Abstract No. Mo0488

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

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Beamlines: X18A

Introduction: Alkane films are of technological interest particularly for their lubricating properties. Films of intermediate-length alkanes such as dotriacontane (n-$C_{32}H_{66}$ or C32) are also of interest as prototypes for more complex polymer films at solid interfaces. Here we report an x-ray reflectivity study of the structure of molecularly thin C32 thin films adsorbed on SiO_2/Si(100) surfaces prepared by two different methods. The results indicate that different stages of film growth are obtained by deposition from solution depending on whether the substrate is "acid-cleaned" or cleaned only with heptane. Both samples had comparable C32 film thicknesses when measured by very-high-resolution ellipsometry (VHRE) [1].

Methods and Materials: Commercial Si(100) wafers were cleaned either in an H_2O_2 + sulfuric acid mixture [1] or pure heptane. C32 films were prepared by dip-coating the wafers in a solution of C32 in heptane (n-C_7H_{16}) [1]. All samples were examined by VHRE to determine the C32 film thickness before the x-ray measurements. The film thickness and other structural parameters were obtained by fitting with a four-slab model consisting of a semi-infinite Si substrate, a slab of SiO_2, and two slabs of C32 differing in their electron densities [2,3].

Results: Sample #1110 was acid cleaned and has a thickness of 66 Å as determined by VHRE [1]. Figure 1 shows its measured x-ray specular reflectivity at room temperature as function of wave vector transfer Q after normalizing to the Fresnel reflectivity. Nice Kiessig fringes were observed for $Q < 0.6$ Å^{-1} but radiation damage apparently occurred at higher Q. The solid line is the fit to the four-slab model, using reflectivity data only below 0.6 Å^{-1}. It gives a total hydrocarbon film thickness of 48.2 Å, consisting of a slab 5.6 Å thick and a second one of thickness 42.6 Å. These slab thicknesses are close to the width and the all-*trans* length of the C32 molecule, respectively, suggesting that the film consists of a monolayer with molecules oriented with their long axis *parallel* to the substrate and a second monolayer with molecules oriented *perpendicular* to the substrate. The same model fit another acid-cleaned sample having a thickness measured by VHRE of 53 Å (not presented here). This distinctive growth mode is similar to one that we have reported earlier [3]. The only difference is that our previous results [3] indicated a "parallel" film thickness about twice the width of the molecule; i.e., a molecular bilayer instead of a monolayer.

It is interesting to compare the x-ray specular reflectivity of a second sample #1150 that was deposited from the same solution as #1110 and had nearly the same thickness (67 Å) but whose substrate was washed in heptane rather than acid cleaned. The specular reflectivity scan of sample #1150 in Fig. 2 shows a qualitatively different behavior characterized by two series of bulk Bragg peaks whose width is resolution limited. One series (roman Miller indices) corresponds to a d-spacing of 42.5 Å, close to the all-*trans* length of the C32 molecule. It is believed to result from a recently discovered surface-stabilized bulk orthorhombic phase [3]. The other series (italic indices) corresponds to a d-spacing of 37.8 Å, the plane spacing along the c-axis in the previously known monoclinic structure of free-standing bulk C32.

Conclusions: The specular x-ray reflectivity curves of C32 films grown on acid-cleaned and heptane-cleaned SiO_2/Si(100) substrates differ dramatically. Although the films had comparable thicknesses measured by VHRE, the "acid-cleaned" substrate allows growth of a uniformly thick C32 film whereas the heptane-cleaned substrate results in the nucleation of preferentially oriented bulk C32 particles.

Acknowledgments: This work was support by the Chilean government under CONICYT Grant No. 018/AT/005NSF and FONDECYT Grant No. 1010548, by the U.S. NSF under Grant Nos. INT-9605227 and DMR-0109057, and by the U.S. Department of Energy under Grant No. DE-AC02-98CH10886 of the MATRIX Participating Research Team.

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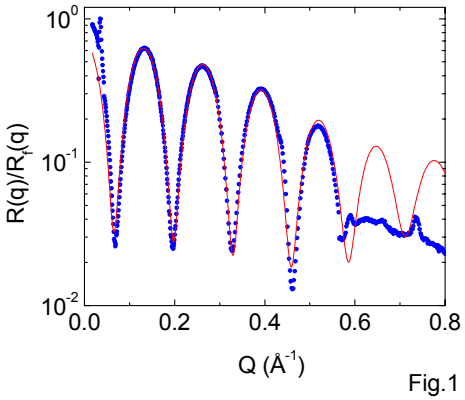

Fig.1

Figure 1. Specular x-ray reflectivity of sample #1110 normalized to the Fresnel reflectivity.

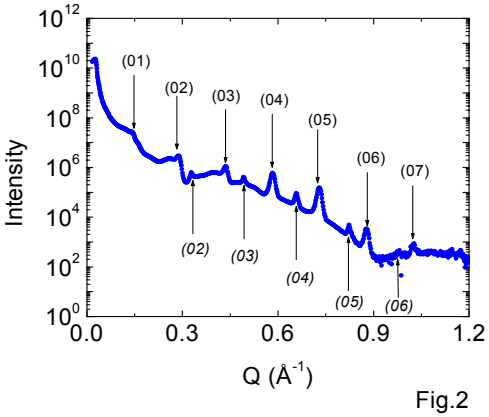

Fig.2

Figure 2. Specular x-ray scattering from sample #1150 showing two series of bulk C32 Bragg peaks.