

A novel growth mode of alkane films on a SiO₂ surface

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Abstract

Synchrotron X-ray specular scattering measurements confirm microscopically a structural model recently inferred by very-high-resolution ellipsometry of a solid dotriacontane (*n*-C₃₂H₆₆ or C32) film formed by adsorption from solution onto a SiO₂ surface. Sequentially, one or two layers adsorb on the SiO₂ surface with the long-axis of the C32 molecules oriented parallel to the interface followed by a C32 monolayer with the long-axis perpendicular to it. Finally, preferentially oriented bulk particles nucleate having two different crystal structures. This growth model differs from that found previously for shorter alkanes deposited from the vapor phase onto solid surfaces.

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Films of alkanes [*n*-C_{*n*}H_{2*n*+2}] are of general interest as prototypes of more complex polymers used in coatings, adhesives, and electronic devices. Alkanes are also of interest as the building blocks of biologically important molecules such as lipids, and, in their own right, as the principal constituents of commercial lubricants [1]. The interfacial structure of alkanes at the molecular level has been the focus of many investigations over the past 25

years [2]. For example, an intriguing surface freezing effect at the bulk alkane fluid/air interface was discovered about 10 years ago in which a solid monolayer phase immediately adjacent to the air persists a few degrees above the bulk melting point [3]. In this monolayer phase, the alkane molecules, predominantly in a *trans* configuration, form a hexagonal lattice with their long-axis oriented perpendicular to the interface.

Riegler and co-workers [4,5] subsequently proposed that a similar structure occurs when air is replaced by a solid substrate, SiO₂. That is, a monolayer of perpendicularly oriented alkane molecules adsorbs immediately adjacent to the SiO₂ interface and remains solid up to a melting

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temperature $T_s \approx T_b + 4$ K, where T_b is the bulk alkane melting point. At higher coverages, they showed that incomplete wetting of the alkane molecules results in nucleation on the solid monolayer phase of either solid bulk particles ($T < T_b$) or bulk droplets ($T_b < T < T_s$). Above T_s , a fluid alkane film wets the SiO_2 surface so that T_s is not only the monolayer melting point but also the wetting temperature [6].

Recently, Volkman et al. [7] performed very-high-resolution ellipsometry (VHRE) experiments to investigate the interfacial structure of an alkane film, dotriacontane ($n\text{-C}_{32}\text{H}_{66}$ or C32), adsorbed onto SiO_2 -coated Si(1 0 0) single-crystal substrates. These measurements revealed a rich structure in the temperature dependence of the polarization angle and stray light intensity previously unobserved from alkane films. Fig. 1 shows the growth mode which they inferred from these VHRE measurements. It differs in an essential way from that in [4–6] by including molecular layers adjacent to the SiO_2 surface in which the long-axis of the C32 molecules is *parallel* to the interface. Above this ‘parallel’ film phase, growth proceeds in the manner proposed by Riegler and co-workers: a

monolayer adsorbs in which the molecules are oriented with their long molecular axis *perpendicular* to the interface followed by the nucleation of either solid ($T < T_b$) or fluid particles ($T_b < T < T_s$).

The ‘parallel’ film phase immediately adjacent to the solid interface in the model of Fig. 1 is consistent with a large number of previous experiments on alkane films as well as molecular dynamics (MD) simulations. Experiments on graphite (000 1) [2,8], Cu(1 1 1) [9], Au(1 1 1) [9], Ag(1 1 1) [10], and Pt(1 1 1) [11] surfaces, using a variety of techniques, have always indicated a first layer in which the molecular axis is *parallel* to the surface. In addition, MD simulations of intermediate-length alkanes ($15 < n < 33$) adsorbed on Au(00 1) [12] and graphite (000 1) surfaces [13] show the molecules in the first layer to be parallel to the interface.

There has been no previous report of a ‘perpendicular’ monolayer above a ‘parallel’ phase in alkane film growth. In the case of short alkanes ($n = 4, 6, 7$) adsorbed on a Ag(1 1 1) surface [10], bulk particles were observed to nucleate upon completion of the ‘parallel’ film phase, excluding the presence of a ‘perpendicular’ monolayer. This behavior has also been observed for butane ($n = 4$) [14], hexane ($n = 6$) [15], and tetracosane ($n = 24$) [16] adsorbed on polycrystalline graphite surfaces. However, in experiments with C32 on polycrystalline graphite [16] and in other experiments [9,11], the coverage was not high enough to reach bulk coexistence so that no conclusion about the presence of a ‘perpendicular’ monolayer phase can be reached.

Although the novel growth mode inferred from VHRE for C32 adsorbed on SiO_2 , is plausible [7], it has not as yet received direct microscopic confirmation. Here we show that it is consistent with X-ray specular scattering measurements and determine the thickness of the ‘parallel’ and ‘perpendicular’ C32 film phases on SiO_2 . In addition, we show that the coexisting bulk phase consists of two different structures both of which are preferentially oriented with respect to the film.

Our X-ray specular reflectivity experiments were conducted at the MUCAT undulator beam line 6ID-B at the Advanced Photon Source (APS). The measurement technique and methods of

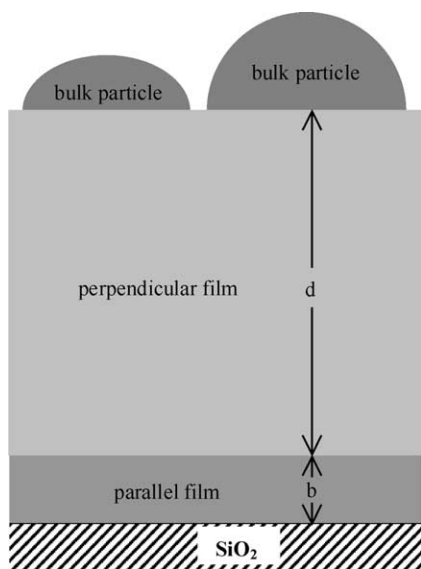


Fig. 1. Model proposed for the C32/ SiO_2 interfacial region based on the VHRE experiments in [7]. The thickness of the parallel and perpendicular films is b and d , respectively.

analysis were similar to those used in earlier studies of alkylsiloxane films adsorbed on Si(1 0 0) wafers [17]. X-rays of wavelength 1.24 Å were reflected off the sample in a vertical scattering plane using slits before the detector to define the divergence of the scattered beam. Background scans were subtracted as in the experiments of Tidswell et al. [17].

As in our earlier ellipsometry experiments [7], the Si(100) substrates were cut from a wafer 0.4 mm thick (Virginia Semiconductor, Inc.) into a square shape 12 × 12 mm and then cleaned in an H₂O₂ + sulfuric acid mixture [17], or they were washed in heptane (*n*-C₃₂H₆₆) which gave similar results. Modeling of X-ray specular reflectivity measurements indicates that the SiO₂ coating of these substrates has a thickness in the range of 12–25 Å (see below). Solid dotriacontane (Aldrich, 97% pure) films were prepared by dipping the silicon substrates into a solution of C32 in heptane for about 5 s. After removal from the solution, the substrate was tilted to let excess heptane run off and any remaining heptane was allowed to evaporate in air. The average C32 film thickness of each sample was measured by VHRE prior to the X-ray experiments just above the wetting temperature ($T_s + 3$ K) where the film should have a planar topology [7].

We show in Fig. 2a the X-ray specular reflectivity scan $R(Q)$ of a 67-Å-thick C32 sample as measured by VHRE. In repeated scans, we observed changes in the X-ray reflectivity attributed to radiation damage (see [17]). However, the reproducibility of the reflectivity measured in initial scans on each sample indicated that radiation damage can be neglected in the results presented here. To emphasize the oscillations in the reflectivity superimposed on the rapidly decreasing background, the reflectivity curve is normalized in Fig. 2b to the Fresnel reflectivity $R_F(Q)$ from a single, perfectly sharp interface. These Kiessig fringes have a period in wave vector transfer ΔQ corresponding to the total thickness of a planar film ($b + d$ in Fig. 1). An estimate of ΔQ made directly from Fig. 2a without fitting a specific model to the reflectivity curve gives a film thickness of $2\pi/\Delta Q \sim 54$ Å. A more accurate model-independent value of the total film thickness can

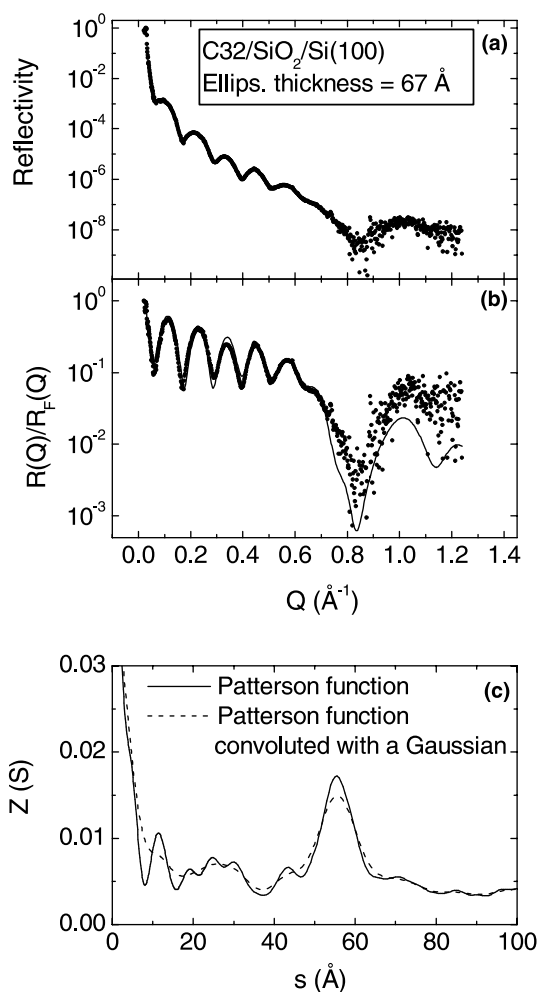


Fig. 2. The X-ray specular reflectivity curves for a C32/SiO₂/Si(100) sample with C32 film thickness 67 Å as measured by VHRE: (a) the measured reflectivity; (b) the reflectivity normalized to the Fresnel reflectivity, $R(q)/R_F(q)$; and (c) the Patterson function $Z(s)$. Roughness of the SiO₂ substrate weakens reflectivity above $Q \sim 0.8$ Å⁻¹ resulting in data scatter.

be obtained from the Patterson function $Z(s)$ shown in Fig. 2c which is calculated from the Fourier transform of $R(q)/R_F(q)$ by the same method used in [17]. We see that the dominant peak in $Z(s)$ is centered at ~ 55 Å consistent with our previous film thickness estimate. There are also weaker peaks in $Z(s)$ at ~ 11 and 43 Å. We verified that these smaller peaks do not result from truncation errors introduced by calculating the Patterson function over a finite Q range. They

survive as shoulders after applying a high- Q Gaussian filter [17] to the data as shown by the dashed curve in Fig. 1c. With the filter present, data above $Q \sim 1.2 \text{ \AA}^{-1}$ contribute negligibly to $Z(s)$.

The solid curve in Fig. 2b is the best fit to a ‘four-slab’ model consisting of a semi-infinite Si substrate, a slab of SiO_2 , and two C32 slabs that allow for different electron densities in the ‘parallel’ and ‘perpendicular’ film phases. The best fit yields thicknesses of $b = 11.7 \pm 0.1 \text{ \AA}$ and $d = 43.2 \pm 0.1 \text{ \AA}$ for the parallel and perpendicular phases, respectively, and $18 \pm 0.4 \text{ \AA}$ for the thickness of the SiO_2 coating. These thickness parameters are insensitive to the initial values used in the fitting routine, and they are consistent with the peak positions in the Patterson function that correspond to distances between the various slab interfaces. The total film thickness $b + d = 55 \text{ \AA}$ is in excellent agreement with the position of the dominant peak in the Patterson function in Fig. 2c, while values of b and d agree with the positions of the weaker peaks in the Patterson function at $s \sim 11$ and $43 \text{ \AA}$, respectively, noted above. Although less certain in that they cannot be resolved after application of the Gaussian filter, the small features in the Patterson function in the range $18 < s < 32 \text{ \AA}$ are also consistent with our slab model; the small peak at $s \sim 19 \text{ \AA}$ corresponds to the thickness of SiO_2 coating, the peak at $\sim 24 \text{ \AA}$ to the distance between the $\text{Si}(100)/\text{SiO}_2$ interface and the interface between the two parallel C32 layers, and the peak at $\sim 31 \text{ \AA}$ to the distance between the $\text{Si}(100)/\text{SiO}_2$ interface and the parallel/perpendicular C32 interface. The electron densities obtained for each slab are in reasonable agreement with bulk values except for a somewhat lower density of the perpendicular C32 slab. We attribute this discrepancy to an incomplete perpendicular monolayer and to bulk particles above it that may effectively reduce the contrast at the monolayer/air interface. The difference in total film thickness determined by VHRE ($67 \text{ \AA}$) and X-ray reflectivity ($55 \text{ \AA}$) will be discussed below.

These X-ray specular reflectivity results support well the structural model in Fig. 1 inferred by VHRE [7]. If there were no ‘parallel film’ phase and only a single layer of molecules oriented per-

pendicular to the interface [4,5], we would expect a smaller film thickness of $\sim 44 \text{ \AA}$, the van der Waals length of the all-*trans* C32 molecule [8]. Moreover, the thickness of $12 \text{ \AA}$ inferred for the parallel film is about twice the width of the C32 molecule, corresponding to a molecular bilayer. X-ray reflectivity results from other samples (not shown) prepared under similar conditions have yielded a parallel film of only monolayer thickness [18]. This may be due to imperfect control over defects in the SiO_2 surface. However, in no cases have we found evidence of the perpendicular film in direct contact with the SiO_2 substrate.

In experiments with films of normal alkanes having carbon number $n < 30$ adsorbed on similarly prepared SiO_2 substrates [19], Merkl et al. [4] inferred a film thickness about 10% *greater* than the all-*trans* length of the molecule. The magnitude of this discrepancy is comparable to a molecular width consistent with the parallel film that we are proposing. It is difficult to explain otherwise, since any tilting of the molecules away from the surface normal would decrease the thickness of the perpendicular monolayer. Also, *gauche* defects known to be present in the molecules at room temperature [12,13] would tend to decrease the thickness of the perpendicular monolayer.

We next present the specular scattering scans for two samples of higher coverage in order to follow the growth mode of the film. As shown in Fig. 3 for a 99- $\text{\AA}$ -thick sample as determined by VHRE, bulk Bragg peaks are now observed consistent with the coexistence of bulk particles as illustrated in the model of Fig. 1. The sample in Fig. 3 actually exhibits two series of bulk Bragg peaks labeled with roman and italic Miller indices, respectively, and whose width is resolution limited. In addition, a Patterson function analysis (not shown) indicates that the Kiessig fringes at low Q have a period corresponding to the same total film thickness of $\sim 54 \text{ \AA}$ as found for the thinner sample in Fig. 2 (VHRE thickness of $67 \text{ \AA}$). Thus an increase in coverage does not result in a thicker film but in the nucleation of bulk particles (islands) as in Stranski–Krastanov growth [10].

In the case of a 153- $\text{\AA}$ sample, we observed no Kiessig fringes as shown in Fig. 4a. However, the same two series of bulk Bragg peaks as seen for the

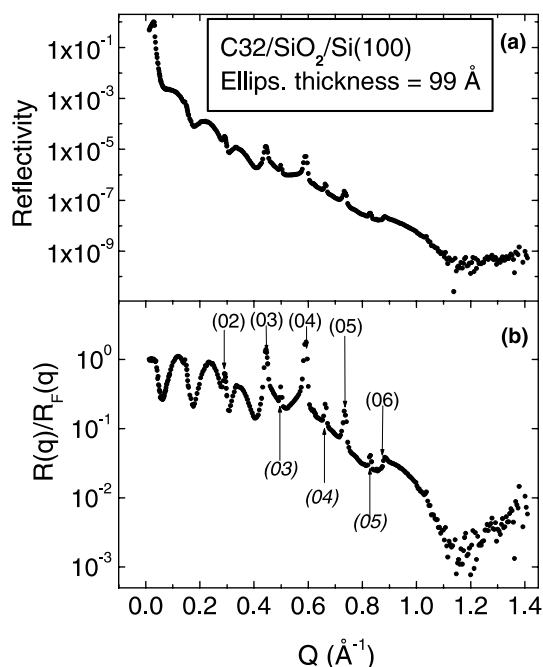


Fig. 3. The X-ray specular scattering curves for a C32/SiO₂/Si(100) sample with C32 film thickness 99 Å as measured by VHRE: (a) the measured reflectivity and (b) the scattering normalized to the Fresnel reflectivity, $R(q)/R_F(q)$.

99-Å-thick sample are present. These peaks are more intense and persist to higher Q than for the thinner sample, apparently obscuring the Kiessig fringes. Analysis of the peak positions in the weaker-intensity series of Figs. 3 and 4 (labeled by Miller indices in italics) yields a d -spacing of 37.8 Å, the spacing between ab -planes in the monoclinic structure reported for bulk C32 crystals [20] shown in Fig. 4b. However, to our knowledge, a bulk structure consistent with the d -spacing of 42.5 Å corresponding to the stronger series of Bragg peaks (roman Miller indices) has not been previously reported. This larger d -spacing closely matches the all-*trans* length of the C32 molecule (~44 Å) and suggests a surface-stabilized orthorhombic phase as depicted in Fig. 4b. It is similar to one that has been proposed previously for n -C₁₆H₃₄ adsorbed on polycrystalline graphite [21].

Except for these two series of peaks, no other bulk Bragg reflections were observed in the specular scattering geometry. This indicates that the

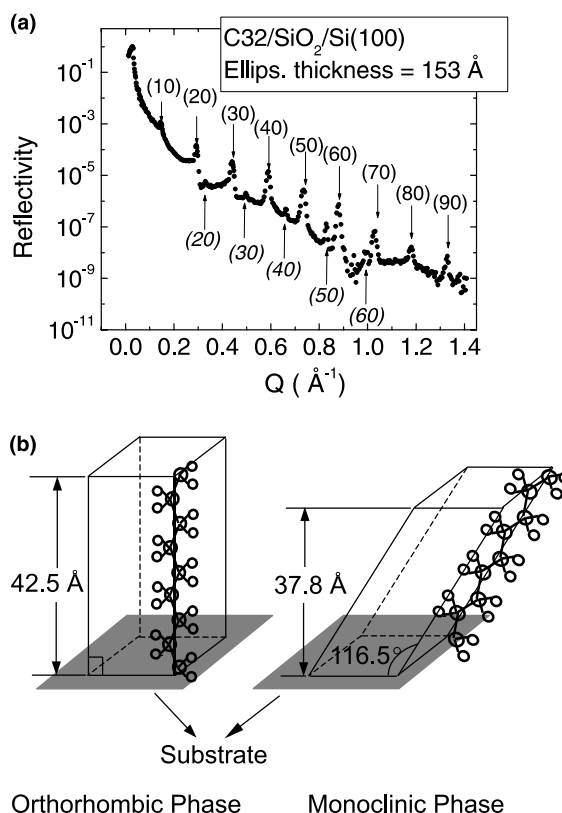


Fig. 4. (a) X-ray specular scattering scan for a C32/SiO₂/Si(100) sample with C32 film thickness 153 Å as measured by VHRE. (b) Models of the bulk C32 crystal structures observed: the proposed 'surface-stabilized' orthorhombic structure (left) and 'free-standing' monoclinic phase (right).

bulk C32 particles of both the monoclinic and surface-stabilized orthorhombic phases grow preferentially with their ab -planes parallel to the film. Since the Bragg peaks of the orthorhombic phase have greater intensity, we speculate that it is growing in equilibrium with the film and that the monoclinic phase is formed metastably during growth from solution.

The discrepancy between the VHRE and X-ray film thicknesses may be caused by the presence of these bulk particles. We speculate that a large fraction of them have a characteristic dimension small with respect to the wavelength of laser light used in the VHRE experiments. These particles would be small enough to contribute to the planar film thickness inferred by analyzing the

ellipsometric data with a Drude model, but large enough to produce Bragg peaks of resolution-limited width in the X-ray experiment. This could explain the systematically larger film thicknesses measured by VHRE compared to those determined from the X-ray measurements.

Although the entropy gain associated with the flexible-chain molecules sampling out-of-plane configurations probably plays a role, the precise mechanism stabilizing the solid ‘perpendicular’ monolayer remains unclear at this point. The intervention of the ‘parallel’ film phase between the SiO₂ surface and the ‘perpendicular’ monolayer may indicate that the scenario proposed for the surface freezing effect at the bulk fluid alkane/air interface [22] does not apply. Presumably, in this theory a ‘parallel’ film phase does not exist at the bulk fluid alkane/air interface because it would inhibit fluctuations along the molecular axis in the ‘perpendicular’ monolayer and hence limit the entropy production needed to stabilize this phase.

Evidence of an incipient ‘perpendicular’ phase has been obtained in MD simulations of Xia et al. [12] of liquid hexadecane (*n*-C₁₆H₃₄) films adsorbed on a Au(001) substrate at 350 K. Their simulations indicate a more compact first layer in which the molecules are nearly parallel to the surface and have some degree of translational and orientational order. Above this layer and extending out to ~40 Å (the limit of their simulation) are molecules which tend to be oriented perpendicular to the surface and contain a larger number of *gauche* defects. Our model in Fig. 1 differs from the liquid structures found by Xia et al. in that both the ‘parallel’ and ‘perpendicular’ films would constitute distinct crystalline phases. In particular, there is evidence from the VHRE experiments that the upper ‘perpendicular’ monolayer supports a crystalline-to-plastic phase transition [7].

A number of questions remain open. For example, is a minimum molecular length required to stabilize the ‘perpendicular’ monolayer phase? What role does the substrate play in its stability? And can a perpendicular phase occur in physisorbed films of other linear molecules? To address these issues, we are conducting MD simulations similar to those of [12] but at temperatures low

enough for the alkane adsorbate to solidify. We are also searching for evidence of a perpendicular monolayer phase in X-ray experiments in progress with C32 vapor-deposited on a Ag(111) surface [23].

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