

X-ray Specular Scattering Study of Dotriacontane Thin Films and Bulk Particles Adsorbed on Si(100)/SiO₂ Substrates

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Introduction

The structure of alkane films adsorbed on SiO₂ surfaces has been the subject of several investigations in the last few years [1-3]. Most recently, we have used synchrotron x-ray specular reflectivity measurements [4] to test a structural model of the alkane/SiO₂ interface inferred from very-high-resolution ellipsometry (VHRE) experiments [3] on solid *n*-C₃₂H₆₆ (C32) films. In this model, one or more layers nearest the SiO₂ surface contain molecules oriented with their long axis *parallel* to the interface. Above this “parallel” film phase is a monolayer in which the long axis of the C32 molecules is oriented *perpendicular* to the interface. Incomplete wetting of the dotriacontane to the SiO₂ surface results in the nucleation of bulk C32 particles on top of these film phases.

Our previous x-ray reflectivity (XRR) measurements [4] showed that for a total film thickness of ~60 Å as measured by ellipsometry, the “parallel” film phase is a bilayer with a thickness of ~11 Å, while the “perpendicular” monolayer thickness is ~43 Å, the length of an all-*trans* C32 molecule.

The purpose of the present experiment was to investigate the structure and wetting behavior of thicker films.

Methods and Materials

The sample preparation method, which used Si(100) substrates coated with their native oxide, is described in Ref. 3. As before, the average C32 film thickness was measured by VHRE before the XRR curves were taken at APS beamline 6-ID-B at room temperature. XRR measurement and analysis techniques were similar to those described in Ref. 5.

Results

We report here on x-ray specular scattering curves for two samples labeled APS5.2 and APS7.3 that had total thicknesses measured by VHRE of 98.6 and 153 Å, respectively. The reflectivity curve for APS5.2 in Fig. 1 shows Kiessig fringes at low wave vector transfer Q that have a period corresponding to a total film thickness of

~54 Å as determined by a Patterson function analysis [4]. This value is in good agreement with that determined for previous samples having a thinner VHRE thickness of ~60 Å [4]. In addition, Fig. 1 shows that sample APS5.2 exhibits two series of bulk Bragg peaks labeled with red and green Miller indices, respectively.

For the thicker sample APS7.3 in Fig. 2, we observed no Kiessig fringes. However, the same two series of bulk peaks as those seen for APS5.2 were present. Each series contained more peaks, and their intensity was greater than those for the thinner sample.

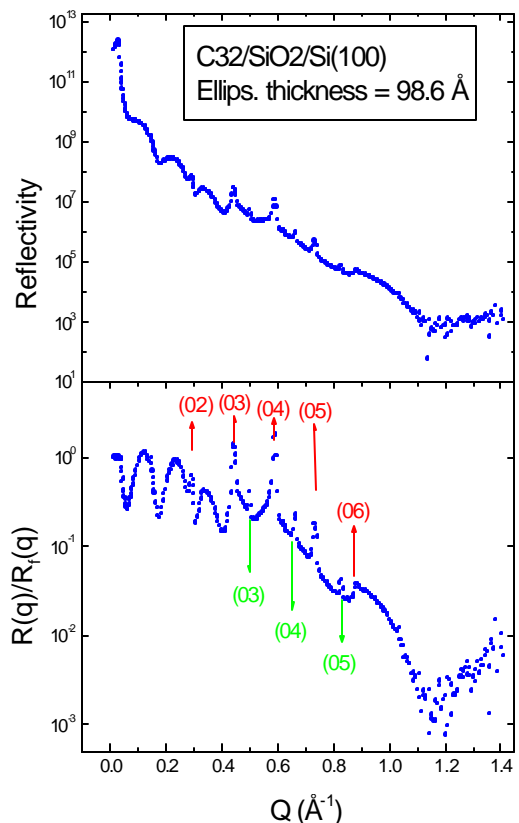


FIG. 1. X-ray reflectivity for sample APS5.2.

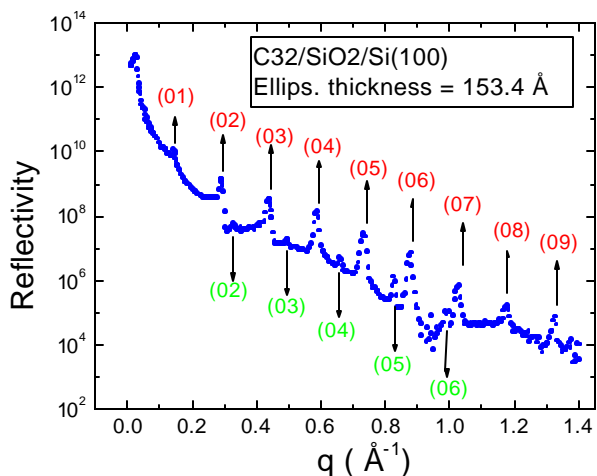


FIG. 2. X-ray reflectivity for sample APS7.3

Discussion

The coexistence of Kiessig fringes and the bulk Bragg peaks in the specular scattering from sample APS5.2 is consistent with incomplete wetting of C32 to the SiO₂/Si(100) substrate at room temperature. Moreover, the total x-ray film thickness of ~ 54 Å for sample APS5.2, which had a VHRE thickness of ~ 99 Å, is in agreement with that found previously for thinner samples with a VHRE thickness of ~ 60 Å [4]. Thus these results strongly support the proposed model for the interfacial structure of solid C32 based on VHRE experiments [3], in which there is sequential adsorption of “parallel” bilayer and “perpendicular” monolayer phases followed by the nucleation of bulk particles.

For the thicker sample APS7.3 (VHRE thickness of 153 Å), the more intense Bragg peaks apparently obscure the Kiessig fringes and suggest a larger number and/or a larger size for the coexisting bulk particles. We note that the weaker series of bulk peaks in Figs. 1 and 2 (labeled in green) corresponds to a d -spacing of 37.8 Å, the largest d -spacing (between ab planes) of the reported monoclinic structure of free-standing bulk C32 crystals [6] (see Fig. 3). However, to our knowledge, a bulk structure consistent with the d -spacing of 42.5 Å corresponding to the stronger series of Bragg peaks (labeled in red in Figs. 1 and 2) has not been previously reported. This larger d -spacing matches the all-*trans* length of the C32 molecules and suggests the surface-stabilized orthorhombic phase depicted in Fig. 3. It is similar to one that was proposed previously for n -C₁₆H₃₄ adsorbed on polycrystalline graphite [7]. Confirmation of such an orthorhombic phase for C32 should be possible by in-plane diffraction measurements that use samples on SiO₂/Si(100) substrates.

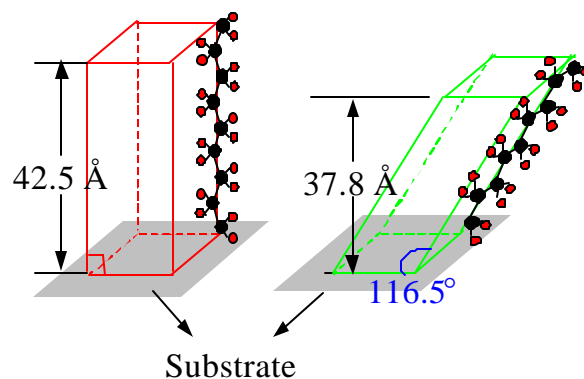


FIG. 3. Bulk C32 structures. Left: “Surface-stabilized” orthorhombic phase. Right: “Free-standing” monoclinic phase.

Except for these two series of peaks, no other bulk Bragg reflections were observed in the specular scattering geometry. This suggests that the bulk C32 particles of both the monoclinic and surface-stabilized orthorhombic phases grow preferentially with their ab -planes parallel to the substrate. We speculate that the Bragg peaks of the surface-stabilized orthorhombic phase are more intense because the underlying “perpendicular” monolayer phase is a more favorable template for the orthorhombic structure.

Acknowledgments

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