NANO SCALE DEFECTS IN LANGMUIR-BLODGETT FILM
OBSERVED BY ATOMIC FORCE MICROSCOPY

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ABSTRACT
In scientific and technical applications, Langmuir-Blodgett films may be useful as nonlinear optical systems, insulating or patterning layers in microelectronics, model systems for two-dimensional phases and templates for protein crystallization. These applications are based on the assumption that a defect-free layered film structure of oriented amphiphilic molecules exists. We here present an atomic force microscopy study of nano scale defects in a typical Langmuir-Blodgett film of fatty acid with hydrocarbon chain length from C_{16} to C_{22}, prepared under conditions often described in the literature. On the surfaces of all films, steps due to the layered structure were found and for a hydrocarbon chain length of C_{20} and C_{22} a surprising number of holes, approximately one monolayer deep, were identified. Molecular resolution showed that the different layers either had the same lattice orientation or a relative orientation close to 0° or 60°. Four observed grain boundaries had a relative orientation close to 60° and the lattice structure was preserved to within less than 1 nm of the grain boundaries. A typical domain size was about 2 μm. All these departures from two-dimensional periodicity may have an important bearing on applications that rely on perfect crystallinity.

INTRODUCTION
Langmuir-Blodgett (LB) films[1] are layers of oriented amphiphilic molecules transferred to a substrate by dipping the substrate through an air-liquid interface where the molecules are spread. The average bulk structure and symmetry of these films have been studied extensively by electron and X-ray diffraction. Recently the atomic force microscope has been used to study the surface topography. This technique has the unique capability of probing only the surface topography and we have resolved both an unexpected buckling superstructure[2] and individual molecules and their surface order[3]. The images with molecular resolution of domain boundaries and steps presented in this paper would be very difficult, if not impossible, to obtain by any other technique.

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For optical applications of LB films, the loss due to scattering from defects, imperfections, etc., is an important parameter and should be kept as small as possible. Conduction through monolayers and multilayers used as insulators is also believed to be dominated by defects. For applications a good understanding of these defects is necessary.

EXPERIMENTAL

Preparation of LB-films

The fatty acids examined were palmitate \((\text{CH}_3\text{(CH}_2)_4\text{COOH})\) i.e. a hydrocarbon chain of \(C_{16}\), stearate (hydrocarbon chain of \(C_{18}\)), arachidate \((C_{20})\) and behenate \((C_{22})\). To prepare the LB film we spread the fatty acid (99% purity) from spectranalyzed chloroform solution (2 mg/ml) onto a water subphase of a trough with \(5 \times 10^{-4} \text{ M CdCl}_2\) and an adjusted pH of 6.5. In the subphase one \(\text{Cd}^{2+}\) crosslink to e.g. two palmitate ions \((\text{CH}_3\text{(CH}_2)_4\text{COO}^-)\) for electroneutrality.

By vertical dipping (1.6 mm/min) the film was then transferred to a polished silicon wafer with orientation (100) at a surface pressures of 30.0 ± 0.1 mN/m. For films with an odd number of layers the wafer was cleaned in a hot solution of \(\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4\) (7:3) at a temperature 90°C for 30 minutes. For films with an even number of layers the cleaning was followed by a 5 second etch in 10% HF, to make the substrate hydrophobic. One film was prepared on freshly cleaved mica.

AFM imaging

For imaging we used a Nanoscope II FM[4] together with microfabricated Si\(_3\)N\(_4\) tips formed on cantilevers with a spring constant of 0.1 to 0.6 N/m. The images (400 × 400 pixels) were recorded in air at room temperature and a relative humidity of 0.5 to 0.8. For molecular resolution we used "force mode", i.e. measuring the \(z\)-deflection of the cantilever while scanning the sample at approximately constant height. When imaging nano scale topography as steps we used the "height mode", i.e. keeping the \(z\)-deflection of the cantilever constant while scanning the sample. The calibrated \(z\)-movement of the sample thereby represents the height of the structures on the sample. The mean force, which was always repulsive and of order 10 to 50 nN, was found not to be critical for the image quality. When estimating the lattice parameters the effect of drift was minimized by using (large) scan areas of 25 × 25 nm\(^2\) to 35 × 35 nm\(^2\) and a (fast) scan rate of 39 Hz. For imaging nano scale topography we used the maximal scan area of 1000 × 1000 nm\(^2\) and a (slow) scan rate of 5-8 Hz.

Approximately 90% of the tips we used immediately gave molecular resolution on the LB-film. These tips were used for further examination of the LB-film, typically for many hours. The AFM scanner was carefully calibrated by fitting linear calibration constants in the \(x\) and \(y\) direction to images of mica.

To estimate a step height we plotted a histogram for an area of 100 × 100 nm\(^2\) around the step. We then measured the height difference between the increased height density due to the surfaces on each side of the step. We subtracted a 3rd order plane to correct for the nonlinearity in the scanning piezos. On some images an average line height (in the \(x\) direction) was subtracted from each line in \(y\), also to reduce nonlinearity. The figures always show the raw data and, unless otherwise mentioned, no image processing or filtering has been applied.
Figure 1: The lattice parameters of 2-5 layer films of cadmium arachidate, measured by AFM. The terminal (topmost) methyl groups, which are probed by the AFM, are drawn as open circles while the black ovals represent the zigzag plane of the alkane chain viewed from above. The methyl group in the centre is shifted relative to the centre of the methyl groups in the corners, but this shift is small compared to the lattice parameters. The standard deviation of a single measurement is $\approx 0.005 \text{ nm}$ for the [10] direction and $\approx 0.008 \text{ nm}$ for the [01] direction. A possible systematic error due to the calibration ($\approx 0.003 \text{ nm}$) is not included.

RESULTS

In the top layer of 2-5 layer films of the fatty acid we found a rectangular lattice with a two molecule basis. The lattice parameters are in good agreement with the “herringbone” structure as examined by Kitagorski[6] and with diffraction data from close-packed, untitled, aliphatic systems. The lattice structure is clearly visible in some of the figures and the lattice parameters are summarized in Fig. 1. The observed thickness of bilayers, as described later, confirm that our images show the terminal methyl groups of the outermost layer with a height corrugation of 0.2 nm due to the silicon substrate.

Film thickness

On the surfaces of all films, occasionally steps due to the layered structure were found. By letting cadmium arachidate (C20) sit in the subphase for half an hour many steps were found. Using the manufacturer’s z-calibration many 2,4 and 6 layer steps could be identified as seen in Fig. 2 (a) and (b). Occasionally steps appearing to be approximately 1.3 or 5 layer were present. The standard deviation for a single measurement of a bilayer step (measured with different tips on different spots) was $6 \pm 1 \%$, which allowed us to unambiguously distinguish 2 layer steps from 1 and 3 layer steps.

The measured lattice parameters are consistent only with the close-packed, untitled, phase. The height of this phase has been examined extensively by x-ray. A least square fit to the bulk thickness of a monolayer as determined by Srivasta and Verma[7], Mann and Kuhn[8] and Matsuda et al.[9] from x-ray experiments has been made. The AFM was then calibrated so the monolayer thickness, determined by the bulk thickness of bilayers of cadmium arachidate (C20), was consistent with these x-ray experiments. This calibration is about 7% higher than the manufacturer’s calibration. The measured monolayer thickness (determined by the thickness of bilayers) is plotted for C16, C18 and C20 in Fig. 3. It is seen that the measured mean height is in good agreement with the x-ray measurements for all chain lengths. The standard deviation on the measured mean height is about 1.5%, comparable to the precision obtained by x-ray.

Due to the amphiphilic nature of the LB-film, one expects steps to be an even number of layers high. However, for a hydrocarbon chain length of C20 and C22 a surprising amount of holes, approximately
one monolayer deep, were identified [see Fig. 2 (c) and (d)]. Molecular resolution at the bottom of these holes was routinely obtained. Five times, the relative orientation between the lattice orientation on the top and the bottom of the holes were the same. Relative orientations of $55.9 \pm 0.5^\circ$ and $68.0 \pm 0.5^\circ$ were discussed later.

The depth of length of squares gives the estimated depth. The filled squares are the standard for the 6 to 7 data point. The depth data from x-ray was discussed later.

Assuming other interfaces or layers or be a hydrophobic hydrophobic

Grain Boundaries
The boundary between two domains is maintained observed at.

Three of $58.4^\circ$, $55.4^\circ$, and $61.4^\circ$ cooled to 74.

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Figure 3: Monolayer thickness as a function of length of hydrocarbon chain. The open squares give the mean monolayer thickness estimated from the thickness of bilayer steps. The filled squares give the mean depth of the holes in the topmost layer. The error bars are the standard deviation of the mean values for the 6 to 30 measurements made for each data point. The solid line is a least square fit to the bulk monolayer thickness determined from x-ray experiments (see text).

$\pm 0.5^\circ$ were also identified. These relative orientations are consistent with hexagonal twinning as discussed later.

The depth of the holes had a standard deviation of about 8%. They could thus be distinguished unambiguously from the bilayer height, and the depth of the holes for C$_{20}$ and C$_{22}$ is plotted in Fig. 3. It is seen that the holes indeed have a depth of approximately one monolayer. However, in particular the depth for cadmium behenic is significant lower than the average height of half a bilayer.

Assuming that the hydrophobic tail group is sticking up in the bottom of the holes, one of the other interfaces beneath the hole must have a hydrophobic-hydrophilic interaction either between layers or between the LB-film and the substrate. The small depth of the holes might indicate that a hydrophobic-hydrophilic interface is higher than the usual hydrophilic-hydrophilic or hydrophobic-hydrophobic interaction.

Grain Boundaries

The boundary between two distinct ordered domains with areas $\geq 10^4$ nm$^2$ is shown in Fig. 4. The two domains have a relative orientation of 55.9 $\pm$ 0.5$^\circ$ with respect to each other and the lattice order is maintained to within about 0.3 nm on each side of the boundary. No holes or other defects were observed at, or near, the boundaries. As the molecular ordering near the grain boundary is similar to that within the grain, it is unlikely that grain boundaries are pathways of enhanced diffusion.

Three other observations of well defined adjacent domains (not shown) gave a relative orientation of 58.4$^\circ$, 55.9$^\circ$ and 68.0$^\circ$.

Transmission electron diffraction (TED) of a 3 layer film deposited on carbon-coated formvar and cooled to 74K showed "hexagonal twinning," i.e. all the domains had orientations close to either 0$^\circ$ or $\pm 60^\circ$ relative to a fixed direction. These TED observations, therefore, suggest that the four relative orientations observed in the top layer by AFM and the two observed relative orientations between layers with a different thickness were clustered around 60$^\circ$ not by coincidence, but because all layers consists of domains which have relative orientations close to either 0$^\circ$ or $\pm 60^\circ$. By considering the number of observed boundaries in comparison to the number of lattice images examined overall, we can estimate the domain size (based on statistical considerations) to be $\approx 2$ $\mu$m.
Figure 4: (a) 25 × 25 nm² image of a 3 layer film of cadmium arachidate prepared on mica. The dashed line marks the boundary between two regions with different lattice orientations. The arrows indicate the lattice directions on the two domains. The bright areas of the image are roughly 0.2 nm higher than the dark areas of the image. (b) 7.5 × 7.5 nm² image of the boundary. The boundary on the images can be identified easily by looking at a grazing angle along the arrows indicating the lattice directions.

ACKNOWLEDGEMENTS
We thank S. Chiruvolu for the TED experiments and Frank Grunfeld of NIMA Technologies for his assistance with the trough and software. This work was supported by the Office of Naval Research Grant No. N00014-90-J-1551, the National Science Foundation Grant CTS90-15537, and the Donors of the Petroleum Research Foundation. JG acknowledges support from the Danish Technical Research Council.

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