Research Article

X-Ray Reflectometry Study of Self-Assembled Ionic Nanolayers

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The self-assembly technique has been applied for the fabrication of thin films including macrocyclic molecules. These multilayered structures, grown by sequential deposition of oppositely charged molecules, were characterised with X-ray reflectometry. The data obtained indicate regular thickness of ion pair layers formed regardless of the number of depositions made as well as the number of ion groups occurring in the molecule. Savitzky-Golay algorithm was used for the calculation of the layer thickness. Formation of self-assembled multilayers (SAMs) occurs not only for polymeric structures but also for small ionic compound systems and results from the electrostatic interaction of many strongly dissipated charges on the whole structure of the molecule.

1. Introduction

Self-assembled multilayers (SAMs) have become of great interest since they were reported by Decher and Hong in the early 1990s [1, 2]. The self-assembly process based on electrostatic attraction can be used to obtain multilayered thin film materials showing unique properties [3–6]. The electrostatic self-assembly (ESA) technique is based on sequential deposition of oppositely charged molecules (polymers) on the substrate surface to form a thin film. Electrostatic self-assembly occurs not only on the solid surface but also in the solution [7] as well as in the air/water interface [8]. ESA is a very simple and versatile method of fabrication of nanoscale thin films. In the past two decades much effort has been made to achieve and improve desired properties of these materials. The role of electrostatic and secondary interactions including hydrophobicity, hydrogen bonding, dispersion forces, ion dipole, and van der Waals interactions has been investigated. Extrinsic conditions are also fundamental, and varying pH or ionic strength of aqueous solution alters the thickness of layers and the nature of thin film obtained [5, 6].

Layer-by-layer (LBL) film structures are promising for commercial applications. Incorporation of metal or inorganic particles leads to interesting electrooptical or magnetic

properties [9] of the material potentially applicable in magnetic recording or as memory. The use of LBL films for modification of surface wettability, adhesion, surface conductivity [10], ion transport, and catalytic [11, 12] or specific binding activity [13] illustrates a wide range of their applications in industry. Permeability is an especially interesting property of the LBL films. It is crucial for applications such as drug encapsulation with controlled release or membrane separation [14]. Encapsulation of a drug molecule is connected with the approach to ESA technique that, instead of a planar substrate, colloidal particles have been coated [15]. Subsequent core removal leads to hollow capsules which are spherical closed thin multilayers [3–5].

It has been reported that ionic liquids consisting of multivalent small molecules can create an extended network through pairwise interactions. They form supramolecular polymers, which is in good agreement with the viscosity of such ionic liquids higher than that of cationic or anionic molecules combined with monovalent counter ions [16]. Macrocyclic compounds employed in this experiment are expected to form supramolecular structures with oppositely multicharged polymers or macrocycles. Formation of thin films formed by sequential deposition of oppositely charged polyelectrolyte and small molecules is reported [17–20].

FIGURE 1: The structures of the compounds studied.

In this work formation of nonpolymeric ionic nanolayers consisting of small molecules with four or six charged functional groups has been studied by X-ray reflectometry measurements [15, 21] utilizing Savitzky-Golay algorithm for the obtained XRR curves [22].

2. Experimental

2.1. Functionalization of Surface. The chemical structures of the compounds studied are shown in Figure 1. Positively charged polymer, PDDA, poly(diallyldimethylammonium hydrochloride), and HACO (1,4,7,10,13,16-hexaazacyclooctadecane hexahydrochloride) were deposited as the first layer because of the negative charge of the native oxide on the silicon surface. The negatively charged layer-building blocks were such macrocycles as copper(II) phthalocyanine tetrasulfonic acid tetrasodium salt (CuPc), 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid tetrasodium salt (DOTA), and mellitic acid hexasodium salt (MA). Azacyclic compounds as cyclen [23] and hexacyclen are known ligands for cations [24] as well as anions if protonated [25]. Metal phthalocyanines are known for their photochemical [26] and conductivity [27] properties.

Silicon plates with oxidized surfaces were cleaned with methanol in an ultrasonic cleaner and subsequently rinsed with deionized water. Then the plates were dipped for 5 minutes in the PDDA (or HACO resp.) aqueous solution of a concentration of $10^{-3} \text{ mol dm}^{-3}$. As the positively charged polymers display an attraction to the negatively charged silicon surface with hydroxyl groups, a monolayer of PDDA (or HACO) was expected to be formed on the surface of the plate. Afterwards the plates were washed with deionized water to remove all nonadsorbed polymers. After washing, the plates were immersed in MA (or CuPc or DOTA resp.) aqueous solution of $10^{-3} \text{ mol dm}^{-3}$ for the next 5 minutes and subsequently washed with deionized water. Consistently

a monolayer of negatively charged MA (or CuPc or DOTA) ions was expected to be dispersed and adsorbed on the PDDA (or HACO)-coated sample. After one dipping cycle including one immersion in PDDA (or HACO) solution followed by one immersion in MA (or CuPc or DOTA solution), a bilayer consisting of PDDA (or HACO) and MA (or CuPc or DOTA) monolayers was expected to be created on the sample's surface. Such a procedure was repeated for 5, 10, 15, 20, 25, 30, 40, and 50 times to form a thin film since the opposite charges of PDDA (or HACO) and MA (or CuPc or DOTA) attract these components and ensure their bonding.

The thin films formed on silica surfaces were examined by the X-ray reflectometry.

2.2. X-Ray Reflectometry. The ion nanolayers were investigated by means of high-resolution X-ray diffractometer supported with Ge(220) four-crystal Bartelss monochromator in the incidence beam, open detector with 0.45 mm slit in the diffracted beam, and $\lambda_{\text{CuK}\alpha 1} = 1.540597 \text{ \AA}$ radiation. X-ray reflectivity is a precise and nondestructive method for the determination of thickness, density, and roughness of a layer on a substrate. The method enables observation of layer thickness of the order of angstroms. In X-ray reflectometry measurements, the X-ray beam is directed onto the sample surface. The angle of incidence beam is above the critical angle for investigated material. Below this angle the X-ray beam is totally reflected. In proper measurement the X-rays are reflected from the air/layer as well as from the layer/substrate interfaces. As a result the reflectivity curves with characteristic oscillations are obtained.

The position and number of the oscillations are used to plot a linear function whose directional parameter is used for the calculation of the layer thickness. In this work Savitzky-Golay algorithm was used to reduce noise of the measured curve. The application of this method, widely used in spectroscopy, considerably improves data analysis [22].

TABLE 1: The thicknesses of the measured ionic nanolayers.

Quantity of ionic layers	The thickness of ionic layers [Å]			
	Series A PDDA and CuPc	Series B PDDA and DOTA	Series C PDDA and MA	Series D HACO and MA
5	17.0	16.7	17.5	17.5
10	17.0	16.7	17.1	17.5
15	17.1	16.6	17.6	17.2
20	16.9	15.8	18.5	17.1
25	17.0	16.6	16.8	17.2
30	17.0	16.8	17.5	16.9
40	16.8	17.4	17.5	17.3
50	17.2	16.4	17.5	17.2
The value average	17.0	16.6	17.5	17.2

FIGURE 2: Reflectivity curves from the measured ionic nanolayers.

3. Results and Discussion

In this work two systems were applied: in the first, the layer deposited on the silicon substrate as well as further positively charged layers were made of PDDA polymer, while in the second the protonated cyclic amine, HACO, was used. A comparison of results obtained for these two systems allowed evaluation of the possibility of SAMs formation when the alternating layers are isolated multicharged molecules instead of polymers.

As prepared thin films were examined by the X-ray reflectometry. The exemplary reflectivity curves obtained for PDDA and CuPc system are shown in Figure 2. The thicknesses of bilayers for all studied ionic SAM are collected in Table 1. The average values of the layer thicknesses, varying in each series not more than about 10%, indicate a regular thin film growth. Lütt et al. [17] studied the formation of self-assembled thin films of cationic polymer PDDA and NiPc by X-ray refractivity method. They have proposed a hypothetical structure of a thin-film made by PDDA and NiPc. The thickness of a PDDA-NiPc bilayer is of about 8 Å.

The results exhibit larger thickness of bilayers deposited at the beginning than those deposited after many depositions. The average layer thickness decreased from about 20 Å for first two immersion cycles to an average and constant

value of about 8 Å after deposition of about 40 bilayers. The authors explain a constant increase in the film thickness as well as a constant increase in the roughness of the growth surface by incomplete and random covering of the substrate surface by blocks representing a bilayer.

In our work we studied an analogous system containing Cu^{2+} ions in the phthalocyanine ring instead of Ni^{2+} ions. For this system the average thickness of a bilayer was determined as 17.0 Å. Such a value indicates that ionic molecules form self-assembled flat layers, in which dissipated charges determine the thickness of a bilayer by electrostatic interaction (Figure 3(a)). The molecules deposited should be lying down as presented in Figures 3(a)–3(d); otherwise, the thickness values would be higher.

The application of multicarboxyl acids salts (MA and DOTA) and ionic polymer PDDA in fabrication of ionic layers confirmed an analogous character of the emerging SAM bilayers as that of the CuPc or NiPc layers [17]. The thickness of these layers depends on the anion used. For an MA system the average thickness of a bilayer is 17.5 Å, whereas for a DOTA system this value decreased to 16.6 Å. The differences are determined by the lability of carboxyl groups induced by the presence of alkyl linkers. These bilayers are closer packed than the other systems studied. Figures 3(b)–3(c) present visualization of ionic thin film structure as obtained from x-ray measurements.

In this work formation of ionic layers by nonpolymeric ions HACO and MA was also studied. The SAM character of the HACO and MA system is analogous to that of the other systems studied. Reflectivity curves enabled determination of the layers thicknesses for this type of SAM. The average thickness of a bilayer was 17.2 Å. Figure 3(d) presents visualization of ionic thin-film structure as obtained from X-ray measurements.

4. Conclusions

Ionic SAMs on silicon substrate require no polymer component. Formation of layers results from the electrostatic interaction of many strongly dissipated charges on the whole structure of the molecule. Strong localization of charge solely on one functional group prevents from formation of the

FIGURE 3: The visualization of PDDA and CuPc (a), PDDA and DOTA (b), PDDA and MA (c), and HACO and MA (d) ionic thin-film structures obtained from X-ray results.

ionic SAMs in an ordered way. A considerable delocalization of charge in the following layers is the condition of the ionic SAMs formation. These layers form a self-healing ordered ionic structure. The thicknesses of bilayers obtained from X-ray measurements indicate that the molecules are laid in flat layers.

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