Crystallization process of Langmuir–Blodgett films of octadecylthiobenzoquinone

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Atomic force microscopy images of the electron acceptor 2-octadecylthio-1,4-benzoquinone prepared as 2–4 Y-type Langmuir–Blodgett films revealed the formation of nanoscale crystals one week after deposition. The crystals have a layered structure with a total height from 3 to 15 nm and they each covered an area of <1 μm² on the substrate. In the plane of a layer, the molecules formed a two molecular rectangular unit cell with sides of 0.51±0.01 nm and 1.35±0.03 nm. The measured step height of a layer was 3.6±0.2 nm and gives a tilt of the alkyl chains of 54±3° relative to the normal to the interface between layers. The packing density of 0.34±0.1 nm² per molecules in the plane of a layer is significantly different from the packing density on the water subphase during deposition and the packing density found on the flat Langmuir–Blodgett bilayer of about 0.26 nm². This means that a transition from a two-dimensional packing to a three-dimensional bulk crystal has taken place. This transition is more easily induced on a hydrophobic silicon substrate than on a bilayer of hydrophobic fatty acid. Six months after preparation, the crystal had grown in size, and now covered a typical area of ≈15 μm². The mobility of molecules necessary for this growth is discussed.

I. INTRODUCTION

The Langmuir–Blodgett technique plays an increasingly important role as a means of organizing molecular materials at the microscopic level.1 In the ideal situation, the structure of a Langmuir monolayer of surfactant molecules floating on an air–water interface is preserved during transfer of the monolayer to a substrate. Transfer is accomplished by dipping a substrate through the air–water interface, and multilayered structures may be obtained.1 The Langmuir–Blodgett (LB) films hence often represent metastable superstructures, because the thermodynamically stable form of the multilayers is different from the stable form of the monolayers floating at an air–water interface. As a consequence, crystallization of the Langmuir–Blodgett film often occurs in time.2,3

The persistence of LB films is hence kinetically determined. This raises important questions about the mobility of molecules in the LB films since a certain mobility is necessary for the crystallization process. While the stability of LB films of fatty acids has been extensively studied (e.g., Refs. 2 and 3), only little attention has been paid4 to the stability of films of molecules encountered in molecular electronics (e.g., Ref. 5), nonlinear optics (e.g., Ref. 6) etc.

We present here investigations of the crystallization process of LB films of the surfactant electron acceptor 2-octadecylthio-1,4-benzoquinone7 (Fig. 1). The investigation is based mainly on atomic force microscopy (AFM) of 2–4 Y-type layers of the molecules deposited on differently prepared silicon substrates. The atomic force microscope (AFM) has been used to study the surface topography of LB films and the technique has shown the unique capability of probing the surface with molecular resolution.8 On multilayers of the salt of fatty acids, the AFM has resolved domain boundaries9 and a different crystalline order depending on the substrate.10 Lattice parameters have been estimated with an uncertainty (68% confidence) of <1%11 and step heights have been measured with an uncertainty of <2%.12

The structure of LB films of simple fatty acids has been extensively studied by electron13–17 and x-ray diffraction.18–24 Molecules with special electronical properties have been designed and the electrical features of the LB films have been investigated.5–7,25

II. EXPERIMENT

A multilayer of the acceptor molecule 2-octadecylthio-1,4-benzoquinone26 was deposited directly on top of a superpolished silicon wafer with orientation (100) or on a bilayer of cadmium behenate which was deposited on top of a silicon wafer, by the following procedure: The silicon wafer was first cleaned in a hot solution of H₂O₂/H₂SO₄ followed by etching in hydrofluoric acid to make it hydrophobic. The behenate was transferred with 2.0 mm/min from a water subphase in a Langmuir trough (KSV Instrum.) with 5×10⁻⁴ M CdCl₂ and an adjusted pH of 6.5. Details are given elsewhere.27

To prepare the multilayer of the acceptor, a solution of the acceptor in CHCl₃ was spread on a water surface and compressed to 20 mN/m giving a molecular area of 0.26±0.01 nm² (see Ref. 26 for details). Transfer to the surface of hy-
drophobic behenate or etched silicon took place at the down and up stroke with a deposition speed of 1 mm/min. The transfer ratios were 1.0±0.1, indicating full monolayer coverage. After deposition, the samples were stored in ambient air.

For imaging, we used a Nanoscope III FM (Digital Instrument) and microfabricated Si$_3$N$_4$ tips formed on cantilevers with a spring constant of 0.1 to 0.6 N/m. The images (512 ×512 pixels) were recorded in air at room temperature and a relative humidity of 50%–80%. 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 nanoscope topography as steps and crystals, we used the “height mode,” i.e., keeping the z deflection of the cantilever constant while scanning the sample. It was necessary to keep the force at ≈10 nN when imaging the flat LB film of the acceptor, and less than ≈50 nN when imaging the crystals. When estimating the lattice parameters, scan areas of 225 to 900 nm$^2$ were used and we minimized the effect of drift by using a fast scan rate of 39 Hz per line (13 s per images). For imaging nanoscale topography, we used scan areas up to 100 μm$^2$ and a slow scan rate of 5–8 Hz per line (1 to 2 min per image).

From two to six images of mica recorded with six different tips, the AFM scanner (1×1 μm) was calibrated by multiplying the same constant on the calibration constants in the x and y direction. The standard deviation of the length of the reciprocal basis vector for mica was then calculated to be $\sigma_m = 1.7\%$. The absolute uncertainty (68% confidence) of the calibrations is then $\sigma_m/\sqrt{6} = 0.7\%$.

To estimate step heights we plotted a histogram for an area of 0.1 to 1 μm$^2$ around the step. We then measured the height differences between the increased height densities due to the surface on each side of the steps. A third-order plane was subtracted to correct the nonlinearity in the scanning piezo. On some images also an average line height (in the x direction) was subtracted from each line in Y to reduce artefacts created by low-frequency noise. Measurements of the step heights on films made of fatty acid with hydrocarbon length from C$_{16}$ to C$_{22}$ show that the standard deviation for a single measurement of a bilayer step of 4.7 to 5.5 nm is 6%. We will assume that the standard deviation for a single measurement on steps of the acceptor molecule with a comparable height is also 6%. The height measurement (z direction) was calibrated from bilayer steps on cadmium behenate with the known height of 6.04 nm. The absolute uncertainty (68% confidence) on this calibration is 6%.

We did not apply image processing or online filtering to any images of molecules.

### III. RESULTS

One week after preparation, images of the bilayer of the acceptor on top of a bilayer of cadmium behenate showed flat and defect-free areas of the acceptor surface with typical size >20 μm$^2$ [see Fig. 2(a)]. By zooming in on the flat
areas, nanometer-scale domains, with molecular order, were seen. In each domain, the molecules formed an oblique unit cell with a packing density of about 0.26 nm$^2$, roughly equal to the packing density on the water subphase during decomposition. The measured height of a bilayer (4.5±0.2 nm) and the packing density corresponds to a tilt of the chain of ≈40°, relative to the normal of the substrate, assuming close packing of straight alkyl chain. Details about the molecular packing will be published elsewhere.$^{29}$

Contrary to the bilayer on top of cadmium behenate, images of the molecules prepared directly on top of the silicon wafer, showed crystals with steps [see Fig. 2(b)] one week after preparation. Images at more than six different places showed a silicon surface uniformly covered with crystals of heights from 3 to 15 nm, and each crystal typical covered an area of <1 μm$^2$. From histograms, from several images, the average height of material, relative to the surface of the substrate, was estimated to be ≈8±2 nm.

The image in Fig. 3(a) shows a piece of crystal with the layered structure. From the histogram in Fig. 3(b), the height of three distinct steps can be identified. The smallest step found on the crystals were between 3.4 and 3.8 nm and the average height could be estimated to 3.6±0.2 nm. Other steps were ≥7.0 nm and within the error bars of 6% all steps heights were consistent with being two, three, or four times the measured minimum step height of 3.6 nm.

By zooming in on the surface layer on the crystals, the packing order of the acceptor molecule was seen. Figures 4(a) and 4(b) show the surface structure and a 2D Fourier transformation. The pattern of strong and weak peaks in the Fourier transformation show that the surface structure is a nearly centered rectangular lattice with a two-molecular unit cell. The large closed circles shown in Fig. 4(c), which is a drawing of the Fourier transformation shown in Fig. 4(b), correspond to the strong spots of the reciprocal lattice vector (h,k), where h+k is even. The small closed circles correspond to the weak spots of the reciprocal lattice vector (h,k), where h+k is odd. These spots would be missing entirely if the lattice structure were centered rectangular (i.e., a one molecular cell could be chosen).

Due to different noise level, only the strong peaks (h+k even) were present in all the images and the calculation of the lattice structure were therefore based on them. From ten high-resolution images from two different crystals, we estimated the length of the reciprocal vectors (20) to be 9.3±0.2 nm$^{-1}$. The vectors (11) and (11) was estimated to be 13.2 ±0.1 nm$^{-1}$. The relative angle between (20) and (11) or between (20) and (11) was found to be 69±2°, consistent with a rectangular unit cell with a two-molecular basis. The unit cell area was calculated to be 0.69±0.01 nm$^2$. The estimated lattice parameters are summarized in Fig. 4(d).

To examine the stability of the crystals, we investigated the sample with the molecules prepared directly on top of the silicon wafer, ≈15 weeks later [see Fig. 5(a)]. The crystals have now increased in size. They have a height from 5 to 30 nm and they cover a typical area of ≈10 μm$^2$. The sample was examined again 30 weeks after preparation by Nomarski microscopy [see Fig. 5(b)]. It is seen that the surface is uniformly covered with crystals with a typical area of ≈20 μm$^2$.

**Fig. 3.** Image (2×2 μm) of a part of a crystal. The numbers correspond to the number of layers estimated from the height above the surface. (b) Histogram of the image in (a).

A typical spacing between crystals was 15 μm.

We found an adhesion force in the range 10 to 50 nN between the AFM tip and, respectively, the surface of the etched silicon substrate, the flat film prepared on top of a bilayer of behenate and the crystals. This force is mainly caused by the van der Waals interaction and the surface tension.$^{30}$ We further compared the attractive force when the tip was pulled down to the surface at the approach and the attractive force when the tip loose contact withdrawing from the surface. This allowed us to estimate the contribution from surface tension$^{30}$ to be from 5 to 45 nN. The adhesion force due to the surface tension tells us conclusively that the surface of the crystal was covered by a fluid. This fluid most
likely consists of water and/or organic molecules.

IV. DISCUSSION

From a standard space filling model, we find that the total length of the acceptor is \(~0.29\) nm.\(^{20}\) The step heights in the crystal were \(3.6 \pm 0.2\) nm. This height is significantly higher than the length of the acceptor molecule and it is therefore impossible that the layers of height \(3.6\) nm consists of a single layer. We must therefore assume that the steps consisted of bilayers with the alkyl chains tilted \(~54^\circ\) relative to the normal of the interface between layers. This is consistent with close packing of the molecules in the plane of a layer. The cross-section area of the alkane chain is \(~0.20\) nm\(^2\) if the alkane chains are close packed. To give the measured area of \(0.34\) nm\(^2\) per molecules, a tilt of the alkyl chains relative to the normal of the interface between layers of \(~51^\circ\) is necessary.

The area per benzoquinone molecule projected onto a plane perpendicular to the benzoquinone plane can be as small as \(~0.23\) nm\(^2\).\(^{31}\) If the alkyl chains are assumed to form a close packing configuration giving rise to a projected area per molecule of \(0.34\) nm\(^2\), a considerable tilt of the benzoquinone headgroup, relative to the normal of the interface between layers of molecules, is possible. Molecular mechanics calculations show\(^{32}\) that the alkyl chain and headgroup can move rather freely relative to each other. It is therefore plausible that the headgroup can adopt an orientation that also fills space. The exact orientation cannot be determined solely from the present investigation. However,
the structural information available is the approximate orientation of the molecule relative to the normal between layers as given in Fig. 1 and the packing within a layer as given in Fig. 4(d).

A distinct 2D packing was found on the smooth bilayer of the acceptor molecules, deposited on a bilayer of cadmium behenate (Ref. 29). However, a film of the acceptor molecule prepared in the same way, but on an etched silicon substrate, revealed only crystals. Both films were investigated after one week. This suggests that a transition from an unstable 2D packing to a 3D bulk crystal takes place more easily on an etched silicon substrate.

The high-resolution images of the nanoscale crystals also allows us to examine the evolution in the size of the crystals. Comparing Figs. 2, 5(a) and 5(b) show that crystal size increases significantly in time. One week after the deposition the area covered by a crystal was typically 1 μm² while after 30 weeks the typical area had grown to 15 μm². The height and distance between crystals were increased as well thereby keeping the total amount of material per unit area constant.

Although some crystals visible one week after preparation [Fig. 2(b)] are connected, many crystals are not. The image recorded 15 weeks after deposition clearly shows that the silicon has large void areas without crystals. This means that the small crystals, not connected to other crystals, have participated in the formation of larger crystals. A plausible assumption, which explains this mobility, is that the whole surface is covered by a water film which makes it possible for the acceptor molecule to move, presumably due to its surfactant nature.

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28 User Guide to Nanoscope III.
29 J. Garnaes et al. (in preparation).

32 N. B. Larsen (private communication, 1993)