecular dipoles, and (v) push back into the metal of the electron cloud spilling over the metal surface.<sup>30</sup> The push back effect reduces the surface dipole lowering the vacuum level relative to the Fermi edge, and thus, it always reduces the substrate work function.<sup>31</sup>

The direct adsorption of a single layer polyelectrolyte thin film over conductive substrates leads to a change in the substrate work function, which is interpreted in terms of the formation of an interfacial dipole. Hence, it is argued that the deposition of polycations lowers the work function as they form a dipole with positive charges at the polyelectrolyte/vacuum interface, whereas the deposition of polyanions increases the work function as they form a dipole layer with negative charges at the polyelectrolyte/vacuum interface.<sup>32,33</sup> However, the manner in which permanent dipoles are generated from the ionic functionalities, the distribution of charges so that global electroneutrality is ensured, and the factors that determine the magnitude of the interfacial dipoles are not explained. Here, we should note that the work function modification of (semi)-conducting substrates by a single polyelectrolyte layer has been recently explained with a qualitatively model based upon the formation of a surface dipole in the polyelectrolyte layer due to the different mobilities of charges in this layer and an image-charge dipole in the substrate.<sup>34</sup> Although this model was used successfully to account for the experimental observations made by the authors, it is a qualitative model that cannot be used directly to rationalize our observations.

We will describe here a semiquantitative model to explain our experimental observations. When the film is in contact with a solution (before drying), global electroneutrality requires the sum of the charges at the topmost layer, the charge of the mobile ions in the diffuse ionic layer, and the charge at the metal to be zero (see the schemes of the system and the electrostatic potential profile in Figure 5a). Note that the LbL film is electrically neutral with the exception of the charge at the topmost layer. As we show below, the charge distribution described in Figure 5a naturally results from solving the electrostatics of the system in solution. However, the work function of dry LbL films is measured; therefore, we must consider how the charge distribution described above changes upon drying. X-ray photoelectron spectroscopy and conductance experiments have shown that drying a charged



**Figure 5.** Schemes showing the proposed structure of the metal/film system before (a) and after (b) drying and the electrostatic potential profiles for both cases. In the case where the metal/film system is immersed in solution (a), the sum of the excess charge in the topmost layer, the charge on the metal surface, and the charge of the diffuse ionic layer is zero. After drying (b), it is proposed that the ions of the diffuse ionic layer collapse onto the polyelectrolyte charges in the topmost layer of the film; however, the charge at the metal remains unaffected. The charge at the metal and the remaining charge at the topmost layer are equal in magnitude but opposite in polarity; therefore, they form a dipole that modifies the work function of the substrate.

substrate collapses the counterions of the diffuse ionic layer onto the surface.<sup>35</sup> On the basis of this result, we propose that drying the LbL film condenses the counterions onto the charges of the topmost layer, partially neutralizing them. The remaining charges at the topmost layer are now electrically compensated by the charge at the metal, which did not change during drying (see the scheme and the electrostatic potential profile in Figure 5b). Therefore, in the dry film, the excess charge at the topmost layer and the charge of the metal have equal magnitude and opposite polarity, and thus, they form an electrical dipole.

Let us consider the system in solution shown in Figure 5a. The charge density of the metal is  $\sigma_M$  and its (Volta) electrostatic potential is  $\Psi_M$  (we use the reference  $\Psi = 0$  for a point in the bulk solution). The electrode potential of a metal electrode immersed in a solution is set by the presence of Faradaic reactions due to redox couples in the solution (added on purpose or present in trace amounts). For example, in “pure” water, a Faradaic reaction may be due to the oxygen dissolved in solution. For a fixed electrode potential, the electrostatic potential difference between the metal and the solution  $\Psi_M$  should be constant and independent of the content of the interface;<sup>36</sup> therefore, we will assume that  $\Psi_M$  is independent of the thickness and nature of the topmost layer of the film. This assumption is supported by LbL-deposition

experiments on indium tin oxide (ITO) electrodes, which showed that the change in the open circuit potential has no clear trends with the number and type of deposited polyelectrolyte layers.<sup>37</sup>

We model the LbL film as a dielectric layer of thickness  $\delta$  and relative dielectric permittivity  $\epsilon_f$ . At the film/solution interface (zone III),<sup>38</sup> there is an excess of charged groups because polyelectrolyte–polyelectrolyte pairing is not stoichiometric in this region; we denote the resulting excess charge density as  $\sigma_s$ . We assume that the magnitude of  $\sigma_s$  is independent of the number and type of layers, but its sign depends on the layer number. Note that for simplicity, we assume that the excess charge at the topmost layer of the film is located on a plane, whereas in reality, it will be more or less distributed along the direction normal to the substrate. The metal/film system is immersed in a water solution, whose ionic strength is  $I$ . For the deionized water used during rising (just before drying), this ionic strength is given by the residual salt ions and products of water self-dissociation, for example, deionized water in equilibrium with atmosphere has  $\text{pH} \approx 5$  because of the dissolution of  $\text{CO}_2$ ; thus,  $I \approx 10^{-5}$  M.

The potential at the film/solution plane,  $\Psi_s$  (see Figure 5a), is given by Gouy–Chapman's equation, which relates the charge and the potential of a substrate immersed in an electrolyte solution<sup>39–42</sup>

$$\Psi_s = \frac{2RT}{F} \operatorname{asinh} \left[ \frac{\sigma_s + \sigma_M}{(8I\epsilon_s\epsilon_0RT)^{1/2}} \right] \quad (1)$$

where  $R$  and  $F$  are the ideal gas constant and Faraday's constant, respectively (this equation assumes that the ionic strength is given by a 1:1 electrolyte). The charge at the metal is given by the equation of a parallel-plate capacitor between the metal/film and film/solution planes

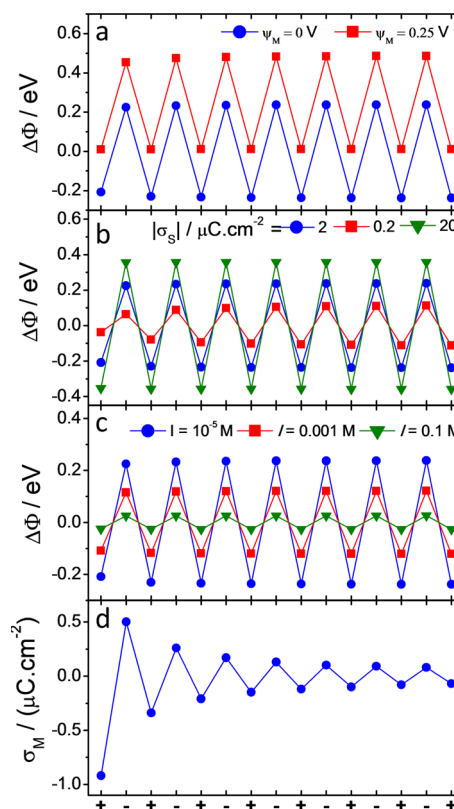
$$\sigma_M = \frac{\epsilon_f\epsilon_0}{\delta} (\Psi_M - \Psi_s) \quad (2)$$

combining eqs 1 and 2 results in an implicit expression for  $\Psi_s$ , which can be solved numerically,

$$\Psi_s = \frac{2RT}{F} \operatorname{asinh} \left[ \frac{\sigma_s + \frac{\epsilon_f\epsilon_0}{\delta} (\Psi_M - \Psi_s)}{(8I\epsilon_s\epsilon_0RT)^{1/2}} \right] \quad (3)$$

upon drying, (i) the counterions condense on the film, and (ii)  $\sigma_M$  remains unchanged; thus, according to eq 2:  $\Delta\chi = -\sigma_M\delta/(\epsilon_f\epsilon_0)$  (see also the electrostatic potential profile in Figure 5b).

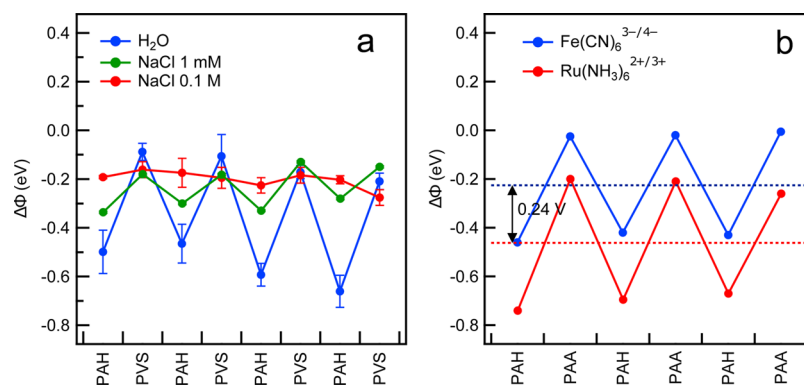
Figure 6a–c shows the evolution of  $\Delta\Phi = -e\Delta\chi$  as a function of the number of adsorbed layers calculated using our model under different conditions. In all cases,  $\Delta\Phi$  is larger for negatively capped films than for positively capped ones, in agreement with the experimental observations in Figures 2 and 3. Moreover, Figure 6a–c shows that our model indicates that the oscillations of  $\Delta\Phi$  are not attenuated at all by increasing the number of polyelectrolyte layers. The blue circles in Figure 6a show that the oscillations of  $\Delta\Phi$  for  $I = 10^{-5}$  M, and a typical set of parameters ( $\sigma_s = 0.12$  e nm<sup>-2</sup>,  $\epsilon = 10$ , a thickness per layer of 2 nm, and  $\Psi_M = 0$  V) have an amplitude of 0.48 eV, which is in the right order of magnitude compared with that in our experimental observations. The red squares in Figure 6a show that increasing  $\Psi_M$  increases all values of  $\Delta\Phi$ , but it does not change the amplitude of oscillations. Because we are interested in the amplitude of the oscillations and not in the absolute value of  $\Psi$  (which has other contributions besides that



**Figure 6.** (a–c) Change in work function ( $\Delta\Phi$ ) as a function of the number of layers (+ and – denote the films terminated in polycation or polyanion, respectively) for different values of the potential of the metal,  $\Psi_M$  (a); the absolute value of the charge density of the topmost layer of the LbL film,  $|\sigma_s|$  (b); and the ionic strength of the solution,  $I$  (c). (d) Charge density of the metal surface as a function of the number of layers. Calculation parameters:  $\sigma_s = 2 \mu\text{C cm}^{-2} = 0.12 \text{ e cm}^{-2}$  (only panels a, c, and d),  $I = 10^{-5}$  M (only panels a, b, and d),  $\Psi_M = 0$  V (only panels b, c, and d),  $\epsilon_f = 10$ , and thickness per layer = 2 nm.

originated due to the LbL film excess charge), we will use  $\Psi_M = 0$  V hereafter. Figure 6b shows that increasing the net charge of the topmost layer,  $\sigma_s$ , increases the amplitude of the oscillations; although the effect is not very strong, increasing  $\sigma_s$  from 0.12 to 1.2 e nm<sup>-2</sup> increases the amplitude from 0.48 to 0.71 eV. This result suggests that the fact that the oscillations of  $\Delta\Phi$  observed for PDDA/PAA and PAH/PAA in Figure 3 were larger than those observed for PDDA/PVS in Figure 2 may be explained by the larger excess of charge in the topmost layer of the former systems. This result can be rationalized by the combination of two arguments: (i) the amount of excess charge should be directly proportional to the thickness of the topmost layer and (ii) we choose the deposition pH so that PAA and PAH are weakly charged; thus, they have coiled conformations and produce thicker layers than those produced by PDDA and PVS, which are strongly charged polyions and adopt rodlike conformations.<sup>43,44</sup>

Figure 6c shows that increasing the ionic strength of the solution decreases the magnitude of the oscillations of  $\Delta\Phi$ . For  $I = 0.1$  M, the oscillations are quite small (0.05 eV), which is in qualitative agreement with the experiment using NaCl 0.1 M for the rising step shown in Figure 3c. The oscillations in  $\Delta\Phi$  are affected by the ionic strength of the solution because the capacitance of the double layer increases with  $I$ ; thus, for a large ionic strength, the charge of the topmost layer will be mostly



**Figure 7.** Work function change as a function of the number of deposited layers of PAH/PVS films rinsed with (a) increasing concentrations of NaCl solutions and (b) solutions containing 0.1 mM of different redox couples.

compensated by mobile ions rather by the induced charge at the metal. Because the mobile ions collapse to the film upon drying, the dipole of the dry film will be very small when the ionic strength is large. In addition to the parameters explored in Figure 6a–c, we also explored the effect of the thickness per bilayer and  $\epsilon_f$  on the oscillations in  $\Delta\Phi$  (results not shown). The thickness per bilayer did not influence the magnitude of the oscillations much, whereas increasing  $\epsilon_f$  affected only a few initial oscillations, slightly dampening them. We should finally note that our model correctly suggests that the amplitude of the oscillations of  $\Delta\Phi$  is independent of film thickness because while the separation of charges increases with film thickness, the amount of separated charge decreases (see  $\sigma_M$  versus number of layers in Figure 6d). Thus, our proposed model captures the main part of the experimental observations reported here and in the literature,<sup>14–18</sup> strengthening the mechanism we propose to explain the oscillations of  $\Delta\Phi$ .

Following the calculations presented in Figure 6, we measured the KP work function change of a PAH/PVS LbL film as a function of the number of layers when (a) films were rinsed with solutions of increasing concentration of NaCl and (b) the potential of the metal was modified by rinsing with solutions containing different redox couples. Figure 7a shows the effect of increasing NaCl concentration in the solution used to rinse the LbL films. Clearly, as the concentration increases, the intensity of the  $\Delta\Phi$  oscillations is dampened, in agreement with the calculations shown in Figure 6c. Figure 7b shows the effect of rinsing with 0.1 mM solutions containing Fe(CN)<sub>6</sub><sup>3-/4-</sup> (standard potential +0.36 V) and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup> (standard potential +0.1 V) as a means of controlling the metal potential. Clearly, increasing the metal potential shifts the offset of the oscillations toward greater values in agreement with the calculations shown in Figure 6a. Thus, the experimental results presented in Figure 7 give strong support to the model we put forward to rationalize the work function change caused by LbL films.

## CONCLUSIONS

In agreement with previous reports, we show that the change in work function of a conductive substrate due to the sequential growth of a polyelectrolyte thin film oscillates with maximum values for negatively capped films and minimum values for positively capped films, independently of the initial surface charge and of the number of deposited layers. Furthermore, we show that the amplitude of the oscillation depends on the nature of the polyelectrolyte employed in the LbL film:

polyions that produce thicker layers result in larger oscillations. This is explained using our semiquantitative model that indicates that the amplitude of the oscillations increases when increasing the charge density at the topmost layer, which is expected to be larger for polyions that produce thick layers (PAA and PAH) than for those that produce thin layers (PVS and PDDA). We propose the following microscopic mechanism for the formation of a dipole layer responsible for the observed work function oscillations. Removing the LbL film from the solution and drying condenses the counterions present in the diffuse ionic layer onto the charges of the topmost layer, partially neutralizing them with the remaining charges electrically compensated by the charge at the metal. Therefore, the excess charge at the topmost layer and the charge of the metal have equal magnitude and opposite polarity, and thus, they form an electrical dipole layer that causes the work function change. We propose a model for this mechanism based on a continuum description of the electrostatics of the system that reproduces the experimental observations. Our findings are relevant in the fields of (i) LbL polyelectrolyte films and of (ii) organic electronics, where energy-level alignment via work function control using polyelectrolyte films is a key parameter in the performance of organic electronic devices.

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### Notes

The authors declare no competing financial interest.

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