Variation of the in-plane structure with depth revealed by grazing incidence x-ray diffraction in a thin Langmuir-Blodgett film

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Grazing incidence x-ray diffraction is used to characterize the molecular arrangement of ultrathin Langmuir-Blodgett (LB) multilayers. Using two angles of incidence of the beam allowing its penetration either throughout the complete depth of the film or only through the external layers, we show that it is possible to discriminate between the molecular packing of the deeper monolayers and that of the external monolayers of the LB film.

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The use of LB films for many applications implies the fabrication of well-ordered films [1]. It is thus essential to have well-adapted techniques to characterize the films at various lengthscales and in different directions: in the plane of the layers and perpendicularly to them. The main difficulty is to find an experimental method which allows one to determine the in-plane structure at the molecular scale of both the external layer and the deeper layers of the LB film. Among the experimental methods used to study thin LB films [2–5], the more suitable techniques to probe the structure at the molecular scale are transmission electron diffraction (TED), atomic force microscopy (AFM) and the x-ray techniques. However, TED and AFM only provide the structure of the external monolayer. Concerning the x-ray techniques [6,7], x-ray reflectivity allows the characterization of the structure of the films in the surface normal direction. The experimental data of reflectivity are compared, in general, to a model electron density profile along the perpendicular direction. They have to be corrected from the signal due to diffuse scattering, which corresponds to long-range lateral correlations of the interface. From diffuse scattering measurements, the film roughness and the correlations between the layers can be deduced [6]. Grazing incidence x-ray diffraction (GIXD) [8] allows the determination of the structure in the plane of the layers; it provides the in-plane molecular packing, the positional correlation length and also the orientation of the hydrophobic chains (tilt angle). In such experiments performed on thin LB multilayers [5,9,10], the angle of incidence of the x-ray beam is usually fixed at about $0.85\alpha_c$, where α_c is the critical angle for total external reflection for the solid substrate; this value minimizes the background scattering of the substrate. With such an angle of incidence, the beam propagates throughout the complete depth of the LB film. The obtained GIXD pattern is thus a measurement of the superposition of the in-plane structure of all the monolayers of the LB sample. In this paper, we use the possibility of varying the angle of incidence α of the x-ray beam to determine the in-plane molecular packing in different depth of a thin LB film. We take advantage that the critical angle for total external reflection for the hydrophobic chains of the molecules, α_{chains} (2.4 mrad for hydrocarbon chains), is lower than that of the solid substrate, $\alpha_{substrate}$ (3.9 mrad for a Si/SiO_2 wafer). Thus, for $\alpha<\alpha_{chains}$, the wave is evanescent in the LB film; its low penetration depth (a few tenth of angstroms) allows to probe the in-plane structure in the external monolayers of the LB film, as the contribution of the first deposited layers becomes negligible. Consequently, by probing the LB film with two angles of incidence α of the x-ray beam such as $\alpha<\alpha_{chains}$ and $\alpha_{chains}<\alpha<\alpha_{substrate}$, it is shown that the structure of the external monolayers of a thin LB film can be distinguished from that of the deeper monolayers. Indeed, for $\alpha_{chains}<\alpha<\alpha_{substrate}$, the contribution of the different monolayers of the LB film to the diffracted intensity is nearly identical. This method is applied to the characterization of 3-layers LB films transferred on air-oxidized silicon wafers. The first two monolayers are behenic acid monolayers while the third monolayer is made of a fluorinated amphiphilic molecule called FEP. All three layers are transferred with cadmium ions.

Behenic acid was purchased from Sigma and 1-(2′-F-hexylethylthio)-3-(2″-ethylhexyloxy)-2-ol-propane (FEP), CF_3-$(CF_2)_5$-$(CH_2)_2$-S-CH_2-CHOH-CH_2-O-CH_2-CH-$(C_2H_5)(C_4H_9)$, was provided by L'Oréal. The two compounds were used without further purification and spread from chloroform solution on a subphase containing 1.9×10^{-6} mol l^{-1} of $CdCl_2$ (Sigma) and adjusted to pH 6.5 by addition of $NaHCO_3$ (Sigma). The experiments were performed at room temperature (20°C). The Langmuir-Blodgett films were prepared by vertical deposition on polished oxidized silicon wafers (Si/SiO_2 wafers) (Applications Couches Minces). The studied samples were made of two behenic acid monolayers and of a FEP monolayer as third layer. The two first layers were transferred at a surface pressure of 35 mN/m whereas the third layer was deposited at a surface pressure of 28 mN/m. The dipping speed was 10 mm min^{-1}.

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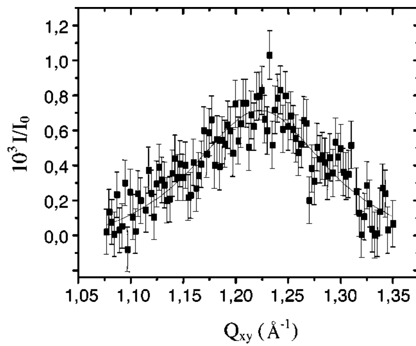

FIG. 1. Grazing incidence x-ray diffraction data in the horizontal plane, integrated over Q_z, for a FEP monolayer transferred at 28 mN/m on a behenic acid bilayer deposited at 35 mN/m. All three layers are transferred with cadmium ions. The angle of incidence of the x-ray beam was set to 1.5 mrad.

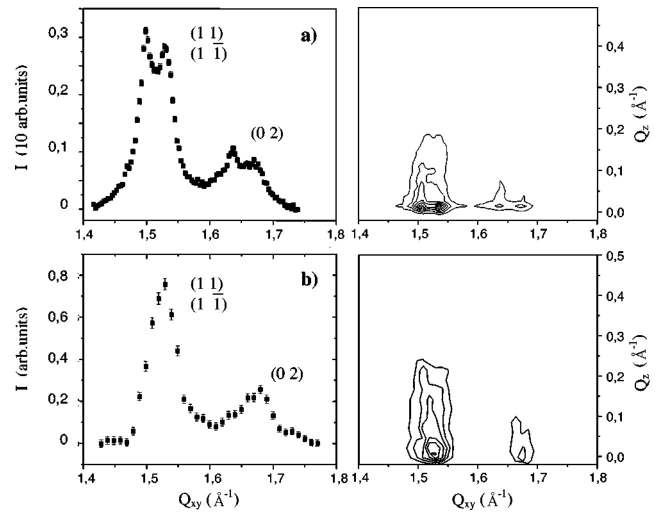

FIG. 2. X-ray diffraction data in the horizontal plane, integrated over Q_z (left) and contours of equal intensity vs the in-plane and out-plane scattering vector components Q_{xy} and Q_z (right) for a FEP monolayer transferred at 28 mN/m on two behenic acid layers deposited at 35 mN/m. All three layers are transferred with cadmium ions. Two angles of incidence of the x-ray beam were used: (a) $\alpha = 3.5$ mrad; (b) $\alpha = 1.5$ mrad.

The grazing incidence x-ray diffraction experiments (GIXD) were performed at the D41B beamline at the LURE (Orsay, France). The selected wavelength was 1.646 Å. The diffracted intensity was monitored by a Ar/CO_2-filled position sensitive detector (PSD, 13°), as a function of the in-plane component Q_{xy} of the wave-vector transfer, selected using a Soller collimator with a resolution of 5 min. The experimental maximum signal to noise ratio is close to 5. The Q_{xy} pattern, corresponding to the diffracted intensity integrated over the vertical component Q_z of the wave-vector transfer, allows one to determine the cell parameters of the two-dimensional lattice. The tilt angle is deduced from the vertical intensity profiles (Bragg rods). The angle of incidence α of the beam was fixed using a polished glass mirror with an accuracy of 0.05 mrad and checked by measuring the incident and reflected beams. Two angles of incidence were used to probe the samples more or less deeply. The first value was fixed to $\alpha = 3.5$ mrad, which is slightly below the critical angle for total external reflection for Si/SiO_2 wafers (3.9 mrad). The second value was 1.5 mrad which is below the calculated critical angle for total external reflection for the hydrocarbon chains (2.4 mrad) (Note that the critical angle for total external reflection for the FEP molecules is slightly higher than that of the fatty acid molecules).

Figure 1 shows the diffraction pattern obtained for Q_{xy} in the range of 1.07 to 1.35 Å^{-1}. For the two angles of incidence of the x-ray beam, a large in-plane peak is detected. By fitting this peak with a Lorentzian shape, one obtains its maximum at $Q_{xy} = 1.225 \pm 0.007$ Å^{-1} and its full width at half maximum (FWHM) that leads to a positional correlation length L (L = 2/FWMH) of the order of 40 Å. This indicates a weak organization of the FEP molecules on a roughly hexagonal lattice. The position of the peak leads to a molecular area A = 30.4±0.1 Å^2, in agreement with a dense packing of fluorinated chains [11].

The diffraction patterns obtained for Q_{xy} in the range of 1.4 to 1.75 Å^{-1} for two angles of incidence of the x-ray beam $\alpha = 3.5$ mrad and $\alpha = 1.5$ mrad are shown respectively in Figs. 2(a) and 2(b). For $\alpha = 3.5$ mrad, two in-plane doublets are clearly visible whereas for $\alpha = 1.5$ mrad, only two in-plane diffraction peaks are detected at $Q_{xy} = 1.529 \pm 0.007$ Å^{-1} and $Q_{xy} = 1.674 \pm 0.007$ Å^{-1}. The splitting of the two peaks for the higher incidence angle of the x-ray beam means that the use of two angles of incidence allows to detect different structure in each of the monolayers of the LB film. Indeed, for $\alpha = 3.5$ mrad, the penetration length corresponding only to the absorption is greater than 100 nm, so the beam penetrates throughout the complete depth of the LB film with approximately the incident intensity. In contrast, for $\alpha = 1.5$ mrad, the wave is evanescent and its penetration depth is close to 65 Å. The diffracted signal is thus mainly provided by the external layers. Indeed, calculating for a 3 layers LB sample the ratio between the intensity of the incident evanescent wave in the external monolayer and in the first deposited monolayer, one obtains a value of about 7 while the experimental maximum signal to noise ratio is close to 5.

One can notice that the Q_{xy} positions of the two peaks detected for $\alpha = 1.5$ mrad correspond exactly to that of the second peaks of each doublet obtained for $\alpha = 3.5$ mrad. Also, for $\alpha = 3.5$ mrad, the first peaks of each doublet are detected at $Q_{xy} = 1.505 \pm 0.007$ Å^{-1} and $Q_{xy} = 1.638 \pm 0.007$ Å^{-1}, which correspond exactly to the Q_{xy} positions of the two peaks measured for 3-layers LB films of behenic acid with cadmium ions presented in a previous study [12]. These peaks can be indexed according to a centered rectangular lattice as respectively the degenerate (11)/(1$\bar{1}$) peaks and the nondegenerate (02) peak. In the studied samples, the peaks are located in the scattering plane indicating untilted molecules. The structure is thus in agreement with the *S* phase of Langmuir monolayers [13,14]. Consequently, the second peaks of each doublet also correspond to a molecular packing of behenic acid molecules in the S phase but with different lattice parameters. These observations evidence that for $\alpha = 3.5$ mrad, each of the two behenic acid monolayers

has a contribution to the diffracted intensity, whereas for $\alpha = 1.5$ mrad, only the signal of the second behenic acid monolayer is detected. Moreover, the lattice parameters of the two behenic acid monolayers are different. From the Q_{xy} positions of the peaks, one can deduce the rectangular cell parameters a and b. One obtains $a = 4.98 \pm 0.02$ Å and $b = 7.67 \pm 0.02$ Å in the first deposited monolayer and $a = 4.91 \pm 0.02$ Å and $b = 7.51 \pm 0.02$ Å in the second monolayer. The area per molecule of the first layer, $A = 19.1 \pm 0.1$ Å^2 is thus larger than that of the second layer, $A = 18.4 \pm 0.1$ Å^2. These results can be compared to that obtained for a 3-layers LB film of behenic acid with cadmium ions [12]. The measured diffraction pattern was identical for the two studied angles of incidence of the x-ray beam, meaning that the in-plane structure of the behenic acid molecules is the same in each of the three monolayers. In the case of the 3-layers sample with FEP molecules as the third layer described in this paper, the contraction of the second behenic acid monolayer indicates a reorganization of the film.

As a conclusion, the use of GIXD with two angles of incidence is a very promising method to characterize the in-plane structure of the different monolayers of LB films with few layers. Reorganizations of the layers after the transfer on solid substrate can be evidenced. For thick films, this method can allow to study the evolution of the molecular arrangement of the layers when increasing the thickness of the film.

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