Structure and growth of dotriacontane films on SiO$_2$ and Ag(111) surfaces: synchrotron X-ray scattering and molecular dynamics simulations

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We report synchrotron X-ray scattering experiments and molecular dynamics simulations of the structure and growth mode of dotriacontane (n-C$_{32}$H$_{66}$ or C$_{32}$) films adsorbed on Ag(111) and SiO$_2$-coated Si(100) substrates. On the SiO$_2$ surface, the X-ray measurements confirm a structural model of the solid film inferred from high-resolution ellipsometry measurements in which one or two layers of C$_{32}$ adsorb with the long axis of the molecule oriented parallel to the interface followed by a monolayer in which the molecules have a perpendicular orientation. At higher C$_{32}$ coverages, preferentially oriented bulk particles nucleate consistent with a Stranski–Krastanov growth mode. On the Ag(111) surface, we again observe one or two layers of the “parallel” film but no evidence of the perpendicular monolayer before nucleation of the preferentially oriented bulk particles. We compare the experimentally observed structures with molecular dynamics simulations of a multilayer film of the homologous C$_{24}$ molecule.

1 Introduction

Films of intermediate length alkanes [n-C$_n$H$_{2n+2}$; 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.

The structure at the molecular level of normal alkane films adsorbed on solid surfaces has been studied by diffraction techniques for over twenty-five years. The first experiments used low-energy electron diffraction (LEED) to investigate shorter alkanes of carbon number n = 3 to 8 on the Pt(111) surface [1] and carbon number n = 4 to 8 on the Ag(111) surface [2]. The LEED experiments were followed by neutron diffraction studies on normal alkanes (n = 2, 4, 6) deposited from the vapor phase onto high-surface-area graphite substrates (Grafoil) as reviewed in Ref. [3]. Neutron as well as X-ray measurements using polycrystalline graphite substrates have continued with recent surveys of the monolayer structure of even alkanes up to n = 14 [4] and odd alkanes up to n = 15 [5]. It has also been possible to use neutron diffraction to determine the monolayer structure of intermediate-length alkane films (n = 24

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and 32) deposited both from vapor phase and from solution onto Grafoil substrates [6, 7]. The development of new scattering techniques has stimulated further studies of alkane film structure on single-crystal substrates in ultrahigh vacuum (UHV). Synchrotron X-ray scattering has been used to determine the structure and growth mode of short-alkanes \((n = 4, 6, 7)\) vapor-deposited on the Ag(111) surface [8].

In addition, He atom scattering has been applied to monolayer structure determination, e.g., alkanes \((n = 8, 9, 10)\) adsorbed on a Cu(111) surface [9]. More recently, Riegler and co-workers have studied the structure and wetting topologies of intermediate-length alkanes \((15 < n < 50)\) deposited from solution onto SiO\(_2\)-coated Si(100) substrates [10–12]. Our own work on these systems has focused on the structure and growth mode of dotriacontane films \((n = 32, \text{denoted } C_{32})\), which we have investigated by both high-resolution ellipsometry [13] and synchrotron X-ray specular reflectivity measurements [14]. Our measurements have revealed a previously unobserved growth mode of alkane films on a solid substrate: in the first one or two C\(_{32}\) layers adjacent to the substrate, the molecules orient with their long axis parallel to the surface. This “parallel” film is followed by a monolayer in which the molecules adsorb with their long-axis perpendicular to the interface. At still higher coverages, preferentially oriented bulk particles nucleate indicating a Stranski-Krastanov growth mode. This growth mode differs from that proposed earlier for these systems [10] by the inclusion of the “parallel” film immediately adjacent to the SiO\(_2\) surface.

Since the “perpendicular” monolayer was not observed in studies of films of shorter n-alkane molecules grown from the vapor phase on a Ag(111) surface [8], it is of interest to ask such questions as whether the growth mode of solid alkane films depends on the length of the molecules, the choice of substrate, and the deposition method. To address these issues, we have undertaken X-ray specular reflectivity measurements on C\(_{32}\) films grown from the vapor phase on single-crystal 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.

2 Methods and materials

For this study, the C\(_{32}\) films were grown \textit{in situ} using a specially designed UHV chamber. Vapor from the C\(_{32}\) 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 25 mm from the aperture. For monolayer coverage, the Knudsen cell was held at a temperature of 73 °C, while the Ag(111) substrate was held at 106 °C to prevent thicker film growth. The multilayer was grown with the Knudsen cell at the same temperature but the substrate at 42 °C, exposing it to the C\(_{32}\) vapor for 20 min. The highest C\(_{32}\) coverage was achieved by increasing the temperature of the Knudsen cell to 110 °C with the Ag(111) substrate fixed at 30 °C for a deposition time of 40 min.

We conducted the X-ray reflectivity measurements at the 6-IDB station of MUCAT at the Advanced Photon Source, Argonne National Laboratory. Specular reflectivity curves were obtained by integrating the intensity of individual “rocking” curves taken at closely spaced intervals along the specular rod (wave vector transfer \(Q < 2.5 \text{ Å}^{-1}\)). After making corrections for beam spillover, other geometrical effects, and \(Q\)-resolution, the curves were fitted with an atomic model that included contributions from both the Ag crystal and the alkane layers [8]. From the fit, parameters such as the height of the alkane layers and their density were obtained.

3 Results

The X-ray specular curves taken at room temperature for a monolayer and a “multilayer” sample are shown in Fig. 1 and Fig. 2, respectively. The solid symbols are data points and the solid lines are the best fits to the model that assumed the first \(N\) molecular layers of the film to be complete followed by up to three partial layers with fractional occupancy \(\theta_1, \theta_2, \theta_3\), respectively (note that the subscript indicates the number of partial layers following \(N\) complete layers). The C\(_{32}\) molecules were taken to be in the all-trans configuration.
In the case of the monolayer, the best fit is obtained with the C32 carbon skeletal plane parallel to the substrate whereas parallel and perpendicular orientations yielded comparable fits for the “multilayer” film. The monolayer fit gives an area of $A_{C32} = 209 \text{ Å}^2$ per molecule, a second layer occupancy of $\theta_1 \sim 9\%$, and a height of the carbon skeletal plane above the Ag(111) surface of $d_{AgC32} = 4.04 \text{ Å}$. Similar measurements of the molecular height in monolayer butane ($n = 4$), hexane ($n = 6$), and heptane ($n = 7$) on the Ag(111) surface have yielded values of 3.60 Å [8], 3.60 Å [15], and 3.79 Å [15], respectively, which are somewhat smaller than the value we find for $d_{AgC32}$. However, our measured value of $d_{AgC32}$ is in reasonable agreement with a recent calculation of 3.90 Å for the height of polyethylene above the Ag(111) surface [16].

Assuming a parallel orientation of the molecules, the fit to the “multilayer” gives about the same area per molecule ($A_{C32} = 208 \text{ Å}^2$) and first C32 layer height ($d_{AgC32} = 3.93 \text{ Å}$) as for the monolayer. Although we estimated the amount of C32 deposited on the substrate for the “multilayer” sample to be greater than that required to grow four layers of parallel-oriented molecules, the best fit gives fractional occupancies $\theta_1 \sim 60\%$ and $\theta_2 \sim 6\%$ of the second and third layers, respectively. It also gives a distance of $d_{C32} = 3.91 \text{ Å}$ between the C32 layers.

To investigate the possibility of growing thicker C32 films on the Ag(111) substrate, we increased both the exposure time to the C32 vapor and the temperature of the Knudsen cell. In Fig. 3, we show the X-ray scan along the specular rod for a sample estimated to have a coverage equivalent to 63 layers in which the molecules are oriented with their carbon backbone plane parallel to the surface. Here we observe Bragg peaks from preferentially oriented bulk particles consistent with the nucleation of an orthorhombic
orthorhombic phase

monoclinic phase

parallel film (1–2 layers)

SiO₂

Ag(111)

Fig. 4 (online colour at: www.pss-a.com)
Model proposed for the growth of C₃₂ films from solution on a SiO₂ surface.

Fig. 5 (online colour at: www.pss-a.com) Model proposed for the growth of vapor-deposited C₃₂ films on a Ag(111) surface.

phase as found for C₃₂ deposited onto the SiO₂-coated Si(100) substrates [14]. The Bragg peaks indicate three different orientations of the orthorhombic particles: (i) an (00l) series corresponding to particles that are oriented with the ab-plane parallel to the surface; (ii) an intense peak indicating a large number of particles with their (110) plane parallel to the surface; and (iii) a weaker peak from particles having a (020) plane parallel to the surface. The lattice constants of the orthorhombic unit cell calculated from these peaks are \( a = 4.95 \, \text{Å}, b = 7.52 \, \text{Å}, \) and \( c = 42.5 \, \text{Å}. \)

4 Discussion

It is interesting to compare the growth mode of C₃₂ on Ag(111) with that on the SiO₂/Si(100) substrate. In both cases, we have inferred that one to two layers of C₃₂ adsorb first with the long molecular axis oriented parallel to the surface as shown in Figs. 4 and 5. Also, for both substrates at sufficiently high coverage, preferentially oriented bulk particles coexist with the film as in Stranski-Krastanov growth. On the SiO₂ surface, two series of bulk Bragg peaks are observed corresponding to particles of a surface stabilized orthorhombic phase as well as the previously reported monoclinic structure [17] both oriented with the ab-plane parallel to the film plane as shown schematically in Fig. 4 [14].

The inferred orientation of the bulk particles on the Ag(111) surface is shown schematically in Fig. 5. Again, we find evidence of an orthorhombic phase but this time with three different possible orientations of the particles as described above.
For C32 film growth on the Ag(111) substrate, we do not observe Kiessig fringes with a period consistent with the presence of a C32 monolayer with molecules oriented perpendicular to the surface as we did for growth on the SiO$_2$ surface. Also, our fits to the reflectivity curves of the multilayer samples (including those not presented here) indicate a much smaller film thickness than that estimated from the vapor deposition times assuming about the same sticking coefficient found for shorter alkanes [8]. We note, in addition, that the quality of the multilayer fits is not as good as for the monolayer in Fig. 1.

To aid in interpreting our X-ray scattering results, we have begun extensive molecular dynamics (MD) simulations of film growth of intermediate-length alkanes on a solid substrate. In the first exploratory simulations, we used the smaller C24 molecule (carbon number $n = 24$) in the unified-atom approximation [18] in order to reduce the computation time and a graphite basal plane-surface as in previous simulations [7]. As an example, we show in Fig. 6 results from a vapor-deposition simulation in which 224 C24 molecules were initially placed in a gas phase above the graphite surface in order to simulate the experiments with a Ag(111) substrate in UHV. The molecules were introduced into the simulation cell at a temperature of 300 K with random positions and orientations and then sent toward the static surface.

Figure 6 shows an $x$–$z$ view ($z$-axis perpendicular to the graphite surface) of the instantaneous configuration of the system after evolving for 17.5 ns. In agreement with the growth mode inferred experimentally for the Ag(111) surface (Fig. 4), the simulation shows nearly two complete layers of molecules oriented with their long axis parallel to the surface. Above these parallel layers, there are regions in which the molecules again have a parallel orientation and other regions where the molecules are either disordered or are tilted with their long axis at an angle of $\approx 55^\circ$ with the surface (the tilt is in the y-direction so that the molecules appear perpendicular to the surface in Fig. 6).

The disordered regions of molecules containing many gauche defects may also explain why fits of $N$-layer models as in Fig. 2 yielded a smaller film thickness than that estimated from the vapor deposition times. Further simulations with a larger cell, more molecules, and longer run times will be required to determine whether the more ordered regions above the parallel layers in Fig. 6 actually represent embryos of bulk particles having different orientation as indicated in Fig. 5. Simulations are also underway involving the freezing of a fluid film in an effort to understand the origin of the perpendicular monolayer phase observed in growth from solution on a SiO$_2$ surface.

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