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Growth of *n*-alkane films on a single-crystal substrate

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Abstract

The structure and growth mode of alkane films (n-C_nH_{2n+2}; n = 4, 6, 7) adsorbed on a Ag(1 1 1) surface have been investigated by synchrotron X-ray scattering. New models are proposed for the butane (n = 4) and hexane (n = 6) monolayer and butane bilayer structures. Specular reflectivity scans reveal that growth of all films is preempted between two and three layers by nucleation of bulk particles oriented with a single bulk crystal plane parallel to the film. In the case of butane, the bulk particles also have a fixed azimuthal relationship with the film resulting in complete epitaxy. © 2001 Published by Elsevier Science B.V.

Interest in the structure of alkane films adsorbed on solid surfaces has increased in recent years. As the principal constituents of commercial lubricants, knowledge of the structure of both solid and fluid alkane [C_nH_{2n+2}] films is important in understanding lubrication phenomena at the microscopic level [1]. In addition, the structure of solid alkane films on metal surfaces enters in such diverse areas as the dynamics of two-dimensional small polaron formation [2].

While there has been considerable progress made in determining the structure of alkanes at the fluid–vapor interface [3], the multilayer structure and growth mode of alkane films at a solid–vapor interface have been less well investigated. Studies of alkane monolayer structure on solid surfaces date back to the first indirect determinations by thermodynamic measurements [4]. These have been followed by investigations with a variety of techniques: low-energy electron diffraction (LEED) [5], neutron diffraction [6,7], scanning

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tunneling microscopy [8], and helium atom scattering [9].

Here we report synchrotron X-ray scattering experiments which have probed the film structure and growth mode of three shorter *n*-alkanes, butane (n = 4), hexane (n = 6), and heptane (n = 7), adsorbed from the vapor phase onto a single-crystal Ag(1 1 1) surface. We find: (1) a butane and hexane monolayer structure which differs from the LEED determination reported earlier [5]; (2) a bilayer structure of butane simply related to that of the monolayer and the (1 0 0) plane of the bulk; and (3) incomplete wetting (a Stranski–Krastanov growth mode) above two layers characterized by nucleation of bulk particles having either partial or complete orientational epitaxy with the film. While epitaxially oriented bulk crystallites have been found in Stranski–Krastanov growth of metals on metal and semiconductor substrates [10], such an epitaxial growth mode, to our knowledge, has not been demonstrated previously for 'soft matter.' In this case, the weak, nondirectional, van der Waals interactions between the film and the bulk particles make it difficult to predict whether orientational epitaxy of the particles can occur.

The experiments were performed at beam line X18A of the National Synchrotron Light Source by the same method used previously for xenon films adsorbed on a Ag(1 1 1) substrate [11]. X-rays of wavelength 1.0 Å were reflected off the sample in the horizontal scattering plane using slits before the detector to define the divergence of the scattered beam. The sample was housed in an ultrahigh vacuum chamber equipped with a low-current LEED system described previously [12]; and the substrate was a single-crystal silver disk of 10 mm diameter and 3 mm thickness with the (1 1 1) direction oriented within 0.2° of the surface normal. After repeated sputtering and annealing cycles [11], its out-of-plane and in-plane mosaic spread were ~0.3° and ~0.17°, respectively. The alkane gases typically had a purity of 99.9%. They were introduced into the chamber through a variable leak valve and emerged from a dosing tube situated 1 cm in front of the Ag(1 1 1) surface. During the experiment, the sample could be cooled below 40 K using a closed-cycle He refrigerator.

Although in-plane diffraction and specular reflectivity X-ray scans were performed with all three alkane adsorbates, the most comprehensive data set was obtained with butane. Fig. 1 illustrates the structural evolution which we propose from these experiments with adsorbed butane. At coverages from one to three layers, two in-plane Bragg peaks were observed whose positions in reciprocal space are incompatible with the hexagonal unit mesh proposed by Firment and Somorjai [5]. To model the monolayer structure, we considered an oblique unit cell similar to that found for butane on the graphite (0 0 0 1) surface and indexed the two Bragg peaks observed as the (11) and (20) diffraction rods [7]. Our LEED patterns show the existence of three equivalent monolayer domains azimuthally separated by 120° so that the radial position and azimuthal separation of the two X-ray peaks uniquely determined the lattice vectors of the monolayer unit cell shown in Fig. 1a [13]. This cell is too large for a close-packed structure to contain a single molecule. Assuming two molecules per cell as is the case for the herringbone monolayer structure of butane on graphite [7] yields an area per molecule about 16% smaller than on graphite. The molecular orientations in Fig. 1a were calculated by minimizing the potential energy of a monolayer cluster having the lattice vectors inferred from the X-ray experiment. Semiempirical nonbonding atom–atom potentials were used to represent the monolayer cluster potential energy as described in [7].

By the same method, we have also inferred a nearly rectangular unit cell containing two molecules for the hexane monolayer on Ag(1 1 1). It has about the same area per molecule as the rectangular cell on the graphite (0 0 0 1) surface (see [6]) but differs from the oblique cell containing one molecule proposed for hexane/Ag(1 1 1) in [5].

We find that all three alkane monolayers have a well-defined azimuthal orientation on the Ag(1 1 1) surface apparently forming a long-period superlattice structure on this substrate [the angle between a monolayer lattice vector and the Ag(1 0) azimuth reproduced to $\leqslant 0.03°$]. The azimuthal orientation of the films varies in a small (< 1°) but reproducible way depending on both temperature and coverage [13]. For example, the butane

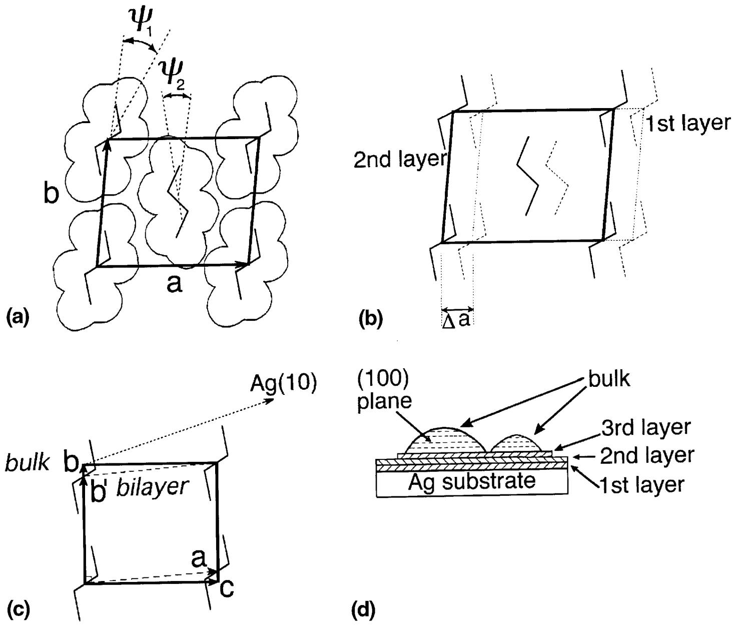

Fig. 1. (a) Unit cell of a butane monolayer on the Ag(1 1 1) surface. The oblique cell contains two molecules arranged in a herringbone pattern and has lattice constants $a = 8.10$ Å and $b = 6.84$ Å (±0.005 Å). The angle between lattice vectors is $84.6 \pm 0.1°$, and the calculated azimuthal angles of the molecules (see text) are $\psi_1 = 24.3°$ and $\psi_2 = 15.2°$ (±3°). (b) Schematic diagram of the proposed butane bilayer. The second layer is identical in structure to the first but shifted by a distance Δa in the direction of the **a** lattice vector. (c) Schematic diagram showing the rotational epitaxy of the bulk butane particles on the bilayer film. The bulk (1 0 0) or *b–c* plane is parallel to the Ag(1 1 1) surface with its **b** lattice vector parallel to **b**′ of the bilayer unit cell. The lattice constants of the bilayer are $a = 8.13$ Å and $b' = 6.76$ Å (±0.005 Å) with an included angle of $84.9 \pm 0.1°$, while the bulk (1 0 0) plane has a rectangular unit cell with lattice constants $b = 7.621$ Å and $c = 8.097$ Å. The angle between the Ag(1 0) azimuth and the bulk **c** lattice vector is 19°. The translational relationship of the bulk (1 0 0) plane to the bilayer crystal is undetermined. (d) Model proposed for a nominal coverage corresponding to three butane layers in which crystalline film coexists with bulk particles as described in the text.

monolayer expands nonuniaxially in area by ~0.6% upon heating from 40 to 90 K, while the monolayer reciprocal lattice vectors rotate by 0.4° [**G**(20)] and 0.9° [**G**(11)] toward the nearest Ag(1 0) azimuth. At 40 K, upon increasing from monolayer to bilayer thickness, the unit cell contracts in area by ~0.7% accompanied by rotations in the opposite sense of 0.4° [**G**(20)] and 0.9° [**G**(11)]. These azimuthal rotations may be caused by the Novaco–McTague effect [14]. Their theory assumes an elastically isotropic monolayer, an assumption which would have to be relaxed for these anisotropic alkane films.

To investigate changes in the butane film structure above monolayer coverage, both in-plane diffraction and specular reflectivity scans were performed at nominal film thicknesses of one, two, and three layers. The films were deposited by dosing the substrate with a constant butane flux, while maintaining a background pressure in the chamber of 1.8×10^{-8} Torr. Deposition began at ~140 K just above the monolayer condensation temperature and continued while slowly reducing the temperature. Nominal coverage was determined by monitoring oscillations in the X-ray intensity at the bulk butane 'anti-Bragg' position on the specular rod [11]. An intensity minimum was observed at monolayer condensation. Two-layer coverage was taken at the following intensity maximum (reached ~10 min in later) and three-layer coverage where the oscillations ceased (~20 min after monolayer condensation).

Specular scans are shown in Fig. 2 after making corrections for X-ray polarization and various geometrical factors as described in [13]. The scattered intensity has been integrated transverse to

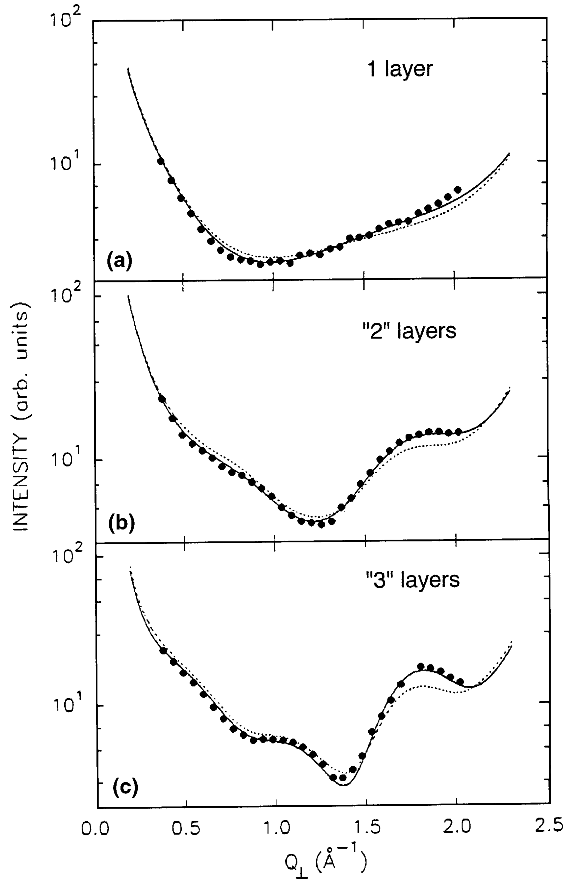

Fig. 2. Integrated specular reflectivity scans as a function of $Q_\perp$ at a temperature of 40 K for butane films of various thickness adsorbed on the Ag(1 1 1) surface: (a) monolayer; (b) nominal bilayer; (c) nominal trilayer. Solid (dotted) curves are best fits to the data assuming the carbon skeletal plane of the molecule is parallel (perpendicular) to the surface as discussed in the text.

the specular rod at each value of $Q_\perp$, the component of the wave vector transfer perpendicular to the surface. These integrated specular scans were modeled assuming the first N layers of the film to be complete followed by three partial layers [11]. For the monolayer scan in Fig. 2a, the best fit (solid curve) was obtained with $N = 1$ and only one partial layer having an occupancy of 5%. It was necessary to assume the same areal density as for the unit cell in Fig. 1a inferred from the in-plane diffraction peaks and that the molecules are in the *trans* conformation with their carbon skeletal plane parallel to the surface. A best fit analysis gave the height of the molecular center of mass as 3.60 ± 0.05 Å above the Ag(1 1 1) surface [13]. Rotating the molecules 90° about their long axis so that their carbon skeletal plane is perpendicular to the surface yielded a slightly poorer fit (dotted curve).

Upon increasing the coverage to a nominal two layers, the specular reflectivity scan becomes more modulated as shown in Fig. 2b. In this case, the best fit was obtained with $N = 1$ complete layers and partial second and third layers having an occupancy of 73% and 14%, respectively, with all layers having the same density as the monolayer. These results indicate that the third layer begins to grow before the second layer is complete. The improvement in the fit for the parallel orientation of the molecules (solid curve) compared to that for the perpendicular orientation (dotted curve) is more marked at this coverage. A similar analysis of the integrated specular reflectivity scan in Fig. 2c at a nominal coverage of three layers yields $N = 2$ complete layers with partial third and fourth layers having 70% and 14% occupancy, respectively, again indicating a departure from layer-by-layer growth [13].

There is an important qualitative change in the specular reflectivity between two and three nominal layers which does not appear in the integrated scans of Fig. 2 due to the coarse grid of data points. This can be seen in the nonintegrated scans of Fig. 3a which can be taken more quickly and therefore allow finer increments in $Q_\perp$. Near $Q_\perp = 1.75$ Å^{-1}, a sharp peak appears at nominal three-layer thickness which grows in intensity at higher coverages. This peak position corresponds to the (1 0 0) *d*-spacing of monoclinic bulk butane [15]. It demonstrates that bulk particles have nucleated at a coverage between two and three layers and are growing with a (1 0 0) plane parallel to the Ag(1 1 1) surface.

Results of our X-ray experiments with hexane and heptane adsorbed on the same Ag(1 1 1) substrate indicate a similar growth mode in which bulk particles nucleate with a particular crystal plane parallel to the Ag(1 1 1) surface. In Fig. 3b,c, we show nonintegrated specular reflectivity scans for hexane and heptane, respectively, at the same coverages as for butane. At each coverage, the

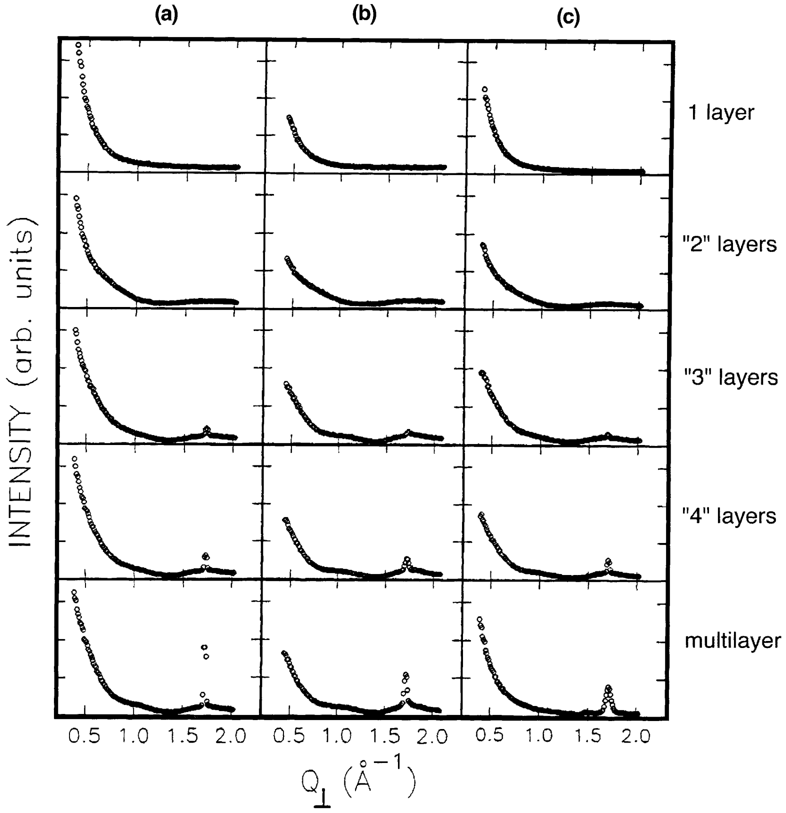

Fig. 3. Nonintegrated X-ray specular reflectivity scans of the solid alkane films at different coverages: (a) butane; (b) hexane; (c) heptane. 'Multilayer' refers to a coverage greater than five layers.

specular reflectivity has qualitatively the same shape for all three alkane molecules. Between two and three layers the lineshape develops a two-component structure with a sharp peak appearing near $Q_{\perp} = 1.7$ Å^{-1}. This peak corresponds to the (1 0 1) Bragg reflection of bulk hexane and the (0 1 3) reflection of bulk heptane, indicating which bulk plane is parallel to that of the film. We suggest that the preferred bulk plane is selected by its compatibility with the molecular orientations and lattice constants of the bilayer film.

The absence of the bulk butane (1 0 0) peak in the two-layer nonintegrated specular scan (Fig. 3a) is consistent with our modeling of the corresponding integrated specular scan in Fig. 2b as a crystalline bilayer film. Further support for this interpretation comes from analyzing an integrated scan along the nonspecular (20*l*) rod at a nominal coverage of two layers [13]. The analysis employs the model shown in Fig. 1b in which the second layer is identical to the first but shifted a distance $\Delta a = 1.77$ Å in the direction of the film's **a** lattice vector. This bilayer structure is similar to that of monoclinic bulk butane in which neighboring (1 0 0) planes are shifted by 1.97 Å in the *c*-direction (see Fig. 1c). However, in the bulk structure, the long axis of the molecules is tilted ~22° out of the (1 0 0) plane [15] whereas, in the bilayer model of Fig. 1b, the molecules are strictly parallel to the surface.

Nonintegrated scans along the (20*l*) rod at coverages above five layers reveal a second Bragg peak of the bulk monoclinic butane structure, the (0 0 2) peak. Using both the (1 0 0) and (0 0 2) peak positions, we can uniquely determine the azimuthal orientation of the bulk butane particles about the surface normal as shown in Fig. 1c. The (1 0 0) plane is parallel to the Ag(1 1 1) surface with the bulk **b** lattice vector aligned parallel to the bilayer **b**′ lattice vector. Because the bilayer unit cell is oblique, the bilayer **a** lattice vector is not parallel to the bulk **c** vector. Nevertheless, the distance between sides b of the bulk unit cell is equal to that between sides b' of the bilayer cell. We speculate that the similarity in the orientational order of the butane molecules in the bilayer film and the (1 0 0) bulk plane promotes the epitaxial growth of the bulk particles, although it is insufficient to allow complete wetting of the film. Possibly, it is the tilting of the molecules with respect to the bulk (1 0 0) plane which prevents complete wetting. We also searched for a second bulk Bragg peak in the case of hexane but were unable to find one consistent with a unique orientation of bulk crystallites as found for butane.

The structural evolution depicted in Fig. 1 for butane on the Ag(1 1 1) surface is similar to the quasiepitaxial growth mode which we proposed earlier for butane on the graphite (0 0 0 1) surface [7]. There, again, bulk butane particles grew with a (1 0 0) plane parallel to the surface. However, since these neutron diffraction experiments required a polycrystalline substrate, the determination of the preferred bulk plane was more indirect; and it was impossible to establish complete epitaxy corresponding to a specific azimuthal orientation of the bulk particles as we have done here. Also, the polycrystalline substrate complicated the interpretation of the butane film growth mode due to possible capillary condensation.

It is interesting to analyze the width of the bulk (1 0 0) peaks appearing at coverages of three layers and above in the nonintegrated specular scans of Fig. 3a. Without deconvoluting the instrumental resolution, we can place a lower bound of 200 Å on the width of the bulk particles in a direction perpendicular to the (1 0 0) planes, corresponding to a bulk particle thickness greater than 55 layers. This implies a very rapid increase in the bulk-particle height, since the dosing rate was constant and the exposure time between nominal coverages of two and three layers was approximately the same as that for the growth of the second film layer. We interpret this behavior as resulting from quasiequilibrium between impinging butane molecules and those adsorbed. The rapid growth of bulk particles occurs as the temperature is lowered below ~80 K, corresponding to bulk vapor–solid coexistence at the effective pressure ($\sim 2 \times 10^{-8}$ Torr).

In summary, we have proposed new monolayer structures for butane and hexane on the Ag(1 1 1) surface and a bilayer structure for butane. Along with heptane, these alkane films exhibit Stranski–Krastanov growth in which bulk particles nucleate in either partial or complete orientational epitaxy with the coexisting film. The relative simplicity of the van der Waals interactions between alkane molecules should enable molecular dynamics simulations of the bulk-particle orientational epitaxy which would be far more difficult to conduct for metal systems.

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