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X-ray scattering studies of imperfect manganese stearate Langmuir–Blodgett films

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Abstract

Metal-organic multilayers of manganese stearate prepared by Langmuir–Blodgett (LB) technique on hydrophobic Si substrate were studied by grazing incidence X-ray scattering techniques. Grazing incidence X-ray diffraction measurements show distorted hexagonal in-plane structure of the molecules. Reflectivity measurements show that the LB films consist of two types of blocks having slightly different bilayer separation, but well arranged. The reasons for which these LB films present such imperfection are discussed.

Keywords: Grazing incidence X-ray scattering; Langmuir–Blodgett films

1. Introduction

Metal–organic multilayer thin films can be prepared by transferring Langmuir monolayers of amphiphilic molecules on solid substrate [1,2]. Such multilayer Langmuir–Blodgett (LB) films are usually expected to have well-ordered structure along the growth (z) direction. However, in practice different parameters such as the surface pressure, temperature, pH, film–substrate interaction, etc. play an important role in the growth of the films [3,4]. According to that one can get highly perfect LB film composed of either tilted or untilted molecules (tails) or an imperfect LB film with phase separation or a mixture of tilted and untilted molecules, which may show film of different thickness, different molecular separation [4,5] and even different in-plane correlation [6–11]. All these make it difficult for the LB films to achieve promised applications such as non-linear optical devices, etc. and make it interesting for the scientist to understand the physics in confined geometry and control the growth to make it viable for the applications.

Grazing incidence X-ray scattering is a powerful technique to study the structure of thin films. In particular, X-ray scattering gives the electron density contrast of the system in a nondestructive way. In-plane grazing incidence X-ray diffraction (GIXD) is useful to determine the short-range correlation, which essentially gives the lattice parameters of the in-plane structure [3,4]. Diffuse scattering, on the other hand, provides us information about the lateral correlation (long range) of in and between rough interfaces [6–11]. Combination of GIXD and diffuse scattering can be used to determine the short- as well as the long-range in-plane ordering in the thin film. Specular reflectivity gives the average film thickness and the information about the stacking of film in the direction normal to the surface, it essentially gives the electron density profile (EDP) of a thin film [9–14]. The analysis of diffuse scattering becomes convenient if the system has conformal or correlated roughness [15], while the analysis of the specular reflectivity is easy if the film is homogeneous laterally. Although it is now possible to make nearly perfect films by the LB technique, it is extremely frequent to get thin films presenting some imperfections. These imperfections can induce strong diffuse scattering (bad lateral coherence) or various effects in the specular reflectivity. It is therefore important to characterise such imperfections from a structural point of view to understand how such imperfections can affect the growth process. Here, we present the results of grazing incidence X-ray scattering from manganese stearate (MnSt) LB

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films, which exhibit some clear indication of imperfections. An attempt to explain the origin of these imperfections is developed.

2. Experiment

A monolayer of MnSt was prepared in water subphase by spreading stearic acid solution in chloroform on manganese chloride solution. The monolayers were transferred to hydrophobic Si substrate at speed, surface pressure and temperature of 5 mm min^{-1}, 28 mN m^{-1} and 20°C, respectively. Si substrates were made hydrophobic by depositing a thin layer of silane after treatment with chromic acid. LB8, LB12 and LB16 MnSt LB films of different thickness, prepared by transferring 16, 24 and 32 monolayers, respectively, in down/up stroke, were studied by surface sensitive X-ray scattering technique.

X-ray scattering experiments were carried out at synchrotron source (X22A beam line, NSLS, Brookhaven National Laboratory) using a wavelength of 1.197 Å. Specular reflectivity measurements were performed by keeping the incidence angle, α, equal to the exit angle, β ($\alpha = \beta = \theta$). Diffuse scattering data were collected in two different modes. The transverse diffuse data were collected by performing rocking scans of the sample keeping the detector in fixed position ($\alpha + \beta = 2\theta$) while the longitudinal diffuse data were collected by performing a specular scan ($\theta - 2\theta$ scan) while maintaining a fixed angular off-set between α and β. The incident radiation was collimated by slits having apertures of 0.05 and 0.4 mm in and perpendicular to the scattering plane, respectively, with the aperture in the scattering plane determining the width of the incident beam in the scattering plane. To measure the scattering intensity back slit of aperture 0.4 and 1.0 mm in and perpendicular to the scattering plane was placed in front of the detector. GIXD measurements were carried out on the same instrument after replacement of the back slits by soller slits.

3. Results and discussion

X-ray specular reflectivity of the three MnSt LB films are shown in Fig. 1. All reflectivity curves exhibit small oscillations known as Kiessig fringes which are the signature of the total film thickness. The intense quasi-Bragg peaks are related to the bilayer separation (distance between Mn layers). The intensity of the odd Bragg peaks is found to be more compared to that of the even ones. In addition, each Bragg peak is composed of two peaks having slightly different periodicity. These peaks are well resolved at high q_z values and for film having higher thickness. This indicates that all the present LB films consist of two separate blocks which have different bilayer separation. Due to the presence of the two separate

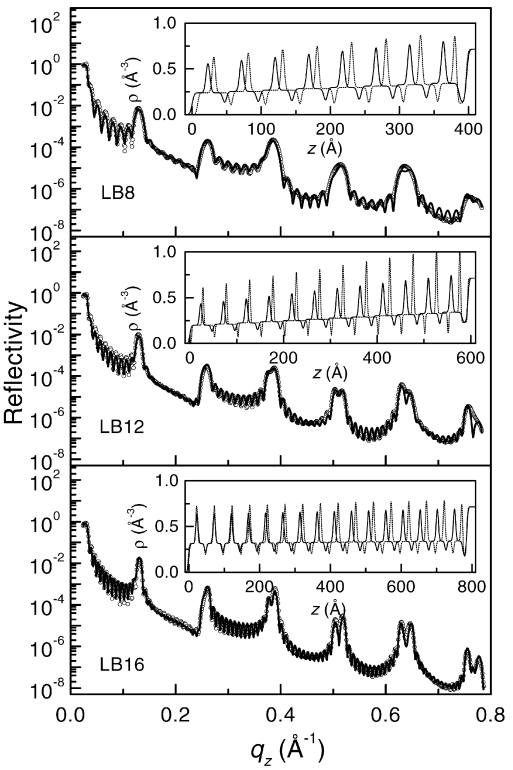

Fig. 1. X-ray reflectivity data (o) along with the best fit curves (solid line) for the three MnSt LB films in three different panels. Inset shows the corresponding EDP: dotted line for block A and solid line for block B.

Bragg peaks, the number (N–2) of Kiessig fringes within two Bragg peaks which is the measure of the number of bilayers (N) in the film is not clear in all the q_z range. N–2 Kiessig fringes are, however, clear between the second and third Bragg peak. It is also clear in the reflectivity curves that the Bragg peak corresponding to the lower bilayer separation is dominant in the lower q_z range while that related to higher bilayer separation is dominant at higher q_z values. Longitudinal diffuse scattering of all the films (not shown here), on the other hand, is about two orders of magnitude less compared to that of the specular value. In the diffuse scattering, only one type of Bragg peaks is observed. The diffuse peak is located at the average position of the two types of Bragg peaks, observed in the reflectivity curve.

In-plane GIXD of the three films is shown in Fig. 2. Each curve shows the presence of two diffraction peaks h_1 and h_2. The intensity of the second peak is stronger compared to that of the first and observed to increase with the thickness, while the intensity of the first peak is decreasing with the thickness. Position of both peaks is also shifting towards higher values with the thickness. The peaks in the GIXD indicate the presence of molecules

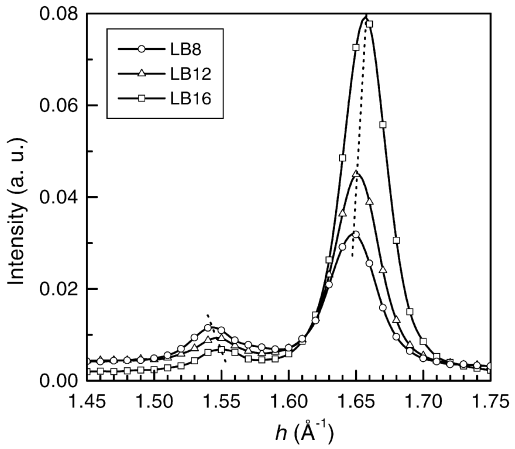

Fig. 2. In-plane GIXD patterns of the three MnSt LB films.

which are well ordered in the x–y plane. The peaks h_1 and h_2 corresponds to the (1 1) and (0 2) Bragg peaks, respectively, of the orthorhombic sub-cell [16] having lattice parameters a and b. The lattice parameters and the area per MnSt molecule obtained from the GIXD measurements are listed in Table 1. This indicates that the molecules are arranged in-plane according to a distorted hexagonal structure in opposition to what can be found in self-assembled films where hexagonal structure is undistorted.

The reflectivity data of all the films were analysed considering the total intensity is the sum of the two intensities arising from two separate blocks A and B having bilayer separation d_A and d_B ($d_A > d_B$), respectively. Each bilayer consists of one head ($Mn[COO]_2$) and two tails ($CH_3[CH_2]_{16}$). In order to explain the difference in the intensities of the odd Bragg peaks compared to that of the even ones we assumed that the two tails were separated by a portion having low electron density. The same roughness was used for each interface of a block considering conformal roughness. As tails are flexible it was assumed that the difference in bilayer separation for the two blocks was due to the difference in tail length in the vertical direction. The EDPs thus obtained by fitting the reflectivity curves are shown in the inset while the best fit curves are shown in Fig. 1. The average total film thickness (D), the bilayer separation for each block and the fractional surface coverage (c) of the block A are listed in Table 1.

We now discuss the reasons for which these LB films may present such an imperfection. The presence of two bilayer separations is clearly related to the presence of two specific length d_A and d_B. These two lengths are found in the three films studied here so that one may conclude that this kind of defect can be easily reproduced during the growth process. Such an imperfection is very likely related to the chemical procedure used to make these films. In particular, possible origins for the observation of such defects may be twofold. A first possibility would be that the LB films are not homogeneous from a chemical point of view. Part of the film (block A) is made of salt-riched molecules while the other part (block B) is made of acid-riched molecules. The film would then be separated into two blocks corresponding to two phases: the unreacted fatty acid and the salt. This picture has the drawback that it is not consistent with the experimental reflectivity. Since the unreacted fatty acid is far less contrasted in electron density than the salt, this would give rise to very faint Bragg peaks coexisting with much stronger ones. We observe the Bragg peaks for blocks A and B, with almost similar intensities. An other possibility may be that the molecules of one part (block B) of the film are tilted with respect to the other (block A), which we do believe is the case for the present films. The bilayer separation d_A of block A is close to that of the untilted molecules. Low fractional surface coverage of block A suggests that most of the film consists of molecules which are slightly tilted (block B). However, the strong short range correlation observed in the GIXD pattern indicates that although molecules are tilted, they are well arranged. This may be an indication of the regular tilt of the molecules. Considering the decrease of bilayer separation of block B with respect to block A is due to such regular tilt of the molecules one can calculate the tilt angle (ϕ) which is listed in Table 1. The reason for which some of the molecules are tilted and others remain untilted can be explained as follows. We treated all the Si substrates initially to make it hydrophobic in order to attach tails in the first deposition. It seems that part of the substrate ($\sim$20%) became hydrophilic, so that $\sim$80% of the surface area was attached with tails in first down stroke, while the rest $\sim$20% of the surface area was attached with the heads in the first up stroke. The mol-

Table 1
Parameters of the MnSt LB films obtained from the analysis of the GIXD and reflectivity data

Sample	a (Å)	b (Å)	Area/mol (Å^2)	d_A (Å)	d_B (Å)	D (Å)	c	ϕ (°)
LB8	4.816	7.625	18.36	49.82	48.73	396	0.20	12
LB12	4.802	7.611	18.28	49.90	48.62	595	0.20	13
LB16	4.796	7.584	18.19	49.88	48.46	792	0.16	14

ecules attached to the substrate through tails are tilted while the molecules attached to the substrate through heads are untilted. When in the first down stroke tails are attached to $\sim 80\%$ of the substrate there is $\sim 20\%$ vacant area. The molecules that are attached, therefore have an excess surface area and can easily tilt. In the up stroke the molecules that attached in the remaining vacant area, do not have such freedom, which essentially force them to remain untilted. The initial attachment of the molecules with the substrate is controlling the growth or arrangement of the rest of the film.

4. Conclusions

MnSt LB films of 8, 12 and 16 number of bilayers deposited on hydrophobic Si substrate were studied by surface sensitive X-ray scattering techniques. Reflectivity measurements show that the films consist of two separate blocks having slightly different bilayer separation. GIXD measurements show the well-ordered in-plane arrangement of the molecules. The structure is a distorted hexagon. Combination of two measurements suggest that the in-plane arrangement of the molecules in the two blocks is well ordered. Analysis suggests that most probably one is composed of molecules which are tilted with respect to the other block. However, the size, separation and formation of such separate blocks of well-ordered structure in all the films is not clear at this moment.

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