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Structure and Growth of Vapor-Deposited *n*-Dotriacontane Films Studied by X-ray Reflectivity

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We have used synchrotron X-ray reflectivity measurements to investigate the structure of *n*-dotriacontane (*n*-C₃₂H₆₆ or C32) films deposited from the vapor phase onto a SiO₂-coated Si(100) surface. Our primary motivation was to determine whether the structure and growth mode of these films differ from those deposited from solution on the same substrate. The vapor-deposited films had a thickness of ~50 Å thick as monitored *in situ* by high-resolution ellipsometry and were stable in air. Similar to the case of solution-deposited C32 films, we find that film growth in vacuum begins with a nearly complete bilayer adjacent to the SiO₂ surface formed by C32 molecules aligned with their long axis parallel to the interface followed by one or more partial layers of perpendicular molecules. These molecular layers coexist with bulk particles at higher coverages. Furthermore, after thermally cycling our vapor-deposited samples at atmospheric pressure above the bulk C32 melting point, we find the structure of our films as a function of temperature to be consistent with a phase diagram inferred previously for similarly treated solution-deposited films. Our results resolve some of the discrepancies that Basu and Satija (Basu, S.; Satija, S. K. *Langmuir* **2007**, *23*, 8331) found between the structure of vapor-deposited and solution-deposited films of intermediate-length alkanes at room temperature.

I. Introduction

As the principal constituents of commercial lubricants, linear alkane molecules of intermediate length (*n*-C_nH_{2n+2}, 15 < *n* < 40; hereafter denoted C_n) are natural candidates for both protective coatings and for lubrication of nanoscale devices. They are also the building blocks of many organic molecules. Thus, knowledge at the molecular level of the structure, the growth mode, and the phase transitions of films of intermediate-length alkanes may provide insight into the behavior of thin films ranging from polymers and biological membranes to surfactants and liquid crystals.

The structure of molecularly thin films of C32 deposited from solution onto SiO₂ surfaces has been studied previously by high-resolution ellipsometry,¹ atomic force microscopy (AFM),^{2–4} and both X-ray reflectivity⁵ and in-plane diffraction² techniques. As found for all normal alkanes bound to solid surfaces by van der Waals forces, film growth at room temperature begins with one or two layers of molecules oriented with their long axis parallel to the SiO₂ surface (hereafter referred to as parallel layers).^{1,3,5,6} As coverage increases, islands form of one or more

layers of perpendicular molecules (hereafter referred to as perpendicular layers) coexisting with preferentially oriented bulk particles.^{2,3,7} Temperature cycling of dip-coated films above the bulk C32 melting point *T*_b = 341 K results in a decrease in the number of molecules in these perpendicular layers and a corresponding increase in the size of the bulk particles.² This behavior suggests that the perpendicular layers are metastable at low temperature and may be pinned to impurities and defects in the underlying parallel layer while the bulk particles are thermodynamically stable. Thus, solid C32 films, like those of all other alkanes, appear to exhibit a Stranski–Krastanov growth mode in which preferentially oriented bulk particles nucleate above parallel layers of film.

Figure 1 contains a sketch of the phase diagram in the chemical potential/temperature plane inferred for C32 deposited from solution onto a SiO₂ surface² at atmospheric pressure. At room temperature, bulk particles having an orthorhombic structure denoted *C'* nucleate above the parallel layers.^{2,5} These orthorhombic particles are preferentially oriented with their *a*–*b* plane parallel to the SiO₂ surface such that the long axis of the C32 molecules is aligned along the surface normal.⁵ On heating, the *C'* phase transforms to a bulk rotator phase *R'*,² which, on further heating to within a few degrees of the bulk melting point *T*_b, becomes unstable to a monolayer phase in which the molecules remain oriented perpendicular to the surface. Just above *T*_b, this monolayer phase undergoes a delayering transition to three-dimensional (3D) droplets (the *L* phase) that remain present up to their evaporation point.

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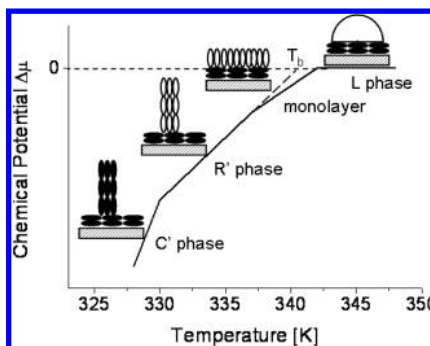


Figure 1. Sketch of the phase diagram of C32 films adsorbed on a SiO₂ surface as proposed in ref 2. The vertical axis $\Delta\mu$ is the chemical potential relative to that of the bulk liquid phase. The cartoons depict the different C32 phases: 3D crystalline (C'), 3D rotator (R'), monolayer, and 3D liquid (L) phases. Filled and open ellipses represent molecules that are orientationally ordered and disordered about their long axis, respectively.

The presence of the metastable perpendicular layers encountered in growth from solution motivated us to consider growing C32 films on the same substrate by deposition from the vapor phase. This method has the advantage of being able to control coverage more precisely, enabling growth of thinner films for which it might be easier to approach quasi-equilibrium conditions. Also, vapor deposition eliminates possible effects of a solvent on both the film structure and morphology⁸ and allows a more straightforward comparison of the experimentally observed film structure with that found by computer simulation.

Basu and Satija⁹ have investigated the structure and morphology of a series of alkane films (C17 to C30) grown from the vapor phase on a SiO₂ surface under quasi-equilibrium conditions. Their results at room temperature agree qualitatively with those obtained on samples grown from solution.^{2–5} That is, for the entire series of alkanes investigated, their X-ray reflectivity measurements can be fit by a model of a single parallel layer of molecules followed by a perpendicular layer.

Nevertheless, the film structure and morphology found by Basu and Satija⁹ differs in some respects from those grown from solution.^{2–5} For example, their vapor-deposited samples showed only one parallel layer, whereas films deposited from solution have more often shown two layers.^{3,5} They also found the single parallel layer to be less dense than the perpendicular layer above it, whereas AFM^{2,3} and synchrotron X-ray reflectivity measurements⁵ on dip-coated samples have indicated a nearly complete parallel bilayer covered by partial perpendicular layers. Perhaps most surprising was their films' instability in air. Both their X-ray reflectivity curves and AFM images indicated a loss of molecules in the perpendicular layer on exposure to air. Finally, for reasons that are unclear, they were unable to grow films of alkanes longer than C30.

In this paper, we extend our previous work^{1–5} by investigating the structure and growth mode of C32 films vapor-deposited in vacuum. Our goal is to reconcile the differences in structure at room temperature found by Basu and Satija in growth of films of shorter alkanes from the vapor phase as well as to investigate the structure of our vapor-deposited alkane films at higher temperatures.

Toward this end, we have conducted a series of synchrotron X-ray reflectivity measurements as a function of temperature on C32 films vapor-deposited on a SiO₂ surface. Films were grown in a vacuum chamber equipped with a Knudsen cell and a high-resolution ellipsometer that allowed monitoring film thickness to

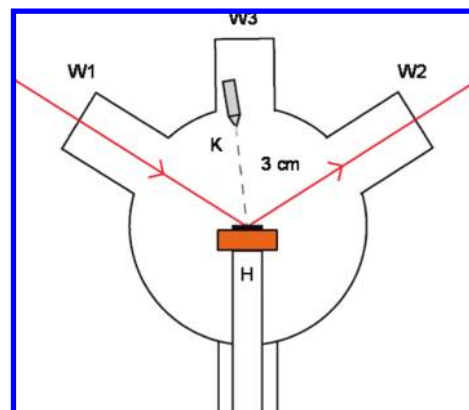


Figure 2. The sample holder (H) is mounted inside a vacuum chamber at a distance of 3 cm from the Knudsen cell (K). For ellipsometric measurements, light enters through window W1 at an angle of 60° from the surface normal, reflects from the sample, and exits through window W2. The stray light intensity is observed through window W3.

within a fraction of a perpendicular layer. After exposure to air, the X-ray measurements were conducted in a helium atmosphere from room temperature to above the bulk C32 melting point. In general, our measurements yield a film structure and morphology similar to that found for films grown from solution.²

II. Experimental Section

A. Film Deposition. As in our earlier experiments,^{1–5} we deposited C32 films on a polished crystalline Si(100) wafer (Virginia Semiconductor, Inc.) 0.4 mm thick that is coated by its native oxide. All of our samples were fabricated from the same wafer. Analysis of the X-ray reflectivity curves (see below) indicates that all samples had the same thickness of the SiO₂ coating (~ 12 Å). Prior to deposition, we cleaned the silicon substrate by immersing it into a solution of sulfuric acid and hydrogen peroxide (70% H₂SO₄ + 30% H₂O₂) at 363 K for 30 min.¹⁰ After cleaning, substrates were stored in ultrapure water and then dried in a jet of dry nitrogen before mounting in the vacuum chamber.

C32 of 99% purity (Aldrich) was loaded into a Knudsen cell, which was mounted in a vacuum chamber about 3 cm in front of the substrate (see Figure 2). Film growth was monitored *in situ* and in real time using high-resolution ellipsometry. Light from a He–Ne laser beam is reflected from the sample, and changes in its polarization angle are proportional to film thickness averaged over the illuminated area (~ 1 mm²). Details of the ellipsometric technique have been given previously.^{1,11} In addition, we used a photomultiplier tube to record the stray light intensity (SLI) scattered isotropically from the sample. The SLI provides a measure of the surface roughness of the film on a length scale comparable to the wavelength of the incident laser light.¹

During vapor deposition, the substrate was held at a temperature of 314 K to anneal the film while maintaining the base chamber pressure of $\sim 10^{-6}$ Torr. Higher substrate temperatures resulted in desorption of C32. As shown in Figure 3a, a ~ 55 Å thick C32 film was deposited at a nearly constant rate over a period of approximately 6 h. This rate was chosen to be slow enough to promote annealing of the film during growth. As expected, though, the SLI (not shown) increased during deposition, consistent with the roughening of the film as it thickened. After completing the deposition, we continued to anneal the film at 314 K in vacuum for ~ 10 h while monitoring its thickness with the ellipsometer. During this time, the film thickness decreased

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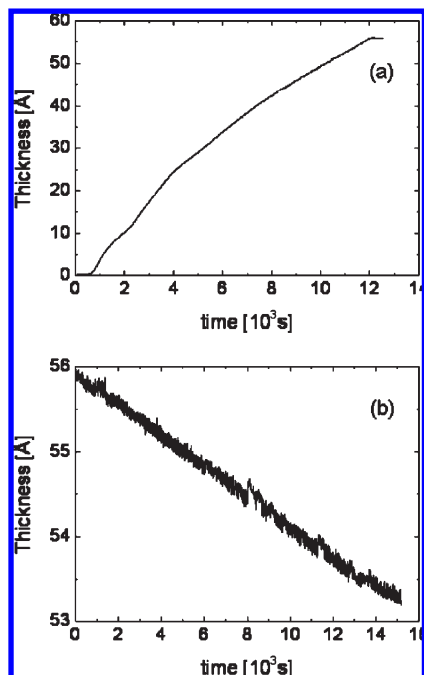


Figure 3. (a) Ellipsometric film thickness versus time. Sample growth took ~ 3.6 h. (b) First 4 h of the annealing process at 314 K in vacuum: film thickness versus time.

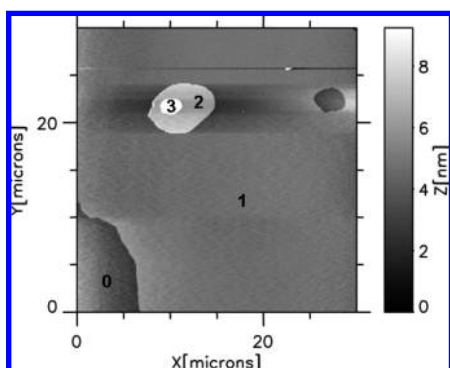


Figure 4. AFM image of a C32 film vapor-deposited onto a SiO₂ surface. The film has an ellipsometric thickness of ~ 50 Å after annealing at 314 K as described in the text. Levels 0, 1, 2, and 3 correspond to a parallel bilayer and first, second, and third perpendicular layers, respectively.

at a constant rate as shown in Figure 3b, while the SLI (not shown) also had a downward trend.

In Figure 4, we show an AFM image taken in the amplitude modulation mode⁴ of the same vapor-deposited sample whose growth and annealing is characterized in Figure 3. After deposition and subsequent annealing for 10 h at 314 K, the C32 film has a thickness measured ellipsometrically of ~ 50 Å. The AFM image shows that the film consists of a bilayer of parallel molecules that completely covers the surface (labeled 0) which is almost covered by a perpendicular layer (labeled 1). Situated on this perpendicular layer are smaller islands of second (labeled 2) and third (labeled 3) perpendicular layers. No bulk particles were seen in the scan areas. AFM images of samples that were prepared identically but did not undergo the annealing treatment showed bulk particles in addition to partial first and second perpendicular layers of larger area than the annealed samples. Thus, annealing in vacuum at 314 K appears to result in slow desorption of molecules from bulk C32 particles as well as from the partial perpendicular layers.

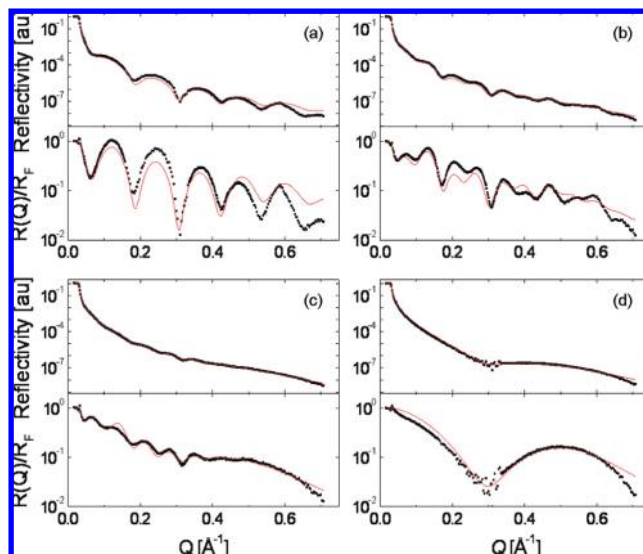


Figure 5. X-ray specular reflectivity curves under different conditions for a C32/SiO₂/Si(100) sample having an ellipsometric thickness of ~ 52 Å: (a) the sample at room temperature after being removed from the growth chamber; (b) the sample again at room temperature after heating in a helium atmosphere to 350 K; (c) the sample at 338 K after the measurement in (b); and (d) the sample at 344 K after measurement in (c). At each condition, both the measured reflectivity (upper panel) and the reflectivity normalized to the Fresnel reflectivity (lower panel) are presented. The dots (black) represent data and the red curves the best fit as described in the text. This sample is believed to have the least radiation damage, as it had the shortest exposure time to the X-ray beam.

B. Reflectivity Measurements. Our X-ray reflectivity measurements were performed on C32 films having an ellipsometric thickness of ~ 50 Å similar to those shown in Figure 4. All reflectivity measurements reported here were conducted at beamline X18A at the National Synchrotron Light Source at Brookhaven National Laboratory. To make a preliminary selection of samples for the synchrotron experiments, we conducted some room-temperature reflectivity measurements in air on the as-deposited samples (not shown) using a laboratory X-ray source. The measurement technique at the synchrotron was similar to that used previously.⁵ During the entire experiment, the sample was mounted on a heating stage inside a chamber equipped with Kapton windows and filled with helium at atmospheric pressure. At each temperature, the sample was translated to expose new material to the beam in order to reduce radiation damage. To perform measurements above room temperature, the sample was heated at a rate of 1 K/min and then held at the desired temperature (uncertainty of ± 0.2 K). The reflectivity and background scans took a total of about 4 h at each temperature.

We conducted specular X-ray reflectivity measurements on a total of four samples. Here, we include results from two of the films on which reflectivity scans were performed as a function of temperature both before and after thermally cycling them above the bulk melting point at atmospheric pressure. Figure 5 contains the reflectivity curves from a C32 film having an ellipsometric thickness of ~ 52 Å. This film had the lowest exposure time to the X-ray beam, and it is believed to have suffered the least radiation damage. The data points are marked by dots (black), while the solid lines (red) are model fits of the data to be described in the following section.

III. Analysis of Reflectivity Data

We have analyzed the X-ray reflectivity data using the Leptos software¹² in which a multislabs structure depicted in Figure 6 is

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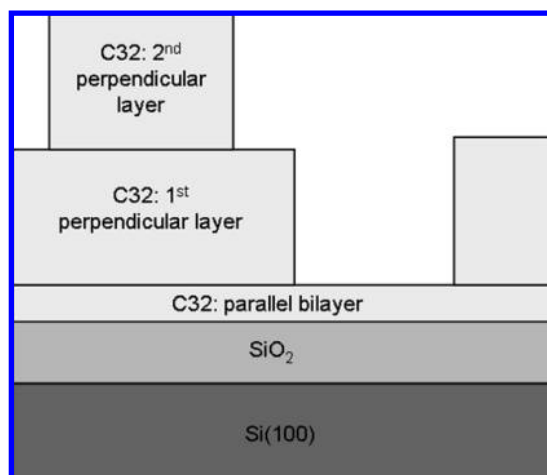


Figure 6. Structural model used to fit all of the reflectivity scans. The single-crystal Si(100) wafer is covered by its native oxide coating. The C32 film consists of a parallel bilayer followed by partial layers of molecules oriented perpendicular to the surface.

treated using Parratt's formalism.¹³ The fitting parameters in the model are the thickness, density, and roughness of each slab. For all samples, we found that the reflectivity curves could be fit well by assuming a native oxide layer of 12 Å thickness with a mass density of 2.20 g/cm³. This density is in reasonable agreement with that found for other SiO₂ thin films.^{10,14}

The reflectivity curve in Figure 5a was taken at room temperature after removal of the C32 film from the growth chamber. A series of Kiessig fringes is observed more easily after normalization to the Fresnel reflectivity corresponding to a single, perfectly sharp interface (see lower panel).⁵ We can estimate the film thickness from the average period ΔQ of the Kiessig fringes corresponding to a total film thickness of $2\pi/\Delta Q \sim 53$ Å. This estimate is confirmed by fitting the reflectivity curve to the multilayer model described above. The best fit corresponds to a multilayer film consisting of a 9.2 Å thick slab adjacent to the substrate having a higher electron density than the slab above it with thickness 42.5 Å. The total film thickness of 51.7 Å is in reasonable agreement with the ellipsometric measurement of ~ 52 Å. Other fitting parameters are listed in Table 1. Assuming a molecular width of ~ 4.8 Å² and an all-*trans* length of the C32 molecule of ~ 43 Å,⁴ we see that the thickness of the lower slab corresponds to nearly two layers of C32 molecules oriented parallel to the surface and that the upper slab has the thickness of a single perpendicular layer. Therefore, we have labeled the lower and upper slabs "parallel bilayer" and "1st perpendicular layer" in Figure 6. This model also provides an explanation for the somewhat deeper minimum in the reflectivity curve at $Q \sim 0.3$ Å⁻¹ in the lower panel of Figure 5a. It results from a superposition of one of the minima in the shorter-period Kiessig fringes arising from the perpendicular layer and the first minimum in the longer period fringes contributed by the parallel bilayer (see Figure 5d).

The fit to the reflectivity curve in Figure 5a yields an electron density ρ_e for the parallel slab of 8.17×10^{-6} Å⁻². Here, $\rho_e = n_e r_e$, where n_e is the number of electrons per Å³ and $r_e = 2.818 \times 10^{-5}$ Å is the classical electron radius.⁹ This density is close to the value for bulk liquid alkanes of $\sim 8 \times 10^{-6}$ Å⁻² (ref 9) and also to that of a C32 monolayer on graphite.⁸ Assuming approximately the same unit cell dimensions for the C32 monolayer on the SiO₂ surface as on graphite, we conclude that the parallel layers are nearly

completely occupied. In contrast, the fit gives a smaller electron density of 6.13×10^{-6} Å⁻² for the slab representing the first perpendicular layer of molecules. We assume that this lower density implies that the first perpendicular layer is incomplete and consists of islands as shown in Figure 4 having the same electron density (9.01×10^{-6} Å⁻²) as the bulk orthorhombic particles (lattice constants $a = 7.57$ Å, $b = 4.98$ Å, and $c = 42.5$ Å).^{2,5} These islands would then occupy about 67% the available surface area. This occupancy factor is about 30% less than that for the parallel bilayer (see Table 1).

After recording the reflectivity curve at room temperature, the sample was heated above the bulk melting point at 341 K and then cooled at the same rate of 0.5 K/min to room temperature where the reflectivity measurement was repeated as shown in Figure 5b. The Fresnel normalized reflectivity shows a doubling of the frequency of the Kiessig fringes compared to those in Figure 5a consistent with the growth of a second perpendicular layer. The best-fit parameters in Table 1 indicate no change in the thickness of each layer and the same thickness for both perpendicular layers. Also, there is no change in the occupancy of the parallel layers, while the occupancy of the first perpendicular layer decreases to 59% and that of the second perpendicular layer is only 27% (see Figure 6). Because the sample is translated after measuring a reflectivity curve in order to reduce radiation damage, the amount of C32 illuminated by the X-ray beam can vary between measurements. Therefore, the total occupancy of the perpendicular layers is not conserved after the heating/cooling cycle. Ellipsometric measurements¹ indicate a negligible amount of C32 desorbs in heating *in air* up to 345 K, although this temperature well exceeds 314 K at which desorption from the solid phase begins *in vacuum* (see Figure 3b). Similarly, we do not expect the thermal cycling performed during the reflectivity measurements with the sample under helium gas at atmospheric pressure to result in significant desorption.

On heating to 338 K in a second heating cycle, the reflectivity curve (Figure 5c) can still be modeled with a parallel slab having the same thickness and density as before (see Table 2). However, the thickness of both the first and second perpendicular layers has now decreased to 40.3 Å, and their occupancy is only 42% and 25%, respectively.

The last reflectivity curve was taken at 344 K (Figure 5d) after heating above the bulk melting point for the second time. At this point, the shorter-period Kiessig fringes characteristic of the perpendicular layers are no longer visible. As seen in Table 2, the reflectivity curve is now fit well by including only a single C32 slab whose thickness of 10.4 Å is about 13% greater than that of the bilayer slab of parallel molecules below the bulk melting point but has the same density as before.

A second C32 film vapor-deposited and annealed in vacuum which also had an ellipsometric thickness of ~ 50 Å gave the same structural parameters as those obtained for the as-deposited film in Table 1 to within the measurement uncertainties. However, after the first heating cycle, we found some quantitative differences with the structural parameters in Table 2. We attribute these discrepancies to radiation damage that occurred through longer exposure to the synchrotron X-ray beam at the higher temperatures.

IV. Discussion

Our modeling of the reflectivity curves in Figure 5a from a vapor-deposited C32 film after 15 h of annealing in vacuum gives a total film thickness at room temperature of 51.7 Å compared to a value of 50 Å determined ellipsometrically. We interpret this good agreement as indicating a multilayered film in which the

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Table 1. Results of Fitting Reflectivity Curves at Room Temperature^a

layer	film as deposited			film after heating cycle		
	thickness (Å)	electron density ($\times 10^{-6} \text{ Å}^{-2}$)	occupancy (%)	thickness (Å)	electron density ($\times 10^{-6} \text{ Å}^{-2}$)	occupancy (%)
parallel bilayer	9.2	8.17	99	9.2	8.17	99
first perpendicular	42.5	6.13	67	42.5	5.37	59
second perpendicular				42.5	2.43	27

^a As deposited film: parameters are from fit to curve in Figure 5a after sample was removed from the growth chamber and before heating. After heating cycle: parameters from fit to curve in Figure 5b after heating sample to 350 K in 1 atm of helium.

Table 2. Results of Fitting Reflectivity Curves Taken above Room Temperature during the Second Heating Cycle^a

layer	$T = 338 \text{ K}$			$T = 344 \text{ K}$		
	thickness (Å)	electron density ($\times 10^{-6} \text{ Å}^{-2}$)	occupancy (%)	thickness (Å)	electron density ($\times 10^{-6} \text{ Å}^{-2}$)	occupancy (%)
parallel bilayer	9.2	8.17	99	10.4	8.17	99
first perpendicular	40.3	3.79	42			
second perpendicular	40.3	2.26	25			

^a Parameters are from fit to curve in Figure 5c taken at 338 K and from fit to curve in Figure 5d taken at 344 K.

bilayer of parallel C32 molecules adjacent to the SiO₂ surface is nearly complete and the first perpendicular layer above it, although incomplete, has a much larger occupancy than the second and higher perpendicular layers. This picture is qualitatively consistent with the AFM image in Figure 4.

An unusual feature of the equilibrium phase diagram in Figure 1 for C32 films deposited from solution² is the presence of a narrow temperature range near the bulk C32 melting point T_b in which a perpendicular monolayer phase of C32 molecules is stable. This monolayer phase undergoes a delayering transition to a three-dimensional (3D) fluid phase on heating to just above T_b and to a solid 3D phase on cooling below T_b . The room-temperature reflectivity curve in Figure 5b taken after thermal cycling of the sample above T_b is consistent with a delayering transition occurring on cooling. Analysis of it indicates a decrease in the occupancy of the first perpendicular layer and the growth of a second perpendicular layer. We interpret the appearance of the second perpendicular layer at the expense of molecules in the first layer as the initial stage of bulk crystal growth. By heating the sample at atmospheric pressure instead of vacuum, we have allowed the film to reach the bulk liquid phase *L* (see phase diagram in Figure 1) rather than desorb from its solid state. Subsequent slow-cooling to room temperature from this liquid phase produces a solid film that is closer to its equilibrium structure (the *C'* phase) than the as-deposited film. Thus, our X-ray reflectivity measurements on vapor-deposited samples appear to be consistent with the Stranski–Krastanov growth mode of solid C32 films inferred from the previous AFM measurements on solution-deposited films.

One of the purposes of our reflectivity measurements above room temperature was to obtain evidence of the stable perpendicular monolayer phase observed by AFM a few degrees below the bulk melting point T_b .² However, analysis of the reflectivity curves in Figure 5c indicates that perpendicular *bilayer* islands are still present at 338 K for reasons that are unclear (see Table 2). We also found that the thickness of these perpendicular layers at 338 K had decreased by about 10% from their room-temperature value. This decrease may be due to conformational changes in the molecules associated with the introduction of *gauche* defects^{15,16} and/or possibly tilting of the molecules.

The reflectivity curve in Figure 5d taken at 344 K, after heating above the bulk C32 melting point T_b , supports the occurrence of a

second delayering transition in which the perpendicular monolayer phase transforms to a 3D liquid phase (see phase diagram in Figure 1). The absence of the short-period Kiessig fringes in Figure 5d that are present in the reflectivity curves in Figure 5a–c is consistent with such a delayering transition. Kiessig fringes result from interference of the X-rays scattered from a planar film of uniform thickness so that they should not be observable in scattering from hemispherically shaped droplets observed in AFM images on heating samples in air.² As noted earlier, our reflectivity measurements were conducted under helium gas at atmospheric pressure so that we do not expect significant desorption of C32 when heating to 344 K.¹

The longer-period oscillations in the reflectivity curve of Figure 5d originate in the parallel layers underneath the droplets. The best fit to the reflectivity curve at 344 K shows an increase in the thickness of the parallel bilayer film to 10.4 Å from its value of 9.2 Å at lower temperatures. This thickening could be caused by a greater number of *gauche* defects in the molecules that increase their width, indicating that the parallel layers are either close to their melting point or have already melted at 344 K.^{15,16} In either case, the reflectivity curves at 344 K provide compelling evidence that the parallel layers have greater stability than the perpendicular ones. In the future, it may be of interest to investigate vapor-deposited samples using in-plane synchrotron X-ray diffraction to determine the lateral translational order in the parallel layers. At this point, it is unknown whether the solid parallel layers are amorphous like the SiO₂ surface or crystalline as is the case of C24 and C32 monolayers on a graphite surface.¹⁵

V. Summary and Conclusion

We have deposited C32 films from the vapor phase onto a SiO₂-coated Si(100) substrate. On removal from vacuum, they are stable in air. Before thermal cycling at atmospheric pressure above the bulk C32 melting point, the structure of these films shares some qualitative similarities with that of the series of alkane films (C17 to C30) investigated by Basu and Satija.⁹ They also grew their films from the vapor phase but thermally cycled them under vacuum.³ Like them, we find a layer immediately adjacent to the SiO₂ surface consisting of molecules aligned parallel to the interface and a layer of perpendicular molecules at the air or vacuum interface.

However, we also find some qualitative differences between our vapor-deposited films and theirs. Basu and Satija⁹ were unable to grow stable films of molecules as long as C32 and all of their films were unstable in air at room temperature. We are uncertain of the reason why they were unable to grow C32 films from the vapor

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phase, but it may simply be that their alkane source was not held at a high enough temperature for a sufficient period of time. As for why their films of shorter alkanes were unstable in air, we suggest that it may be a manifestation of the Stranski–Krastanov growth mode of the solid film. The perpendicular layers present at room temperature in air may be unstable to 3D clustering that initiates the growth of bulk crystallites. While the films reside in their growth chamber, these perpendicular layers are being continually replenished by the evaporation of molecules from the source wafer.

The structure of our vapor-deposited films also shows some quantitative differences with those of Basu and Satija.⁹ All of their films have only a single parallel layer having a lower density than the perpendicular layer above it. On the other hand, all of our vapor-deposited films have two parallel layers with a higher density than the perpendicular layer above them, although we did find some cases of single parallel layers in dip-coated films.⁵ Possibly, a single parallel layer results from uncontrolled variation in the quality of the amorphous SiO₂ surface related to its cleaning procedure or the thickness of the oxide layer. We also

note that the reflectivity curves measured by Basu and Satija⁹ only extend up to $Q \sim 0.45 \text{ \AA}^{-1}$, making them less sensitive to the presence of parallel layers.

In conclusion, our X-ray reflectivity measurements are consistent with a Stranski–Krastanov growth mode of both solid and liquid C32 films grown on a SiO₂ surface. Under quasi-equilibrium conditions, a bilayer of molecules aligned parallel to the surface precedes the nucleation of bulk particles or droplets depending on whether the temperature is below the rotator-to-monolayer phase transition or above the monolayer-to-3D liquid transition, respectively. Quasi-equilibrium conditions can be approached for films of intermediate alkanes grown either from solution or from their vapor phase by first thermal cycling them at atmospheric pressure above their bulk melting point.

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