Structural assembly of Cd-arachidate molecules in multilayers

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The three-dimensional (vertical and lateral) structure of Cd-arachidate multilayers prepared on two different substrates, glass and silicon, is studied simultaneously by grazing incidence x-ray reflection/diffraction. The grazing incidence reflectivity studies indicate the formation of a well-ordered layered structure on both the substrates. The reflectivity simulations show that the bilayer spacing in the case of a glass substrate is 5.54 nm while that on a silicon substrate is only 5.44 nm, indicating a vertical tilt of the Cd-arachidate molecules on a glass substrate by about 9.5°. The interface roughness is found to be 0.3 nm for multilayers on a glass substrate and 0.4 nm on the silicon substrate. The interface topography, determined by studying the nonspecular scattering behavior, is found to be replicated between the various interfaces in the multilayers, independent of the type of substrate. The lateral topography of the interfaces in multilayers on a glass substrate shows a self-affine nature with no lateral length limit for the roughness fluctuations. The interfaces in multilayers on a silicon substrate, however, exhibit a saturation behavior for the roughness fluctuations. In the plane of the multilayers the Cd-arachidate molecules on a glass substrate have a centered rectangular lattice arrangement while they have a distorted hexagonal lattice arrangement on a silicon substrate. © 1999 American Institute of Physics. [S0021-9606(99)70548-9]

INTRODUCTION

The current trend in materials technology is towards the preparation of chemically and structurally ordered materials down to the atomic/molecular scale. Towards this end thin films and multilayers made from organic molecules are the subject of intense research activity as they are proposed to have potential applications in molecular electronics, nonlinear optics, chemical sensors, and so on. The realization of such applications however requires the formation of well-ordered, defect-free stable (thermodynamically and mechanically) structures. The different types of structural defects commonly observed in organic thin films and multilayers range in size from several micrometers to submicrometers and are made of domains/grains, subdomains/subgrains, pin holes, steps, and buckles. Since these defects affect their useful properties and the attainment of a truly ordered structure is still elusive, the problem of assembly and structural development in organic films is of great interest.

The arrangement of organic molecules in a monolayer and the subsequent structural development in a multilayer depends on intermolecular interactions such as Coulombic forces, van der Waals forces, hydrogen bonding and additionally the substrate-molecular interactions. It has been known that the in-plane structure and the vertical alignment of the organic molecules in a monolayer is very different compared to bulk structural parameters. The transition from a monolayer to bulk structure is found to depend on the molecular arrangement in the monolayer. In the case of a monolayer with disordered arrangement of molecules addition of a single inverted bilayer structure which has an internal headgroup–headgroup interface was found to lead to the formation of an ordered structure similar to the bulk solid. On the other hand, if the molecules in the monolayer have a more ordered structure, the structural evolution in a multilayer is found to be more gradual and not abrupt as in the previous case. These results clearly show that the substrate–molecular interactions also play an important role in molecular assembly and structural development in multilayers.

In the present work the assembly of Cd-arachidate molecules and their structure in multilayers prepared on two different substrates, glass and silicon, under identical transfer conditions has been studied in detail. Cd-arachidate has been chosen because it is one of the prototypical fatty acid salts whose bulk crystal structure is well characterized. Schwartz et al. studied the molecular ordering on the surface of the multilayers made on different substrates and found that it has a centered orthorhombic arrangement independent of the substrate. These studies however did not investigate in detail the interface topography and its role on in-plane ordering of the Cd-arachidate molecules. The only studies reported on a detailed investigation of the interface topography are on tricosenoic acid salt, stearic acid salts, and a liquid crystal polymer. In these studies the lateral
molecular ordering was not investigated. Hence in the present work both interface topography and lateral molecular order were simultaneously studied to understand the structural development in Cd-arachidate multilayers.

The structural characterization of organic monolayers or multilayers in general is nontrivial. Several techniques like electron microscopy/diffraction, optical microscopy, atomic force microscopy, and infrared spectroscopy have been used for characterization. In the present work, however, the grazing incidence x-ray scattering technique has been used which has several advantages. The technique is non-destructive in nature and allows determination of lattice structure, molecular tilt, interface topography, and correlation lengths estimation. Also, in contrast to various microscopy techniques the x-ray technique provides volume information averaged over relatively large areas.

**EXPERIMENTAL METHODS**

The substrates, glass and silicon, were both chemically cleaned before depositing the Cd-arachidate multilayers. The glass substrates were cleaned ultrasonically with a dilute detergent solution at room temperature and also at 353 K to remove grease and proteins from the surface. Insulating substrates such as glass usually develops an electrostatic charge on the surface which can affect the organization of amphiphilic molecules. Hence, the surface charge was neutralized by dipping the substrates in hot chromic acid for a duration of 10 minutes. The substrates were then cleaned with a solution of ammonium peroxide and hydrogen peroxide at 353 K before ultrasonically rinsing and cleaning with isopropyl alcohol. The glass substrate was finally degreased again with isopropyl alcohol before depositing the multilayers. The silicon substrates on the other hand were degreased in trichloroethylene, acetone, and isopropyl alcohol. They were then boiled in concentrated sulfuric acid for 30 minutes followed by cleaning with 2% hydrogen fluoride before subjecting to the RCA cleaning procedure. The multilayers were deposited using the conventional LB deposition technique onto both the substrates under identical conditions. Arachidic acid solution prepared in chloroform was spread on pure water, deionized through a Millipore system, subphase which contained $4 \times 10^{-4}$ M CdCl$_2$ at a pH of 6.4. The layers were then transferred onto the substrates at a surface pressure of 29 mN m$^{-1}$ and 283 K to achieve near unity transfer ratio. A 1D position sensitive detector (PSD) was used to detect the diffracted beam which has a sensitive length of 45 mm at a distance of 959 mm behind the sample. In this scattering geometry a momentum transfer component $Q_z$ which lies outside the plane of incidence is realized. The individual components of the scattering vector that are operative in the various scan geometries are given by the relations

$$Q_x = \frac{2\pi}{\lambda} \sin \theta$$

where, $\theta$ is the incident angle.

RESULTS

The multilayers show clearly the presence of up to 12 orders of Bragg reflections extending to $Q_z \approx 14$ nm$^{-1}$. However, the longitudinal $Q_z$ scan in the range $0 < Q_z < 7$ nm$^{-1}$ only from the Cd-arachidate multilayers on glass and silicon substrates is shown in Fig. 1 for the sake of clarity. These results clearly indicate the presence of well-formed layers on both the substrates, glass, and silicon. The actual multilayer period $d_0$ can be determined directly from the position of the Bragg reflections $\theta_B$ using the refraction corrected Bragg relation,

$$d = d_0 \left( 1 - \delta \sin^2 \theta_B \right),$$

where $d$ is the apparent period at the different Bragg orders and $\delta$ the real part of the effective index of refraction of the multilayer structure. The multilayer period $d_0$ on the glass substrate is 5.54 nm, in agreement with the bulk lattice parameter of untitled, Y-type Cd-arachidate. The period $d_0$ for multilayers on the silicon substrate however is lower than the bulk value at 5.44 nm, indicating a tilted arrangement of the molecules. The angle of tilt with respect to the untitled arrangement can be determined from geometrical considerations using the relation $\cos \theta = d \left( \text{tilted} \right)/d \left( \text{untitled} \right)$ and is found to be $\sim 9.5^\circ$. This is in close agreement with near edge x-ray absorption fine-structure determination of Cd-arachidate...
molecules in multilayers on different substrates, studied by Kinzler et al.\textsuperscript{25} They found that the films deposited on the Ag substrate were unilted while those on the Si substrate were tilted by $8\pm3^\circ$. The total thickness $t$ of the multilayers can be determined from the separation of the intensity oscillations between the Bragg peaks using the relation, $t = \frac{2 \pi}{\Delta Q_z}$. These intensity oscillations arise as a result of interference of the reflections from the air/film and film/substrate interfaces. The peaks separation, however, depends on the radiation wavelength and this becomes extremely small for Mo $K_a$ radiation which has a wavelength of 0.154 nm was used to determine the total thickness of the multilayers in the two cases. The total thickness of the multilayer on the glass substrate is $\sim 40$ nm corresponding to 15 monolayers, in agreement with the layer transfer conditions. The thickness $t$ on the silicon substrate is $\sim 83$ nm corresponding to 31 monolayers, in agreement with the layer transfer conditions.

The longitudinal $Q_z$ scan mentioned above is sensitive only to the electron density variation along the multilayer growth direction and hence does not provide information about the lateral structure. The diffuse component of scattering on the other hand is sensitive to the lateral structural inhomogeneities in the individual interfaces and/or the layers that make up the multilayer. Hence the diffuse, nonspecular scattering was measured in the longitudinal offset scans, $(Q_x - Q_z)$, and the transverse rocking scans $(Q_y)$. The longitudinal offset scans performed with an offset of $0.2^\circ$ and $0.4^\circ$ from the specular condition are shown in Fig. 1 together with the specular scans. The results show several salient points in the two cases and the difference in structure between the two multilayers. The nonspecular scattering exhibits peaks at the position of the Bragg reflections in both the cases indicating that the structural inhomogeneities have a repeat length along the layers growth direction which is identical to the multilayer period $d_0$. The diffusely scattered intensity in the two cases, however, shows different trends. In the case of multilayers made on the glass substrate the diffuse intensity is significant compared to the specular intensity at the Bragg peak positions and nearly the same as the specular intensity at non-Bragg peak positions. The ratio of true specular to diffuse intensity at the Bragg positions decreases from $\sim 30$ at the first peak to $\sim 1$ at the fourth and fifth peak positions indicating that the scattered intensity at higher orders is predominantly diffuse in nature. In the case of multilayers on silicon substrate however the diffuse component of scattering remains low, 1/20–1/40, compared to the specular scattering at all positions. These results clearly show that the lateral topography of the interfaces in the two cases is not identical in spite of the identical layer transfer conditions.

The transverse rocking scans performed at the five Bragg peak positions from multilayers on glass and silicon substrates are shown in Fig. 2. All the five diffuse scans along $Q_y$ exhibit a pronounced peak at $Q_y = 0$ position in the case of the silicon substrate. In the case of a glass substrate however prominence of the central peaks at $Q_y = 0$ decreases with increasing Bragg order. The diffuse scans exhibit a clear central peak only at the first and second peak positions and no clear peak can be seen at the fourth and fifth peak positions. These results are in agreement with the longitudinal offset scan results which show that the specular-to-diffuse intensity ratio decreases with increasing Bragg order in the case of multilayers made on the glass substrate while the ratio remains high in the case of the silicon substrate. A noticeable feature in the transverse scans is the presence of clear peaks at the condition $\theta_{iff} = \theta_c$, where $\theta_c$ is the critical angle for total reflection. These peaks are referred to as the transmission or Yoneda peaks. The implication of all these results to the interface topography in the two cases will be discussed in the next section.

The grazing incidence diffraction spectrum from the Cd-arachidate multilayers deposited on glass substrate is shown in Fig. 3. The scattering vector $Q_{xy}$ in this case is given by the relation $Q_{xy} = (Q_x^2 + Q_y^2)^{1/2}$. The diffraction spectrum shows clearly six peaks indicating that the Cd-arachidate molecules are regularly arranged with a long range periodicity in the plane of the multilayers. The peaks in the diffraction spectrum can be indexed based on an Orthorhombic unit cell$^{26}$ with lattice parameters; $a = 0.486$ nm and $b = 0.745$ nm and these values are in close agreement with the lattice parameters of bulk Cd-arachidate.$^{13}$ The diffraction spectrum shown in Fig. 3 from the multilayers on the silicon substrate however shows very weak peaks at the positions correspond-
ing to the first two strong diffraction peaks at 15 nm\(^{-1}\) and 16.4 nm\(^{-1}\). The other higher order peaks were too weak to be detected with the PSD. These results show that the Cd-arachidate molecules on the silicon substrate have a disordered crystalline arrangement in the plane of the multilayers. The molecular arrangement, distorted hexagonal, is similar to that observed in a Cd-arachidate monolayer on the liquid subphase.\(^{27}\)

**DISCUSSION**

The various parameters that describe the three-dimensional structure of a multilayer in general are; the thicknesses of the individual layers that make up the repeating unit of the multilayer and their optical constants, the macroscopic topography of the interfaces and the microscopic in-plane arrangement of the molecules. The topography of the interfaces in turn is defined by the following parameters: (1) roughness \(\sigma\), (2) roughness correlation length in the plane of the interfaces \(\xi\) and the type of relation between these two parameters expressed by the roughness exponent \(H\), and the nature of roughness correlation between all the different interfaces. Among the various parameters mentioned above, the repeating unit thickness \(d_0\), and the in-plane molecular arrangement (regular or disordered) are the only two parameters that can be determined directly from the different x-ray scattering experimental data. All the other parameters can only be estimated by a simulation of the x-ray scattering behavior of the multilayers.

The x-ray scattering from an imperfect multilayer is made of two distinct components: (1) the coherent part which is due to scattering from an ideal multilayer with smooth interfaces; and (2) the incoherent or diffuse part which is due to scattering from nonideal or rough interfaces. The intensity scattered along the longitudinal specular direction consists of predominantly the coherent part together with the incoherent part that lies in this direction. Hence, this type of scan is sensitive to the electron density variation along the \(z\)- or the growth direction and contains information regarding the individual layer thicknesses, the electron density in the individual layers and the root-mean-square (rms) roughness \(\sigma\) of the interfaces. A simulation of the specular scattering behavior will provide quantitative information of these parameters. The specular scattering behavior from the Cd-arachidate multilayers has been simulated using Parrat’s recursive optical formalism\(^{28}\) and the interface roughness was taken into account assuming the interface height fluctuations to have a Gaussian distribution.\(^{29}\) The structure of the Cd-arachidate multilayer was subdivided into two alternating repeat layers for the purpose of scattering simulation as
shown in Fig. 4. The first layer is made of the four organic tails which consist of the low electron density CH$_2$ units and the second high electron density layer consists of two Carboxylic group heads with two Cd ions. This type of subdivision of the Cd-arachidate molecules is justified as the phenomenon of x-ray scattering is sensitive only to the interfaces formed between low and high electron density layers. However, it should be noted here that although this model is appropriate to simulate the x-ray scattering behavior, it is inconsistent with the Cd-arachidate molecular structure wherein the real interfaces exist between the low density tails and the high density heads, and not between the tails and heads. The various parameters used in the simulation are given in Table I and the results of the simulation together with the experimental data are shown in Figs. 5(a) and 5(b).

It can be clearly seen from the figures that the simulations fit the experimental data well in the complete range of $Q_z$ investigated and that it describes the multilayer structure along the growth direction. The significant factor however is that the interface roughness $\sigma$ in the case of the glass substrate is $\approx$0.3 nm and that in the case of the silicon substrate is $\approx$0.4 nm. Similar roughness values have been estimated for organic films on liquid surfaces$^{30,31}$ and also in multilayers.$^{15,16}$ In the case of films on liquid surfaces the extremely low value of roughness has been attributed to thermally induced capillary wave nature of the liquid surfaces. In the case of solid multilayers however the origin of such small interface roughness is still not clearly known.

The transverse scans from the Cd-arachidate multilayers on both the glass and silicon substrates shown in Fig. 2 exhibit the presence of pronounced transmission peaks at $\theta_{\text{off}} = \theta_c$. The observation of transmission peaks in the transverse scans has conventionally been attributed to be due to the presence of large interface roughness $\sigma$, which attenuates exponentially the reflectivity $R$ and enhances the transmittivity $T$ exponentially.$^{29,32}$ The simulation of specular scattering however shows that the interface roughness is only 0.3 nm and 0.4 nm on glass and silicon substrates, respectively. These results show that the transmittivity enhancement is due to the extremely low value of $\beta/\delta$, the ratio of optical constants and not due to the interface roughness $\sigma$. This, low value of $\beta/\delta$ is a characteristic feature of the organic multilayers and is not common to inorganic multilayers.

The magnitude and spatial distribution of diffuse scattering in reciprocal space depends on the exact nature of the topography of the interfaces. The diffusely scattered intensity from the Cd-arachidate multilayers along the longitudinal off-specular direction exhibits a $Q_z$ dependence which is similar to that along the specular direction (Fig. 1). The intensity modulations and the position of the peaks are nearly independent of the magnitude of the angular offset indicating the highly correlated or conformal nature of the interface.

![FIG. 4. A schematic diagram showing the two layer model used to simulate the specular scattering behavior of the Cd-arachidate multilayers. The interfaces in the actual multilayers are present between the tails and between the heads. In the model however the interfaces are present between tails and heads.](image)

![FIG. 5. The longitudinal specular scattering from the Cd-arachidate multilayers is simulated as per the two layer model shown in Fig. 4. The specular scattering data was obtained by subtracting the 0.2° longitudinal offset scan data from the $Q_z$ scan. The simulated specular scan is shown by the solid line and the experimental scan by the •. The results of simulation from the multilayers on glass substrate are shown in (a) and those from the silicon substrate are shown in (b).](image)

### Table I. The layer parameters used to simulate the specular scattering behavior of the Cd-arachidate multilayers. The interface roughness $\sigma$ between the tails and the heads in the case of a glass substrate is 0.3 nm and is 0.4 nm in the case of a silicon substrate. The interface roughness is assumed to be identical at the two interfaces; head/tail and tail/head. $\delta$ and $\beta$ are the optical constants of the individual layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness $t$ nm</th>
<th>Interface roughness $\sigma$ nm</th>
<th>$\delta$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>Tails</td>
<td>5.0</td>
<td>0.3</td>
<td>$1.36\times10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Heads</td>
<td>0.54</td>
<td></td>
<td>$3.12\times10^{-6}$</td>
</tr>
<tr>
<td>Silicon</td>
<td>Tails</td>
<td>4.9</td>
<td>0.4</td>
<td>$1.36\times10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Heads</td>
<td>0.54</td>
<td></td>
<td>$2.56\times10^{-6}$</td>
</tr>
</tbody>
</table>
roughness between all the different interfaces, independent of the type of substrate. This type of scattering behavior is predicted from self-affine surfaces and interfaces. The characteristic feature of self-affine surfaces is that the geometric size scaling factor is anisotropic and differs along one of the directions. The height difference function $g(X,Y)$ for an isotropic rough surface can be written as

$$g(X,Y) = \langle [z(x',y') - z(x,y)]^2 \rangle,$$  \hspace{1cm} (2)

where $X$ and $Y$ are the relative spatial coordinates, $(x'-x)$ and $(y'-y)$, respectively. The mean square roughness of all physical self-affine surfaces saturates at a finite length scale, correlation length $\xi$ and the height difference function in such cases is given by

$$g(R) \approx R^{2H} \text{ for } R \ll \xi,$$  \hspace{1cm} (3)

where $R = (X^2 + Y^2)^{1/2}$ is the horizontal distance of separation between all pairs of points on the surface and $H$ is known as the roughness exponent which determines the texture of the surface. The structure factor $S(Q)$ for x-ray scattering within the Born approximation from such a surface becomes

$$S(Q) = \frac{2\pi}{Q} \int_0^\infty \exp \left[ -\frac{Q^2 A R^2 H}{2} \right] R J_0(Q x,y,R) dR,$$  \hspace{1cm} (4)

where $A$ is a constant related to the surface height fluctuations and $J_0(Q x,y,R)$ is the Bessel function of zero order. This expression has no delta functions along $Q_x$ or $Q_y$, i.e., the scattered intensity does not exhibit a true specular component for scans along these directions but only a diffuse component. This type of scattering behavior is observed from the Cd-arachidate multilayers made on the glass substrate and shown in Figs. 1 and 2. The longitudinal offset scans exhibit significant diffuse intensity and the transverse scans exhibit a broad diffusely scattered intensity superposed on the central resolution limited Bragg peak, especially for $Q_x < 3.4$ nm$^{-1}$ (third order Bragg peak). An analytical solution for the structure factor $S(Q)$ given by Eq. (3) exists only for special cases when $H = 0.5$ or 1.0. For the case of $H = 0.5$ the structure factor reduces to

$$S(Q) = \left( \frac{A \pi}{Q_{11}^2 + (A/2)^2 Q_{22}^{3/2}} \right)^{1/2},$$  \hspace{1cm} (5)

and the scattered intensity in this case has a Lorentzian distribution. A fit of the transverse scans (third to the fifth Bragg peaks) obtained from the Cd-arachidate multilayers on the glass substrate to the above-mentioned scattering behavior is shown in Fig. 6. It can be clearly seen that the close agreement between the experimental data and the theoretical predictions indicates the presence of self-affine interfaces with $H = 0.5$ in these multilayers. A similar scattering behavior has been observed in LB multilayers of tricosenoic acid substituted with Cd-headgroup. These results indicate that the layer transfer and the microstructural development in these multilayers is stochastic in nature and the molecules undergo very little surface relaxation after the transfer process.

The transverse scans from the Cd-arachidate multilayers on silicon substrate, shown in Fig. 2, however, show a markedly different diffuse scattering behavior. This type of scattering behavior has been observed earlier and has been attributed to the presence of self-affine interfaces which have small interface fluctuations $\sigma$ and a short in-plane correlation length $\xi$ for these fluctuations. Hence, this type of scattering behavior from the multilayers on silicon substrate is not discussed here in detail.

The Cd-arachidate molecules organize themselves into an ordered orthorhombic structure in the plane of the multilayers on glass substrate. The observation of split peaks in the $14-20$ nm$^{-1}$ wave vector vicinity, (110) and (020), clearly indicates the absence of a hexagonal arrangement. These results are in agreement with earlier observations including the unit cell parameters. The addition of a second layer to a monolayer introduces head–head and/or chain–chain interactions which are known to stabilize the vertical layered structure and also arrange the molecules in the plane of the multilayers into an ordered structure. The lateral arrangement of the Cd-arachidate molecules in the 15 monolayers multilayer on silicon substrate has a disordered arrangement conforming to a distorted hexagonal lattice structure. This result is in agreement with the x-ray scattering results which show that the Cd-arachidate molecules are vertically tilted and the interface has a rough self-affine topography. The vertical tilting of the molecules is known to increase the mean molecular area compared to the unitltiled structure and also result in a loosely packed molecular arrangement. The molecular arrangement in the deposited films is known to depend strongly on the deposition conditions and on the nature of the substrate surface. Small variations in the effective pH of the subphase lead to changes in the concentration of the cations on the liquid surface which in turn affects the structure of the deposited film. The observation that different substrates lead to different structural arrangements under identical deposition conditions can only be understood by assuming that the nature of the substrate surface has a strong influence on the local pH of the sub-
phase. The exact mechanism by which the substrate surface changes the local pH and hence the concentration of the cations on the liquid surface is however still not completely understood.

CONCLUSIONS

The LB multilayers offer a wide variety of structural arrangements as the structure in these materials depends on the different molecular interactions and the processing conditions. When prepared using ‘‘identical’’ processing conditions the structural arrangement depends only on the interactions between the molecules and with the substrate. Hence in the present work Cd-arachidate multilayers were used as model systems to study simultaneously the interface topography vis-a-vis molecular arrangement, on two different substrates, glass and silicon. The structure in the two cases was found to be very different in spite of ‘‘identical’’ layer transfer conditions. The interface roughness fluctuations, ~0.3–0.4 nm have a different in-plane distribution. The interface modulations in the case of multilayers on the glass substrate do not saturate and thus have an in-plane correlation length larger than the coherence length of the incident x-ray beam. These modulations in the multilayers on the silicon substrate however saturate at a finite length. The molecules in the plane of the multilayers are arranged in a periodic fashion on the glass substrate while they have a disordered arrangement on the silicon substrate. All these results clearly indicate that the interface topography, vertical alignment of the molecules and the lateral arrangement of the molecules are all correlated. An untilted configuration of the molecules produces a tight packed, ordered arrangement in the plane while a tilted arrangement produces a loose packed and disordered arrangement of the molecules as seen in the case of silicon substrate. Also, although the macroscopic transfer conditions are identical in the two cases the actual microscopic conditions during the layer transfer process appear to be different resulting in different molecular organization.

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