

In-plane Structure of Dotriacontane Films Adsorbed on a Ag(111) Surface

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Introduction

Films of intermediate length alkanes [n -C_nH_{2n+2}; $20 < n < 40$] are of interest as prototypes of more complex polymer films used in coatings, adhesives, and electronic devices. Alkane films are also of interest in their own right, since alkanes are the principal constituents of commercial lubricants. A microscopic understanding of the structure, phase transitions, and dynamics of alkanes near solid interfaces could potentially lead to significant advances in polymer-based technologies and, in particular, lubrication.

We have previously conducted synchrotron x-ray specular reflectivity measurements to investigate the structure and growth mode of dotriacontane ($n = 32$) films on both SiO₂ and Ag(111) surfaces [1–3]. For C32 films deposited from solution onto a SiO₂ surface, the x-ray measurements [1] confirm a structural model of the solid film inferred by high-resolution ellipsometry [4] in which one or two layers of C32 adsorb with the long axis of the molecule oriented parallel to the interface followed by a layer in which the molecules have a perpendicular orientation. At higher C32 coverages, preferentially oriented bulk particles nucleate consistent with a Stranski-Krastanov growth mode. For C32 films grown from the vapor phase on single-crystal Ag(111) substrates in ultrahigh vacuum (UHV), we also observed one or two layers of the “parallel” film but no evidence of a perpendicular layer before nucleation of the preferentially oriented bulk particles [2,3].

From modeling the specular reflectivity scans on the Ag(111) substrate, we have been able to infer the number of C32 layers adsorbed, the interlayer spacing, the area per molecule, and the layer occupancy [2,3]. However, specular scattering does not provide structural information on the in-plane translational and molecular orientational order within the C32 films. Low-energy electron diffraction [LEED] measurements [5] have shown evidence of a crystalline monolayer phase of C32 on the Ag(111) surface at temperatures below 60 °C. Although consistent with a rectangular unit cell, the resolution in the LEED patterns was too low to obtain reliable structural parameters. At higher temperatures, a decrease in the LEED spot intensity indicated a transition to a more disordered phase at ~110 °C.

In order to determine more precisely the in-plane structural order in C32 monolayer and multilayer films, we have undertaken grazing incidence x-ray diffraction measurements on films vapor-deposited onto Ag(111) substrates in UHV. These experiments are part of a larger program to study the structure of both solid and fluid alkane films adsorbed on well-characterized metal surfaces with the aim of better understanding lubrication phenomena at the microscopic level.

Methods and Materials

As in our specular reflectivity measurements, in-plane diffraction experiments utilized a specially designed UHV chamber. Vapor from the C32 liquid reservoir in a Knudsen cell effused through a small aperture (0.5 mm diameter) onto the Ag(111) substrate (10 mm diameter) located at a distance

of 2.5 cm from the aperture. During all depositions, the Knudsen cell was maintained at a temperature of 74 °C. For monolayer coverage, the Ag(111) substrate was held at 105 °C to prevent thicker film growth using deposition times of 20–30 min. The multilayer was grown with the substrate at about 40 °C, exposing it to the C32 vapor for 60 min.

To perform the in-plane diffraction measurements, our UHV chamber was mounted on the four-circle Huber diffractometer at the 6-IDB station of MUCAT at the APS. The measurement technique was similar to that used previously for shorter alkanes [6].

Results

Consistent with the low-resolution LEED patterns, we observed two strong in-plane Bragg peaks in grazing incidence x-ray diffraction from a C32 monolayer adsorbed on the Ag(111) surface at a temperature of ~28 °C. The two peaks are located at a parallel wave vector transfer of $Q_{\parallel} = 1.26 \text{ \AA}^{-1}$ symmetrically placed about the azimuth of the Ag(10) rod (at -90°) as shown in Fig 1(a). The azimuthal separation of the two peaks could be measured with high precision as 6.72° . Assuming a rectangular-centered unit cell as found on a graphite surface [7], the peaks can be indexed as the (-11) and (11) rods, respectively. The rectangular-centered cell has lattice constants $a = 85.06 \text{ \AA}$ and $b = 5.00 \text{ \AA}$

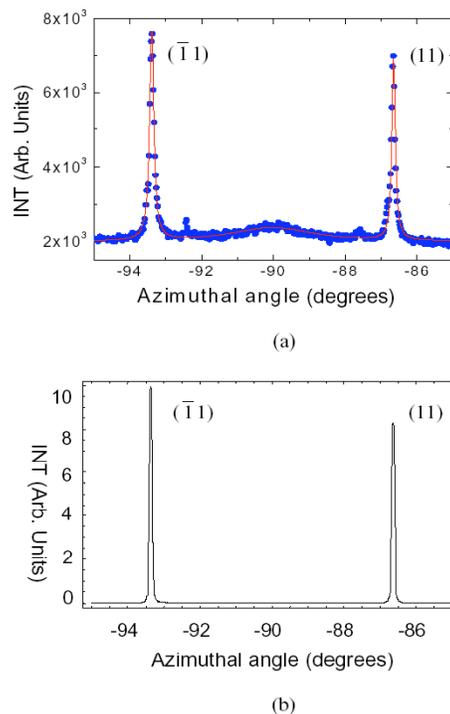


Fig. 1.

corresponding to an area per molecule of 213 \AA^2 in excellent agreement with the value of 209 \AA^2 obtained from analysis of the specular reflectivity scans on similarly prepared films [2,3].

The structure that we have inferred from in-plane x-ray diffraction for the C32 monolayer on the Ag(111) surface is shown in Fig. 2. The solid gray circles are Ag atoms; and the large and small black dots are carbon and hydrogen atoms, respectively. The dashed arrow indicates the direction of the Ag(10) azimuth. **A** and **B** are the lattice vectors of the hexagonal Ag(111) surface.

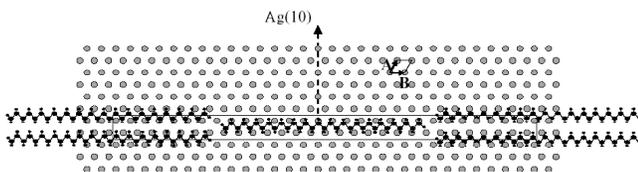


Fig. 2.

The in-plane diffraction scan indicates that the C32 unit cell is at least partially commensurate with the Ag(111) substrate. From the azimuthal separation of the (-11) and (11) Bragg peaks in Fig. 1(a), their value of Q_{\parallel} , and their symmetric location with respect to Ag(10) azimuth, we can conclude that the C32 monolayer is commensurate with the substrate along the direction of the Ag(10) azimuth. In Fig. 2, we see that the **b** lattice vector of the C32 monolayer is along the azimuth of the Ag (10) rod with *b* equal to the distance between Ag atoms in this direction; i.e., $\mathbf{b} = 2\mathbf{A} - \mathbf{B}$. The lattice vector **a** is along the direction of **B**, and *a* is about 29.5 times the nearest neighbor distance of Ag atoms in the Ag(111) plane. However, since *a* is much larger than the Ag lattice constant and no superlattice peaks from the C32 were observed, it is not clear whether or not the monolayer unit cell is also commensurate with the Ag(111) surface in the **B** direction.

Figure 2 shows the orientational relationship between the C32 monolayer unit cell and the substrate. Since the exact adsorption site of the molecules is unknown, the unit cell is placed onto the substrate at an arbitrary location but with known orientation. Potential energy calculations are needed to determine the adsorption site.

Structure factor calculations [5] indicate that the nearly equal intensity of the (-11) and (11) peaks in Fig. 1(a) can be explained by the long-axis of the C32 molecule being oriented along the **a** direction of the unit cell as shown in Fig. 2. In Fig. 1(b), we have calculated the diffraction intensity expected for the transverse scan of Fig. 1(a) assuming a single domain of the unit cell in Fig. 2 and the coherence length ($L \approx 3000 \text{ \AA}$) determined from the width of the diffraction peaks in Fig. 1(a). The apparent agreement of the calculated intensity with that observed in Fig. 1(a) may be affected by the inclusion of other domains.

Figure 3 shows the temperature dependence of radial and transverse in-plane scans through the C32 monolayer (11) Bragg peak located at $Q_{\parallel} = 1.26 \text{ \AA}^{-1}$ and an azimuthal angle of -86.7° [the Ag(10) azimuth is at -90°]. In the temperature range 30–52 $^{\circ}\text{C}$, one sees little change in the peak position observed in either the radial or transverse scans. By $\sim 60^{\circ}\text{C}$, the peak shifts to lower Q radially and closer to the azimuth of the Ag(10) rod. This indicates expansion of the unit cell in both the **a** and **b** directions as well as a smaller ratio *b/a*. The peak disappears just above 70 $^{\circ}\text{C}$ where the monolayer has a transition to a less ordered phase. The transition is reversible in that the (11) peak reappears when the temperature of substrate is lowered.

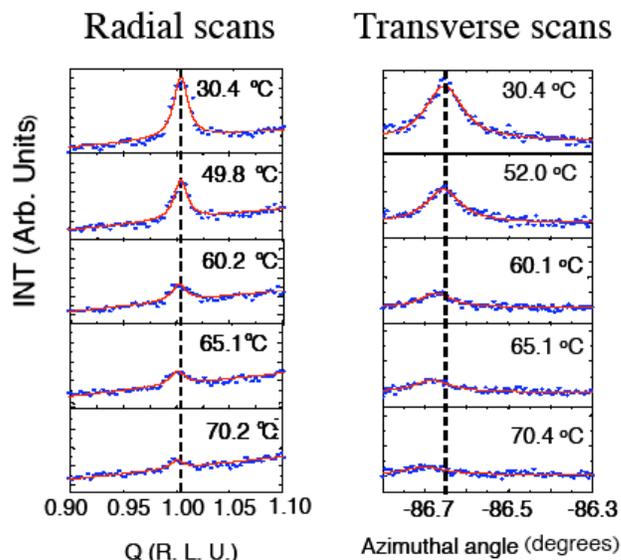


Fig. 3.

We also performed specular reflectivity and in-plane diffraction measurements on multilayer C32 films adsorbed on the Ag(111) substrate. Modeling of the specular reflectivity scans on these samples indicates two complete layers followed by at least two partial layers [5]. As shown in Fig. 4, in-plane transverse diffraction scans taken at a temperature of 28 $^{\circ}\text{C}$ show pairs of Bragg peaks at two different wave vector transfers, $Q_{\parallel} = 1.27 \text{ \AA}^{-1}$ (bottom) and 1.35 \AA^{-1} (top). The peaks within a pair are symmetrically located about the Ag(10) azimuth; but at $Q_{\parallel} = 1.35 \text{ \AA}^{-1}$, their azimuthal separation is too small for both to originate from the same domain. Therefore, we interpret the peaks of each pair as having the same Miller indices but coming from different domains.

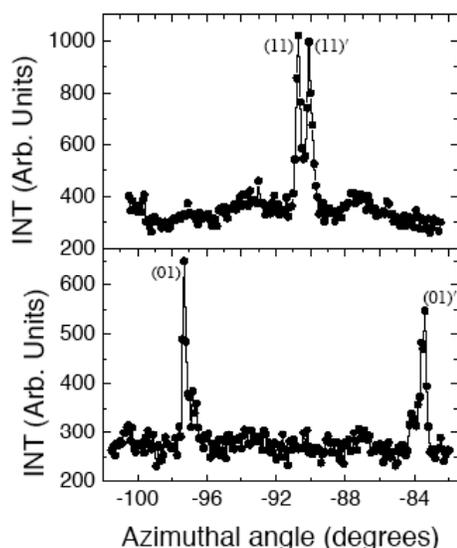


Fig. 4.

Assuming the peaks labeled (11) and (01) in Fig. 4 originate from the same domain, we can fit their position with an oblique unit cell having parameters $a = 41.23 \text{ \AA}$, $b = 5.46 \text{ \AA}$ and included angle $\gamma = 114.8^\circ$ [5]. Furthermore, assuming the cell contains one molecule, these parameters give an area per molecule of 204 \AA^2 in good agreement with the value of 207 \AA^2 inferred from analysis of specular reflectivity scans on similar multilayer samples [5].

As at monolayer coverage, we also made in-plane radial and transverse diffraction scans through the (11) Bragg peak of a multilayer C32 film at higher temperatures. The peak disappeared at $82 \text{ }^\circ\text{C}$ about $10 \text{ }^\circ\text{C}$ higher than for the monolayer.

Discussion

The structure of the C32 monolayer on the Ag(111) surface inferred in this study is similar to its structure on graphite as found by neutron diffraction [7]. The unit cell of both monolayers is rectangular-centered with the long-axis of the molecules parallel to longest lattice vector. The principle difference is that the area per molecule of the C32 monolayer on the Ag(111) surface is about 15% larger than for the commensurate monolayer phase of C32 on the graphite (0001) surface at room temperature ($a = 87 \text{ \AA}$ and $b = 4.26 \text{ \AA}$). The denser monolayer structure on graphite is probably driven by the larger corrugation in the molecule-substrate potential.

In addition to the intense (-11) and (11) peaks observed from the C32 monolayer in Fig. 1(a), we also see a much weaker and broader peak (FWHM = 2.36°) at the same $Q_{\parallel} = 1.26 \text{ \AA}^{-1}$ and centered on the azimuth of the Ag(10) rod. This feature may come from a small amount of C32 in a second layer whose presence is suggested by modeling of the specular reflectivity of other films having nominal monolayer coverage [3]. Molecules in the first layer may serve as a template for those in a partial second layer so that the second-layer molecules, which are also aligned with their long axis parallel to the surface, have the same azimuthal orientation. A bilayer crystal structure of this type has been proposed for C32 adsorbed on graphite [8]. Thus the position of any second-layer molecules could be correlated in the **b** direction but be uncorrelated or have only weak correlation in the **a** direction of the monolayer unit cell. Such a structure would give rise to a broad peak centered at the Ag(10) azimuth corresponding to the same d -spacing as in the first layer.

Two weaker and sharper peaks also appear in the transverse in-plane scan on the C32 monolayer shown in Fig. 1(a). These are located at azimuthal angles of -92.4° and -87.6° , respectively. Because they survived heating of the sample to $600 \text{ }^\circ\text{C}$, they appear to originate from some unknown chemisorbed phase.

It is not clear whether the oblique unit cell inferred for the multilayer C32 film represents a bilayer crystal or a compressed monolayer structure. We note, though, that the lattice parameters of this cell are close to those in the a - c plane of the bulk C32 monoclinic structure ($a = 5.46 \text{ \AA}$, $c = 42.23 \text{ \AA}$, and $\gamma = 116.5^\circ$) [9].

The origin of the phase transition that we find upon heating the C32 monolayer to $\sim 70 \text{ }^\circ\text{C}$ also is uncertain at this time. Molecular dynamics simulations and neutron diffraction measurements indicate a transition from a "smectic" to an isotropic fluid phase in a C32 monolayer adsorbed on graphite at a temperature of $77 \text{ }^\circ\text{C}$ [10]. Such a transition might also be occurring on the Ag(111) surface; however, this interpretation leaves some doubt as to the origin of another phase transition at $\sim 110 \text{ }^\circ\text{C}$ found in LEED

measurements [5]. The transition temperature of $82 \text{ }^\circ\text{C}$ observed for the multilayer film is about 14 degrees higher than the bulk melting point of C32. This perhaps favors the interpretation that the oblique unit cell that we have inferred at this coverage represents the structure of a compressed first layer of the film rather than that of a multilayer crystal.

Acknowledgement

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