

# X-ray Specular Reflectivity Study of Dotriacontane Thin Films Adsorbed on a Ag(111) Substrate

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## Introduction

Our previous studies by very-high resolution ellipsometry [1] and synchrotron x-ray specular reflectivity [2] of dotriacontane ( $n\text{-C}_{32}\text{H}_{66}$ , denoted C32) adsorbed from solution onto  $\text{SiO}_2$ -coated Si(100) substrates revealed an interesting solid film structure [2]. In the first one or two C32 layers adjacent to the substrate, the molecules orient with their long axis parallel to the substrate. This “parallel” film is followed by a monolayer in which the molecules adsorb with their long axis perpendicular to the substrate. At still higher coverages, preferentially oriented bulk particles nucleate, indicating a Stranski-Krastanov growth mode.

Since the “perpendicular” monolayer was not observed in studies of films of shorter  $n$ -alkane molecules grown from the vapor phase on a Ag(111) surface [3], it is of interest to ask such questions such as whether the growth mode of solid alkane films depends on the length of the molecules, choice of substrate, and deposition method. To address these issues, we have undertaken x-ray specular reflectivity measurements on C32 films grown from the vapor phase on single-crystal Ag(111) substrates in ultrahigh vacuum (UHV). These experiments are part of a larger program to study the structure of both solid and fluid alkane films adsorbed on well-characterized metal surfaces with the aim of better understanding lubrication phenomena at the microscopic level.

## Methods and Materials

For this study, the C32 films were grown *in situ* by using a specially designed UHV chamber. Vapor from the C32 liquid reservoir in a Knudsen cell effused through a small aperture (0.5-mm diameter) onto the Ag(111) substrate (10-mm diameter) located at a distance of 2.5 cm from the aperture. During deposition, the Knudsen cell was held at a temperature of 73°C. For monolayer coverage, the Ag(111) substrate was held at 106°C to prevent thicker film growth. The multilayer was grown with the substrate at 42°C, exposing it to the C32 vapor for 20 min.

We conducted the x-ray specular reflectivity measurements at the 6-ID-B station of MU-CAT at the APS. Specular reflectivity curves were obtained by

integrating the intensity of individual “rocking” curves taken at closely spaced intervals along the specular rod ( $Q_{\perp}$  of  $<2.5 \text{ \AA}^{-1}$ ). After making corrections for beam spillover, other geometrical effects, and  $Q$ -resolution, the curves were fitted with an atomic model that included contributions from both the Ag crystal and the alkane layers [3]. From the fit, parameters such as the height of the alkane layers and their density were obtained.

## Results

The x-ray specular curves taken at room temperature for a monolayer and a “multilayer” sample are shown in Fig. 1 and Fig. 2, respectively. The circles are data points, and the solid lines are the best fits to the model that assumed the first  $N$  molecular layers of the film were complete and were followed by up to three partial layers with fractional occupancies of  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$ , respectively. The C32 molecules were taken to be in the all-*trans* configuration.

In the case of the monolayer, the best fit was obtained when the C32 carbon skeletal plane was parallel to the substrate, whereas parallel and perpendicular orientations yielded comparable fits for the multilayer film. The monolayer fit gives an area of  $A_{\text{C32}} = 209 \text{ \AA}^2$  per molecule, a height of  $d_{\text{AgC32}} = 4.04 \text{ \AA}$  for the carbon skeletal plane above the Ag(111) surface, and a second layer occupancy  $\theta_1$  of ~9%.

When a parallel orientation of the molecules is assumed, the fit to the multilayer gives about the same area per molecule ( $A_{\text{C32}} = 208 \text{ \AA}^2$ ) and first C32 layer height ( $d_{\text{AgC32}} = 3.93 \text{ \AA}$ ) as that given by the monolayer. Although we estimated the amount of C32 deposited on the substrate for the multilayer sample to be greater than that required to grow four layers of parallel-oriented molecules, the best fit gives fractional occupancies for  $\theta_1$  of ~60% and for  $\theta_2$  of ~6% of the second and third layers, respectively. It also gives a distance of  $d_{\text{C32}} = 3.91 \text{ \AA}$  between the C32 layers.

To investigate the possibility of growing thicker C32 films on the Ag(111) substrate, we increased both the exposure time to the C32 vapor and the temperature of the Knudsen cell. In these cases (not shown here), we observed that Bragg peaks from preferentially oriented

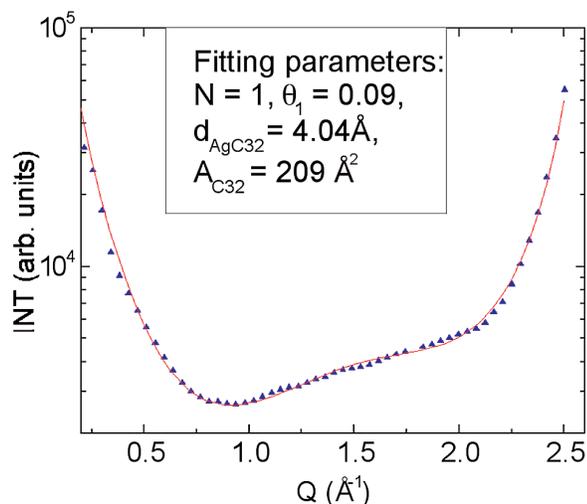


FIG. 1. X-ray reflectivity from C32 monolayer on Ag(111).

bulk particles were consistent with the nucleation of an orthorhombic phase, as found for C32 deposited onto the SiO<sub>2</sub>-coated Si(100) substrates [2].

## Discussion

It is interesting to compare the growth mode of C32 on Ag(111) with that on SiO<sub>2</sub>/Si(100). In both cases, one to two layers of C32 adsorb first, with the long molecular axis oriented parallel to the substrate. Also, for both substrates at sufficiently high coverage, preferentially oriented bulk particles having an orthorhombic structure coexist with the film, a finding that is consistent with a Stranski-Krastanov growth mode. This orthorhombic phase appears to be surface-stabilized, as it had not been reported previously in the literature.

Results for C32 film growth on the Ag(111) substrate differ from those for growth on SiO<sub>2</sub>/Si(100) in that for the Ag(111) surface, we did not observe Kiessig fringes with a period corresponding to a C32 monolayer, with its molecules oriented perpendicular to the surface. Also, our fits to the reflectivity curves of the multilayer samples (including those not presented here) indicated a much smaller film thickness than that estimated from the vapor deposition times, when about the same sticking coefficient found for shorter alkanes was assumed [3]. Note, though, that the quality of the multilayer fits was not as good as that for the monolayer in Fig. 1.

A possibility suggested by molecular dynamics simulations of alkanes on metal surfaces [4] is that a significant number of molecules do adsorb above the

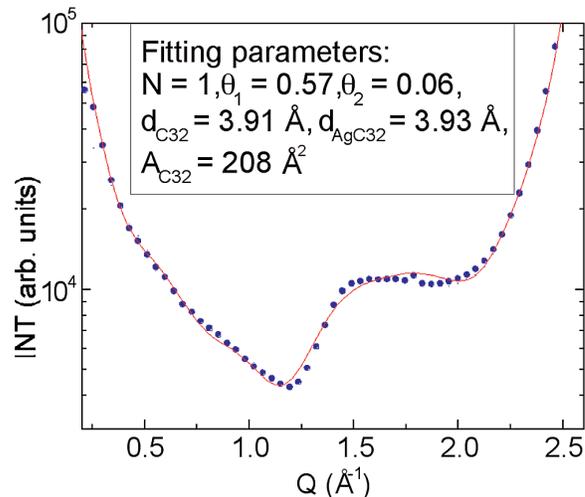


FIG. 2. X-ray reflectivity from C32 multilayer on Ag(111).

“parallel” layers, but, because of slow kinetics and the presence of *gauche* defects in the molecules, they are unable to crystallize into a “perpendicular” monolayer. Thus their contribution is not represented well by the simple layering model used here. In the case of the SiO<sub>2</sub>/Si(100) substrate, deposition of the C32 was from solution, which may allow faster adsorption kinetics and result in crystallization of the perpendicular monolayer.

## Acknowledgments

This work was supported by the National Science Foundation under Grant Nos. DMR-9802476 and DMR-0109057. The MU-CAT sector at the APS is supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), through Ames Laboratory under Contract No. W-7405-ENG-82. Use of the APS was supported by the DOE BES under Contract No. W-31-109-ENG-38.

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