X-ray Specular Reflectivity Study of Dotriacontane Thin Films Adsorbed on Si(100)/SiO_2 Substrates

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Introduction

Recent investigations of the structure and phase transitions of intermediate-length alkane films adsorbed on SiO_2 substrates have agreed on three different wetting topologies of the alkane films, depending on coverage and temperature [1-3]. However, these studies differ with regard to the inferred orientation of the alkane molecules adsorbed closest to the SiO_2 surface in the solid film. Riegler and co-workers [1, 2] have concluded from optical, ellipsometric, and x-ray scattering experiments that a monolayer phase adsorbs adjacent to the SiO_2 surface in which the molecules are oriented perpendicular to the interface. More recently, very-high-resolution ellipsometry experiments [3] have provided evidence that one or more layers of molecules oriented with their long-axis parallel to the interface are nearest the SiO_2 surface and that the previously proposed "perpendicular" monolayer adsorbs above this "parallel" film phase. The purpose of this experiment was to confirm the existence of a "parallel" phase adjacent to the SiO_2 surface and, if it was present, to determine its thickness.

Methods and Materials

The Si(100) substrates were cut from a 0.4-mm-thick wafer into a 12×12-mm square shape and then cleaned in a mixture of H_2O_2 plus sulfuric acid. Solid dotriacontane (n-$C_{32}H_{66}$ or C32) films were prepared by dipping the silicon substrates into a solution of C32 in heptane (n-C_7H_{16}) for about 5 s and then letting the heptane evaporate. The average film thickness was measured ellipsometrically before taking the x-ray reflectivity curves at the APS beamline 6-ID-B. Measurement and analysis techniques were similar to those described previously [4].

Results

The x-ray specular curves for Samples AR4.2 and AR4.1 are shown in Figs. 1 and 2, respectively, showing the (a) relative intensity along the specular rod, (b) reflectivity normalized to the Fresnel reflectivity, and (c) Patterson function $P(z)$ calculated from the Fourier transform of $R(q)/R_F(q)$. The solid curve in Figs. 1(b) and 2(b) is the best fit to a "four-slab" model consisting of a semi-infinite Si substrate, a slab of SiO_2, layers of C32 molecules oriented with their long molecular axis parallel to the interface, and a C32 monolayer with molecules oriented perpendicular to the interface. The slab thicknesses were taken from the peak positions in the Patterson functions in Figs. 1(c) and 2(c).

Ellipsometric measurements give total film thicknesses of 67 and 60 Å for Samples AR4.2 and AR4.1, respectively. For both samples, a rough estimate from the period of the Kiessig fringes Δq in Figs. 1(a) and 2(a) gives a film thickness of $2\pi/\langle\Delta q\rangle \approx 54$ Å. This value is consistent with the Patterson functions in Figs. 1(c) and 2(c), which show the dominant peak in a range of ~53-55 Å for both samples.

Discussion

The total C32 film thickness of ~54 Å inferred from our x-ray reflectivity measurements strongly supports the structural model proposed in Ref. 3. If there were no "parallel phase" and only a single layer of molecules oriented perpendicular to the interface, we would expect a smaller film thickness of ~44 Å, the all-*trans* length of the C32 molecule. Moreover, a total film thickness of ~54 Å implies a "parallel film" that is about 10-Å thick (i.e., a bilayer twice as thick as the width of the C32 molecule). A "parallel" bilayer film is also consistent with a peak in the Patterson function of both samples at z of ~11 Å, as shown in Figs. 1(c) and 2(c). We verified that this peak did not result from a truncation error produced by calculating the Patterson function from a reflectivity scan of finite range. It survives as a shoulder after applying a Gaussian filter to the data, as shown by the solid curve in Fig. 1(c).

We note that the abrupt disappearance of Kiessig fringes for Sample AR4.1 at ~0.6 $Å^{-1}$, as shown in

Fig. 2(a) and 2(b), may indicate damage to the sample by the intense x-ray beam.

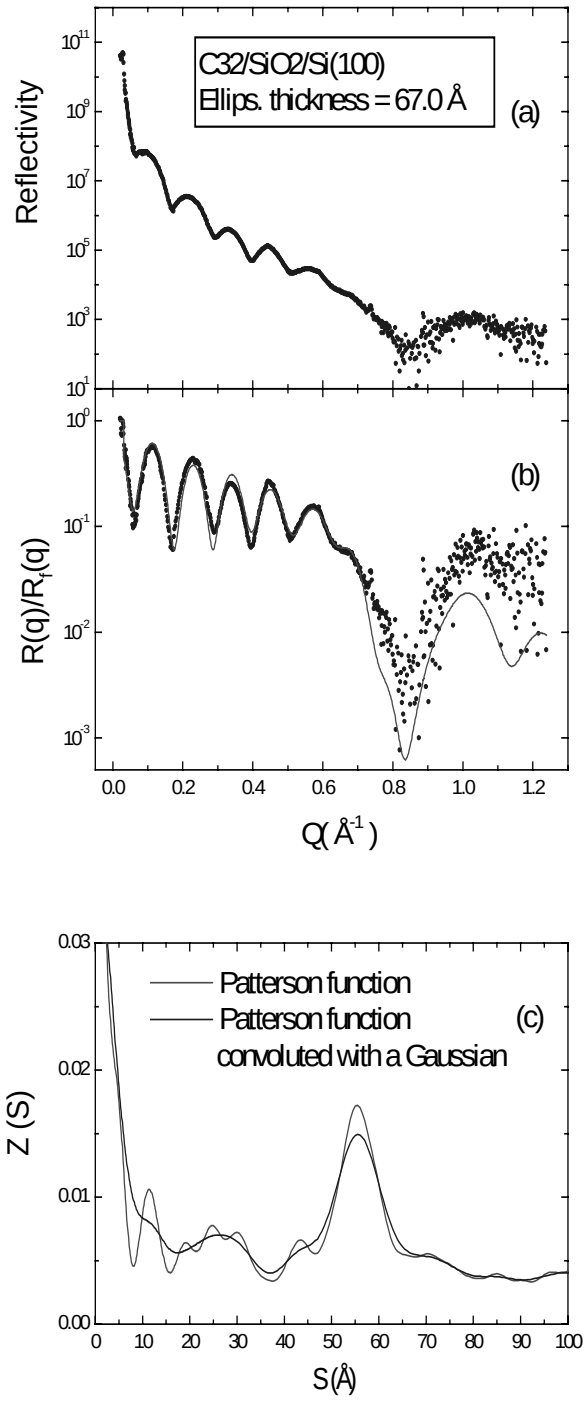

FIG. 1. X-ray reflectivity and Patterson function for Sample AR4.2.

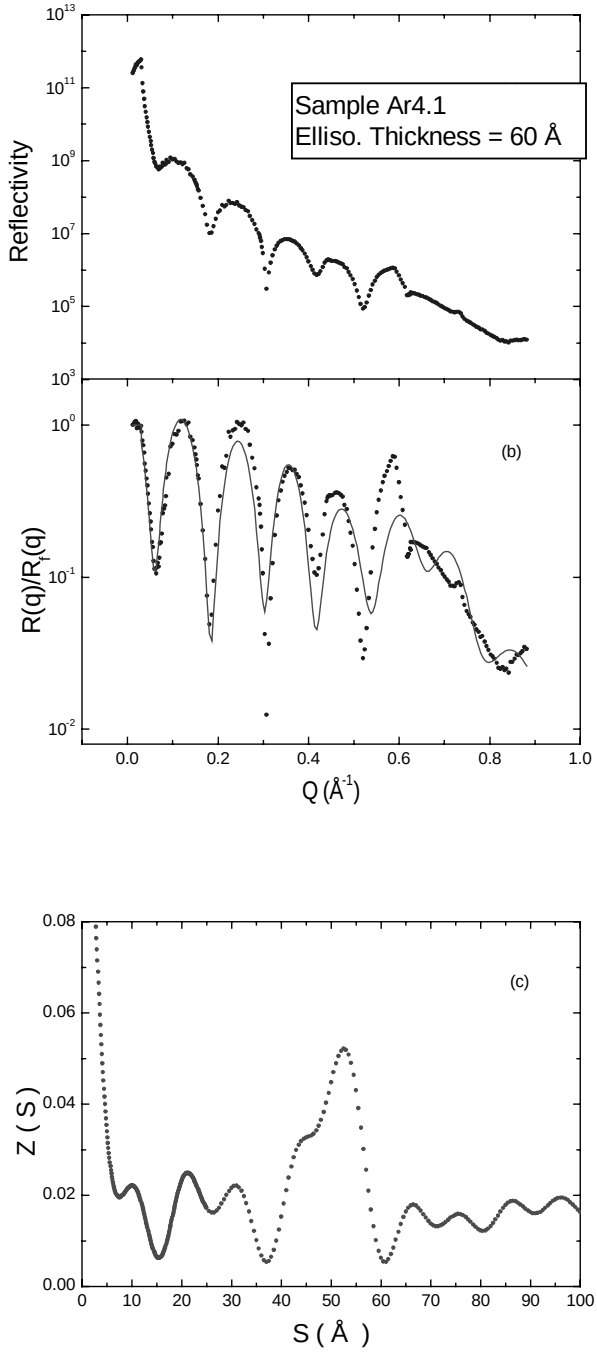

FIG. 2. X-ray reflectivity and Patterson function for Sample AR4.1.

Acknowledgments

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