Morphology of Langmuir-Blodgett multilayers: A near-total external fluorescence and reflectivity study

J. Mati Bloch*
Exxon Research and Engineering Company, Clinton Township, Annandale, New Jersey 08801
and Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439

Wenbing Yun
Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439

K. M. Mohanty
Physics Department, Building 510B, Brookhaven National Laboratory, Upton, New York 11973
(Received 15 September 1988; revised manuscript received 7 March 1989)

X-ray reflection and near-total external fluorescence (NTEF) of Langmuir-Blodgett multilayers of stearate salt were found to be in significant disagreement with a simple-layered structure. The different samples contained one foreign Mn stearate double layer deposited at a different predefined depth for each sample. A binary model of voids accumulated in successive layers is proposed. The lacunar structure for the multilayer that originates with this model fits our reflectivity and NTEF results remarkably well and resolves long-standing discrepancies between optical and x-ray measurements.

The structural aspects of Langmuir-Blodgett (LB) multilayers deposited on a solid substrate have been investigated for several decades now on various length scales.[1-5] For thick LB multilayers, the total thickness of the multilayer $L_{\rm opt}$ obtained from optical interference measurements seemed to be consistently smaller than that inferred from the repeat distance d obtained from x-ray-diffraction measurements[1,2] N, i.e., $L_{\rm opt} < L_{\text{x-ray}} = dN$. The deposition process of the multilayers is discrete and accurately defines the number of layers N in the sample. Recently, the structure by which the molecules arrange themselves in each mono molecular plane was reported to be of a highly ordered orthorhombic nature with a well-defined stacking order between layers.[3] This further confirmed the discreteness of the layers and underscored the incongruity between the x-ray and the optical measurements. Resolving this long-standing and widely documented discrepancy provides an opportunity to understand a fundamental underlying morphological quality of LB multilayers. It also carries practical significance since the organization of LB multilayers is of prime consideration in attempted applications of LB multilayers, e.g., x-ray mirrors, filters, and integrated-optics devices.[6] We have devised a set of reflectivity and NTEF x-ray experiments that constitutes in its entirety a novel approach to the study of the registry of LB multilayers. In NTEF the x-ray fluorescence from an impurity ion is monitored as a function of the angle of incidence of a primary x-ray beam.[7] It allows the identification of the concentration profile of the impurity next to the interface. The information obtained in NTEF is complementary to that obtained from shallow angle reflection in that the dielectric constant of the interface enters in both cases in the Fresnel equations for the primary x-ray beam. The LB samples all contained 51 layers of stearic salt deposited on a flat glass substrate using a conventional LB deposition procedure. The samples were withdrawn at a surface pressure of 30 dyn/cm from a subphase solution of 10^{-3} mole of $CaCl_2$ or $MnCl_2$ in distilled water, at pH$=6.5$ and 22 °C. The metal counter ion in all the samples was 49 layers of Ca and a single "tagged" double layer where the Ca counter ion was exchanged with a Mn ion [cf. inset of Fig. 1(b)]. For each of the samples the foreign layer was deposited at a different depth; this takes advantage of the discreteness of the deposition process. The experiments were conducted using Cu radiation from a rotating anode x-ray source and a Huber two-circle diffractometer. A Ge[111] monochromator was employed to select the CuK_β radiation used throughout these experiments. The x-ray fluorescence was collected using a Si/Li dispersive detector positioned at 2 mm from the sample surface.

The reflectivity and NTEF results. The two Bragg diffraction peaks at $\alpha_m \approx 0.809° \pm 0.004°$ and $1.598° \pm 0.004°$ in the high-angle region, $\alpha > \alpha_{c_1} = 0.20°$, originate with the repeat distance $2d$ of each bilayer of the multilayer [cf. inset of Fig. 1(a)]. Here α_{c_1} and α_{c_2} are the critical angles of the multilayer and the substrate, respectively. α_c is the angle below which the x-ray beam is almost totally reflected from the matter. It relates to the deviation δ of the index of refraction n of the material by the equation $\delta = 1 - n = \alpha_c^2/2$. The fit of these peaks using a modified Bragg equation[8]

$$m\lambda \approx 2d \sin\alpha_m [1 - (\alpha_{c_1}/\alpha_m)^2]^{1/2} \quad (1)$$

yields thickness $d = 25.10 \pm 0.01$ Å, in general agreement with previous results.[4] For an ideal sample with $N = 51$ layers, the thickness L_e of the samples would have been expected to be $L = dN = 1280.1$ Å. This result is in

disagreement with the total thickness of the sample as obtained from the analysis of the interference pattern [Fig. 1(a)] discussed in the following. The peaks in this region $\alpha_{c_1} < \alpha < \alpha_{c_2}$ are the result of the interference between the incident beam and the beam reflected from the substrate. A complete analysis of the spectra requires the solution of the coupled Fresnel equations including the dynamic scattering among the different strata.[5] For the derivation of the reflectivity we have followed the propagation matrix formulation,[9] and the intensity of the electric field inside the matter was calculated using an extension of this technique.[10] A simulation using this formalism for an ideal $N=51$ layers sample with $d=25.1$ Å demonstrates the inadequacy of a simple layered model for the description of the LB multilayer [Fig. 1(a)]. The discrepancy is also evident from the NTEF experiments [Fig. 2(a)]. The coupled Fresnel equations formalism does not lend itself easily to an intuitive interpretation. The approximate modified Bragg approach [Eq. (1)] is also useful here in gaining insight into the cause of the discrepancy.[11] A fit using (1) with the sample thickness L substituted for d yields an effective sample thickness $L_e \approx 1065 \pm 20$ Å and an averaged

$$\delta = 1 - n = \alpha_{c_1}^2/2 = 3.692 \times 10^{-6} .$$

This is in very good agreement with a calculated value of $\delta = 3.63 \times 10^{-6}$. The apparent discrepancy between the thickness $L_e = 1065 \pm 20$ Å of this fit and the one expected from the repeat distance in a simple layered model ($L = 1280$ Å) cannot be excused as an experimental error since it appeared consistently in all three samples, with only a minor deviation of less than 10 Å in the fitted sample length. The ideal layered sample also predicts oscillations in reflectivity and NTEF for angles larger than α_{c_2} that are missing in the experimental data [cf. Figs. 1(a) and 2(a)]. These oscillations are a signature of the sharp surface boundary of the ideal layered model. Graduated surfaces tend to smooth the oscillations.

A morphological model for the structure of a Langmuir-Blodgett multilayer. The LB multilayers exhibit two qualities important to the understanding of their morphological structure: (1) They maintain discrete layered structure with a well-developed self-acquired in-plane orthorhombic registry that extends for at least 100 Å. They also maintain a degree of orientational and positional correlation between the different deposited layers indicating that rafts of the monolayer exhibit an intact self-acquired 3D structure. This is surprising since (2) the monolayer that is spread on the liquid is made of many 2D crystallytes randomly oriented in the plane. It would be unlikely to find the corresponding crystallytes in two successively deposited layers to be appropriately aligned to have interlayer correlation. The process of creating the LB 3D "jigsaw puzzle" requires the LB

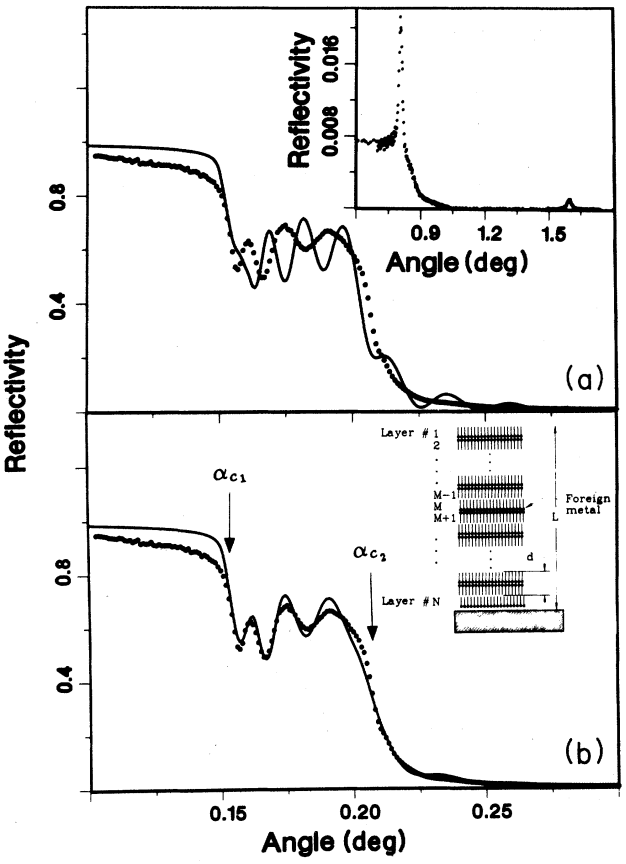

FIG. 1. Experimental reflectivity from a 51-LB-layer sample of Ca/Mn stearate (Mn bilayer 10 bilayers deep). The solid line in part (a) is a reconstruction with an ideal layer sample using the coupled Fresnel equations. Inset in part (a): Higher angle reflectivity from the same sample. In part (b) the fit is done with the same optical parameters as in (a) but using our binomial void model with a single free parameter $p=0.87$ [Eq. (3)]. Inset in part (b): Schematic structure of the ideal composite LB multilayer.

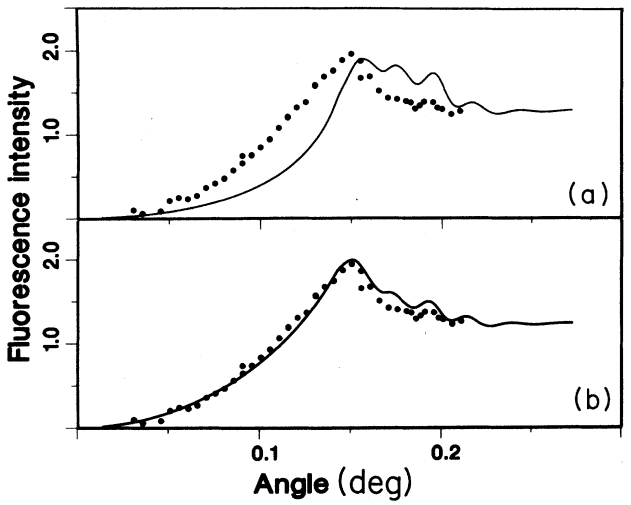

FIG. 2. Experimental NTEF from the sample in Fig. 1. The fit using the binomial void model [Eq. (4)] with the same fraction of voids $p=0.87$ as in Fig. 1 and the same optical constants as in Fig. 1 yields the fit in part (b) [compared to the simulation for an ideal layered structure in (a)].

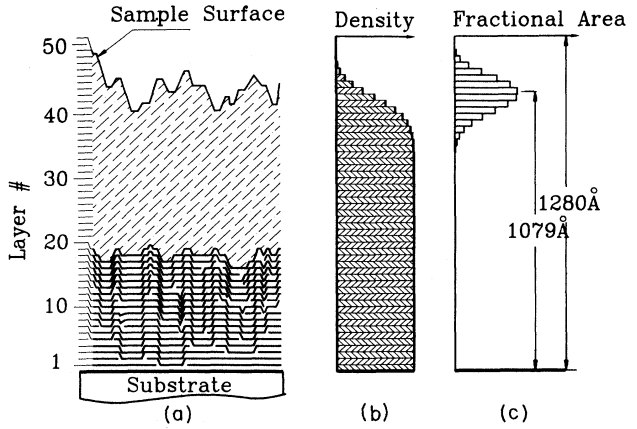

FIG. 3. A model for a Langmuir-Blodgett multilayer with fractional coverage $p=0.85$. The concentration profile of the sample [part (b)] and the fractional area of the surface [part (c)] calculated using Eq. (3) are compared with a "perfect" multilayer sample ($p=1$).

monolayers to rearrange at the time of the deposition process. Each individual monolayer must therefore be ruptured and voids are inevitable in the process of obtaining the 3D structure. The in-plane lattice constant derived from x-ray diffraction changes several percent under temperature changes.[12] This is not likely to be physically possible for a fully covered monolayer since it will require an inordinate reversible glide of macroscopic dimension of the monolayer on the substrate. We propose therefore, that every single monolayer deposited on the solid is a collection of patches of a single layer each of which has a well-defined single layer thickness and ordered in-plane structure. The fraction of the nominal area of the substrate that is covered by the monolayer is indicated by p. The next deposited layer largely duplicates the preceding layer by filling in the voids left out by the preceding layer. In addition, it also adds a small fraction $1-p$ of voids intrinsic to this new layer [Fig. 3(a)]. The probability that the next deposited layer will not contain a void at the same lateral position is also p. The successive application of more layers results in the accumulation of voids from the different layers.[13] If no correlation between the voids on different layers is assumed, then the probability $\mathcal{P}(n)$ of reaching the sample surface after n layers is given by the binomial distribution

$$\mathcal{P}(n)=\binom{N}{n}p^n(1-p)^{N-n},$$

where $\binom{N}{n}=N!/[n!(N-n)!]$. The outer surface of the sample appears fractured and with a lacunar shape where step high terraces of layers make up the surface [see Fig. 3(a)]. The effective total thickness L_e of the multilayer is therefore shorter than the sum of the thicknesses of the deposited layers, and the density profile of the sample is graduated with width ΔL given by the first and second binomial moment distribution:[14]

$$L_e/L=p,\quad \Delta L/L=\sqrt{p(1-p)/N}\ . \tag{2}$$

The average density $\rho(n)$ of the multilayer at layer n is then given by discrete integration over the surface fractions $\mathcal{P}(n)$ up to this layer:

$$\rho(n)=\rho_0 p\left[1-\sum_{k=1}^{n}\mathcal{P}(k)\right],$$

where ρ_0 is the density of a void-free Langmuir-Blodgett multilayer. Substituting the values $L=1280$ Å and $L_e=1065$ Å obtained from the interference peak fits in (2), the fractional coverage p is estimated for our sample to be $p\approx 0.83$. This value is substituted in the equation displayed above to yield the sample profile [cf. Fig. 3(b)]. The reflectivity from such a structure is calculated by convoluting the reflectivity $R_0^{(n)}(\alpha)$ for an n layer sample obtained from the coupled Fresnel equations with the fractional area of the sample surface $\mathcal{P}(n)$:

$$R(\alpha)=\sum_{n=1}^{N=51}R_0^{(n)}(\alpha)\mathcal{P}(n)\ . \tag{3}$$

The fit to our experimental reflectivity results using (3) shows good agreement with the positions of the interference peaks. The obtained value of $p=0.87$ also yields an effective sample thickness very close to the one suggested using the modified Bragg equation (1) that required a length $L_e=1065$ Å for a good fit. The density of the sample (Fig. 3) indeed confirms that the thickness of the sample is about the same effective length as obtained from our binomial model. Notably the calculated reflectivity curve is also monotonic above α_{c_2}: This conforms with the experimental results [cf. Figs. 1(a) and 1(b)]. This is the signature of the graduation inherent to our model. (The substrate roughness, measured independently, was included in the fit.)

Satisfactory agreement was also obtained using the binomial void model to fit the NTEF results from the single foreign layers embedded in the different samples [cf. Figs. 2(a) and 2(b)]. The Mn $K\alpha$ x-ray fluorescence intensity is proportional to the intensity of the primary beam inside the sample at the position of the Mn ions. The distribution of the positions of the Mn ions in the sample is given by the joint probability

$$\bar{\mathcal{P}}(N,n,K,k)=D(N,n,K,k)\mathcal{P}(N,n)$$

of finding the Mn ions in layer k, where

$$D(N,n,K,k)=\binom{K}{k}\binom{N-K}{n-k}\Big/\binom{N}{n},$$

n is the effective number of layers, N is total number of deposited layers, and K is the layer where the Mn ion was originally deposited. The fluorescence from the sample is then given by

$$I(N,K,\alpha)=\sum_{\substack{n=1\\ k=K-N+n}}^{\substack{n=N\\ k\le N \text{ and } k\le K}} I_k^{(n)}(\alpha)\bar{\mathcal{P}}(N,n,K,k)\ . \tag{4}$$

The fits using (4) [Fig. 2(b)] were done with the same refraction indices used to obtain the reflectivity data fit and with the same $p=0.87$ [Fig. 1(b)]. Even a 5% deviation in the value of p results in an observable deterioration of the fit. Furthermore, the model is also highly sensitive to the position at which the Mn double layer was

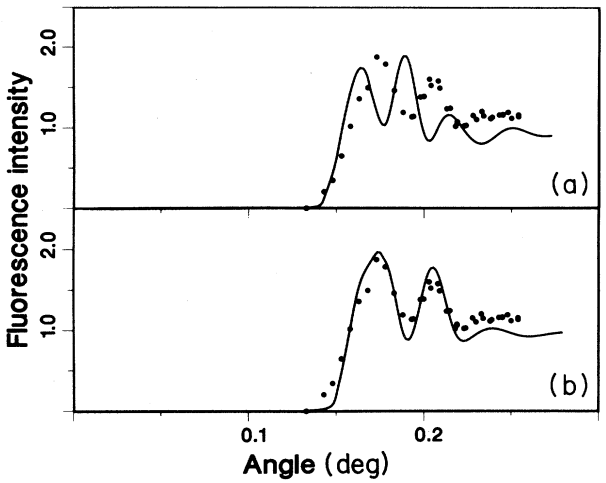

FIG. 4. Experimental NTEF from 49 layers of Ca stearate LB sample and one foreign double layer of Mn stearate deposited on the surface (solid circles). The fit with the ion positions predicted by the binomial model for a monolayer deposited on the surface [part (b)] is significantly better than for a model sample where the foreign metal is displaced by one double layer deeper (50 Å) [part (a)].

originally deposited. For example, an attempt to fit the NTEF results obtained for a sample with the Mn double layer at the surface, with theoretical NTEF calculated for a sample with the Mn double layer at only a single double layer deeper (75.3 Å compared to 25.1 Å from the surface), results in a clearly unsatisfactory fit [cf. Figs. 4(a) and 4(b)]. It is evident that in spite of the highly fractured surface, the deposited layers maintain their relative positions as predicted by our model. This same fact was also demonstrated for other samples where the Mn was originally deposited at various other depths below the surface.

We conclude that a simple statistical binomial void model for the structure of LB multilayers yields remarkable agreement with both depth-dependent NTEF and x-ray reflectivity results. The agreement is especially reassuring since the model is highly constrained, and a single parameter p defines both the effective thickness and the density profile of the LB multilayer. Furthermore, it settles a long-standing discrepancy between optical and x-ray measurements in thick LB multilayers, a phenomenon that was observed and pointed out numerous times in the past. We therefore suggest that the lacunar structure is a universal feature of Langmuir-Blodgett multilayers and that the degree of imperfection depends on the preparation conditions of the samples. It should be noted that an alternative model, where the voids of one layer were not to be filled in by the next deposited layer, but rather that the next layer was to be suspended over the voids of the preceding layer, would have resulted in thickness equal to that of a sample with no voids and therefore would have not fitted our data. Generalization of the binomial void model can be tested for multilayers prepared by other deposition techniques (MBE, etc.), where voids as well as excess material can be simulated using a three-state model.

ACKNOWLEDGMENTS

We thank Dr. Leonid Rozenstein from Forward Technologies for preparing the samples and stimulating discussions. This work was partially supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. One of us (J.M.B.) would like to acknowledge the hospitality of the National Synchrotron Light Source at the Brookhaven National Laboratory, where the work was carried out, and the support of P. Eisenberger and S. Sinha, without which this work could not have been completed.

*Present address: Brookhaven National Laboratory, the National Synchrotron Light Source, Bldg. 510E, Upton, NY 11973.

[1]G. L. Gaines, in *Insoluble Monolayers at Liquid-Gas Interfaces,* edited by I. Prigogine (Interscience, New York, 1966); V. K. Srivastava, Indian J. Pure Appl. Phys. **19**, 780 (1981), and Refs. 22–36 therein.

[2]See Ref. 2, p. 342; A. E. Alexander, J. Chem. Soc. 777 (1939); G. Knott, J. H. Schulman, and A. F. Wells, Proc. R. Soc. London **176**, 534 (1940); S. Bernstein, J. Am. Chem. Soc. **62**, 374 (1940); C. Holley and S. Bernstein, Phys. Rev. **52**, 525 (1937).

[3]J. M. Bloch, L. D. Chapman, S. Garoff, M. Alvarez, and P. Eisenberger, National Synchrotron Light Source Annual Report, 1985 (unpublished), p. 240; J. M. Bloch, L. D. Chapman, S. Garoff, and P. Eisenberger, 1986 Gordon Conference, Santa Barbara, California (unpublished); 1985 NSLS Users Meeting, Brookhaven, New York (unpublished); S. Garoff, H. W. Deckman, J. H. Dunsmuir, M. S. Alvarez, and J. M. Bloch, J. Phys. (Paris) **47**, 701 (1986); M. Prakash, J. B. Ketterson, and P. Dutta, Thin Solid Films **134**, 1 (1985); J. M. Bloch and P. Eisenberger, Nucl. Instrum. Methods B **31**, 468 (1988).

[4]G. L. Clark and P. W. Leppla, J. Am. Chem. Soc. **58**, 2199 (1936).

[5]A. Segmuller, Thin Solid Films **18**, 287 (1973); M. Pomerantz, F. H. Dacol, and A. Segmuller applied the coupled Fresnel formalism in a pioneering work to thin LB films [Phys. Rev. Lett. **40**, 246 (1978)]. Their samples were thin and therefore did not detect the sample thickness discrepancy.

[6]G. G. Roberts, Adv. Phys. **34**, 475 (1985); G. G. Roberts, M. C. Petty, S. Baker, M. T. Fowler, and N. J. Thomas, Thin Solid Films **132**, 113 (1985).

[7]Description of the near total external fluorescence is given in J. M. Bloch, M. Sansone, F. Rondelez, D. G. Peiffer, P. Pincus, and P. M. Eisenberger, Phys. Rev. Lett. **54**, 1039 (1985).

[8]R. W. James, *The Optical Principles of the Diffraction of X-Rays* (Ox Bow, Woodbridge, Connecticut, 1982).

[9]M. Born and E. Wolf, *Principles of Optics,* 6th ed. (Pergamon, New York, 1980), Chap. 1.6.

[10]Our model requires the summation of several hundreds of in-

tensity spectra [cf. Eq. (3)] each involving the propagation matrices of about 200 different strata (for a 51-layer sample). Numerical shortcuts were developed in order to make the intensity calculations required by the morphological model feasible. A full account of the experimental details and calculations are planned to be outlined in a separate publication.

[11]H. Kiessig, Ann. Phys. (N.Y.) **10**, 769 (1931). Note that his Eq. (2) contains an additional factor of $\frac{1}{2}m$ that originates with an opposite optical density ratio between the substrate and the sample. The use of his equation to LB systems may have caused a misinterpretation of the interference results in an interesting earlier reflectivity report: D. S. Kapp and N. Wainfan, Phys. Rev. **138**, A1490 (1965).

[12]W. B. Yun, J. M. Bloch, X. Yang, and J. Viccaro, Abstract to APS March meeting, 1988; and (unpublished).

[13]Defects that are consistent with such voids can be seen in electron experiments. See R. C. Waldbillig, J. D. Robertson, and T. J. Mcintosh, Biochim. Biophys. Acta **448**, 1 (1976).

[14]P. G. Hoel, *Introduction to Mathematical Statistics,* 4th ed. (Wiley, New York, 1971).