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Structure of self-assembled layers on silicon: Combined use of spectroscopic variable angle ellipsometry, neutron reflection, and atomic force microscopy

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Neutron reflection (NR), spectroscopic ellipsometry (SE), and atomic force microscopy (AFM) have been used to characterize the structure of self-assembled octadecyltrichlorosilane (OTS) layers on silicon. The first two of these techniques rely on modeling of the experimental data and may thus result in the unrealistic representation of the composition and structure at the interface. Ambiguities arise from model-dependent analysis complicated by the lack of sufficient external constraints to converge nonunique solutions to a unique one. We show in this work that AFM measurements provide extra constraints to allow us to obtain a physical description closer to the actual structure of the film. It was found that “the simpler the better” modeling strategy very often employed during the fitting of ellipsometric and neutron reflection data is, therefore, not necessarily the best way to obtain a reliable description of the interfacial structure. Our AFM findings necessitated the refit of both neutron and ellipsometric data that were previously described by a single-layer model. Interpretation of the structure of thin layers that is based only on indirect measurements such as SE, NR, and x-ray reflection techniques may be, therefore, misleading. A combined analysis of SE, NR, and AFM data suggests that the OTS film may comprise a rough layer, with pinholes down to bare silicon oxide surface, consisting at least of mono-, bi- and trilayers of OTS molecules. © 1999 American Institute of Physics. [S0021-8979(99)01902-7]

I. INTRODUCTION

This article addresses the fundamental question of the uniqueness of models developed during the analysis of spectroscopic ellipsometry (SE) and neutron reflection (NR) data. SE and NR techniques provide an indirect method of measuring surface structures. The system of interest here is a self-assembled layer (SAL) of octadecyltrichlorosilane (OTS). Self-assembled films from alkyltrichlorosilanes have been widely studied^{1–5} because they are interesting for both technological and scientific applications. Chlorosilanes are attractive because they can chemically react with various surfaces^{6–8} and form closely packed, grafted hydrophobic films, which are used as precursor layers in the study of protein adsorption.⁹ OTS is commonly used for the formation of a hydrophobic layer that has high physical and chemical stability on silicon, quartz, and glass surfaces.

The details of the structure and coverage of self-assembled monolayers, apart from their general scientific interest, are relevant to technological applications. In particular, the use of SALs is currently being exploited in various techniques of “soft lithography.”^{10,11} Monolayers of OTS, which are studied in the work presented here, have been used in a microfabrication process.¹² Consequently, reliable techniques for the analysis of SALs, such as SE, NR, and AFM

are required for technological advances. Moreover, SALs are used for surface modification of substrates when constructing multilayer samples for scientific studies using NR,¹³ and adequate modeling of the SAL is a prerequisite for subsequent analysis of a multilayer structure.

Ellipsometry has been employed extensively for the measurement of the thickness and optical properties of thin organic films.¹⁴ However, for very thin films, like self-assembled OTS films, either thickness or the refractive index of the film must be known in order to find the other parameter because of correlation between the two in data analysis. Additional information about the thickness of a thin layer can be obtained from a neutron specular reflection experiment.¹⁵ Atomic force microscope (AFM) measurements of the surface layers can also give information about the thickness of the film¹⁶ but only when there are holes or scratches (natural or purposeful) that expose the bare substrate. AFM has the advantage of direct observation of surface morphology and, in particular, can provide information about the surface coverage.¹⁷ A combination of either ellipsometry and AFM¹⁸ or ellipsometry and neutron reflectivity¹⁹ is often used as a means of better characterization of the system under study. This study uses simultaneously three techniques—a rare combination, which results in a more accurate description of the OTS structure at the solid surface. We pinpoint some problems associated with the interpretation of data obtained by reflectivity methods.

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It has already been recognized that experimental constraints such as a finite range of incident angles and energy spectra of radiation preclude one from finding a unique structural description of the system during mathematical manipulations of the data. In the fitting of reflectivity data (including SE and NR data) to a physical model, conventional wisdom suggests that one should use the “simpler-the-better” strategy. That is, a materials system should be described with the minimum possible number of unknown parameters. In effect, this approach is a means of restricting the number of models that are eligible for consideration. Other workers have pointed out the need to restrict the number of models used in fitting ellipsometry data.²⁰ In this article, we first follow the simpler-the-better strategy and apply a single-layer model in the analysis of a SAL on silicon substrate. We demonstrate a strategy to obtain fits to the data from *both* SE and NR. We then test our model with a third technique, AFM, and discover that the model is inadequate. Using surface roughness information obtained from AFM, we restrict the range of acceptable models, and finally obtain a physical description of the surface structure based on a trilayer model that is consistent with all three techniques.

II. EXPERIMENTAL DETAILS

Optically polished silicon single crystals block (125 mm×55 mm×25 mm) and wafers (0.4 mm) with (111) orientation were used in this study. The silicon blocks were cleaned in a surfactant (Decon-90) followed by rinsing in water, immersing in a 7:1 H₂SO₄/H₂O₂ solution at about 110 °C, and lastly rinsing in high purity water.²¹ Then the samples were treated with ozone [generated by an oxygen flow in ultraviolet (UV) radiation] for 1 h.²² The thickness of the native oxide layer was measured using ellipsometry, AFM and neutron reflection for each sample prior to the chemical grafting of OTS to the surface. OTS (Aldrich, UK) was used as received. The coating procedure²³ involved first the preparation of 20% *v/v* CH₂Cl₂ in hexadecane solution, protected against moisture, and equilibrated at 12–14 °C in an ultrasonic bath. Second, OTS was added to make a concentration of 10^{−3} M at 12–14 °C, and silicon samples were immersed in the solution and the samples were sonicated in the ultrasonic bath for 1.5 h. They were removed, rinsed in CH₂Cl₂ and ultrasonicated for another 20 min in CH₂Cl₂ in order to remove nonreacted OTS molecules. Finally, the samples were copiously rinsed in CH₂Cl₂, then ethanol and lastly high-purity deionized water.

The SE measurements were performed using a variable angle spectroscopic ellipsometer (VASE Woollam Inc, USA) with a rotating analyzer configuration. Data were fitted to a multilayer model (in which each layer was characterized by its thickness and refractive index) using a Levenberg–Marquardt algorithm. The quality of the SE fit was determined by the mean-square error (MSE):

$$\text{MSE} = \frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^2 \right],$$

where N is the number of (Ψ, Δ) pairs, M is the number of variable parameters in the model and σ are standard devia-

tions of the experimental data points. The superscript “mod” and “exp” refer to values obtained from modeling and experiment, respectively.

The neutron reflectivity measurements were carried out on the CRISP neutron reflectometer at ISIS (Rutherford Appleton Laboratory, Didcot, UK).²⁴ The quality of the NR fit was evaluated by the mean-square standard deviation (χ^2):

$$\chi^2 = \frac{1}{N} \sum_{i=1}^N \frac{(x_i^{\text{exp}} - x_i^{\text{mod}})^2}{x_i^{\text{exp}}},$$

where N is the number of reflectivity values x_i and the superscripts are the same as before. For the solid/liquid NR experiments a special sample cell was used.²¹ Fitting of the NR data involved the calculation of the reflectivity profile for a model interfacial structure using the optical matrix method. A model typically consists of several layers that are characterized by their thickness and scattering length density. More detailed information about the use of specular reflection of neutrons to study interfaces is in the literature.¹⁵

The AFM measurements were carried out using a Nanoscope III (Digital Instruments Inc.) AFM microscope in tapping/phase mode.

III. RESULTS

A. Characterization of silicon oxide layer using SE and NR

Prior to silanating the samples, SE and NR measurements were carried out on all silicon blocks and wafers. Modeling of the ellipsometric data requires a good knowledge of optical properties of species on the surface. In the case of silicon and silicon dioxide, very reliable tabulated optical data of the refractive index dispersion are readily available.²⁵ In order to model the layer of native oxide on the surface of silicon, tabulated data for the optical constants of amorphous silicon dioxide were used.

The oxide layer was measured with ellipsometry at five different points on each silicon sample. The average thickness of the oxide layer was 24 ± 3 Å when the optical data for bulk amorphous silicon dioxide was used. In further modelling, a 24 Å silicon dioxide layer is assumed. Previous work has found that the density, structure, and optical constants of native oxide are not greatly different from bulk amorphous oxide.

Neutron reflection technique is not particularly sensitive to the presence of a native oxide layer when measurements are performed in air. However, neutron reflection data should not *disagree* with the ellipsometric data and could be used as an approximate means to test the validity of the ellipsometric findings. Figure 1 shows the measured neutron reflectivity profile together with the fitted curve for the native oxide layer on the silicon block. Neutron reflectivity is plotted as a function of the neutrons' momentum transfer k ($k = 4\pi \sin \theta / \lambda$, where θ is the incident angle and λ is the wavelength), perpendicular to the surface, as in the standard presentation.

The continuous line in Fig. 1 was calculated based on a single uniform oxide layer model ($\chi^2 = 1.2 \times 10^{-5}$). The

FIG. 1. Neutron reflectivity profile and fitted curve for the air/silicon interface. The solid line shows the best fit model; $\diamond$ shows experimental data. Mean-square deviation (χ^2) is 1.2×10^{-5} .

thickness of the layer was 24 ± 4 Å, which agrees with our value from ellipsometry and with ellipsometric findings of 23¹³ and 25 Å²⁶ reported elsewhere.

B. Characterization of OTS film using SE and NR

NR and SE measurements of silicon blocks and wafers were made after the silanating procedure. Figure 2 shows that there is considerable difference between the ellipsometric spectra for coated and uncoated surfaces, which is well beyond the noise in the data of $\pm 0.1^\circ$ in Δ and $\pm 0.02^\circ$ in Ψ .

FIG. 2. A comparison between ellipsometric measurements for bare silicon (solid lines) and the same wafer coated with an OTS layer (dotted lines). Measurements were performed at three different angles of incidence: 70° - --- line; 75° - - - - and 80° - - - - -.

TABLE I. Properties of OTS and calculated refractive index.

OTS type	Density, g/cm ³	R , cm ³ /mole	M , g/mole	Refractive index, n
Liquid	0.777	84.7	253.5	1.432
Crystalline OTS	0.932	84.7	253.5	1.527

Similarly to the SE model of the oxide layer, the OTS layer can be characterized by two unknown parameters: thickness and refractive index. The two parameters cannot be determined independently for a very thin film. Thus, modeling of such data requires good knowledge of either the refractive index of OTS or its thickness.

The refractive index for OTS layers can be estimated from known values of molecular refractivities²⁷ and material density (d). The relationship is given through the Lorentz–Lorenz equation:

$$R = \frac{M}{d} \frac{n^2 - 1}{n^2 + 2},$$

where M is the molecular weight of the substance, obtained from a knowledge of chemical composition. R is molecular refractivity calculated using known values of molecular refractivities R_i for each chemical constituent of the material:²⁸

$$R = \sum_i R_i.$$

The density of the OTS film on the silicon surface is unknown and is affected by the presence of voids and by the degree of molecular ordering. If the OTS layer is amorphous, its density can be approximated by that of liquid octadecane (0.777 g/cm³).¹³ A 20% increase in density of the surface layer of liquid alkanes has been observed and interpreted as the result of the formation of a crystallized surface layer.²⁹ If the OTS layer is crystalline, its density is expected to be about 20% higher than in the liquid state. Table I provides the expected range of refractive indices for OTS layer that does not contain voids. In the presence of air voids the values will be lower. The complication thus arises from the uncertainty in the physical state of the OTS molecules and the presence of air voids in the layer.

With such a broad range of possible indices of refraction, SE results can be fitted to a number of models, each representing a composite of OTS and voids in the grafted layer. The refractive index of a composite material is calculated using an effective medium approximation (EMA).³⁰ In this approximation, the size of voids is assumed to be less than the wavelength of light used.

Reported literature values for the thickness of an OTS layer on silicon substrates vary from 16 to 25 Å. The thickness of 25 Å corresponds to a fully extended hydrocarbon chain (18 carbons) protruding normal to the surface.³¹ These authors reported that a 16-Å-thick OTS layer was measured by ellipsometry when OTS was coated on a dry silicon substrate. On a substrate which was soaked in water for 12 h prior to the OTS deposition, the thickness was reported to be about 24 ± 2 Å.

FIG. 3. Ellipsometric data measured at 70° (circles), 75° (triangles), and 80° (squares) and fitting curves (25 Å layer, with 40% voids) for the OTS-coated silicon block. Mean square error is 4.7.

Thus, ellipsometric data alone cannot provide a unique answer and additional information is required. A Fourier transformed infrared (FTIR) study reported that the hydrocarbon chains in the OTS molecules stand almost normal to the silicon surface.³¹ With this orientation, the thickness of a molecular monolayer would be about 25 Å. Because the propagation of the light depends on the product of the thickness of the layer and its refractive index (i.e. the optical path), there is strong correlation between the thickness of the layer and its refractive index for a layer that is substantially thinner than the wavelength of the probing light: In modeling the data an increase in the thickness must be compensated by a decrease in the value of refractive index. A liquid-like OTS layer has a lower refractive index than the crystalline one and can be used as a simple alternative model. The ellipsometric data shown in Fig. 3 were fitted to an EMA model which takes into account the suggested vertical orientation of the OTS molecules. The model comprises a liquid-like OTS film of fixed thickness of 25 Å with 40 vol % of air in the layer.

In order to test this model of the OTS film, neutron reflection measurements were performed on the same silicon block studied by SE. Neutron reflection allows measurements of the same interface at different contrasts of the ambient phase by mixing deuterated and protonated materials that scatter neutrons with different scattering amplitudes.¹³ The scattering ability of each species constituting the interface is characterized by the scattering length density (SLD). The SLD of a layer at a solid/liquid interface is

$$\text{SLD}_{\text{layer}} = (1 - \gamma)\text{SLD}_2 + \gamma\text{SLD}_1,$$

FIG. 4. Neutron reflectivity profiles (diamonds) and fitted curves (solid lines) for the OTS film on silicon surface. Isotopic composition of ambient phase is (a) air; (b) D₂O; (c) D₂O/water contrast 4; (d) D₂O/water contrast 2.07 (silicon contrast match). The size of the diamonds represents error bars.

where γ is the volume fraction of species 1 (SLD_1) in the layer and SLD_2 corresponds to the ambient medium. Under proper experimental setup, the ambient scattering length density will match exactly that of the solid substrate, thereby giving the reflectivity profile arising only from the interfacial region. Mixing water with an SLD of $-0.35 \times 10^{-6} \text{ Å}^{-2}$ and D₂O with an SLD of $6.35 \times 10^{-6} \text{ Å}^{-2}$ allows one to obtain any desired contrast of the ambient liquid phase from -0.35×10^{-6} to $6.35 \times 10^{-6} \text{ Å}^{-2}$. Neutron reflectivity profiles were measured for the OTS-coated silicon block using four different contrasts of the ambient medium: air ($\text{SLD} = 0.0 \times 10^{-6} \text{ Å}^{-2}$), D₂O ($\text{SLD} = 6.35 \times 10^{-6} \text{ Å}^{-2}$) and H₂O/D₂O mixtures giving SLDs of 4.0×10^{-6} and $2.07 \times 10^{-6} \text{ Å}^{-2}$. Figure 4 shows the experimental data and fitted curves using the parameters listed in Table II. As seen in Table II, four measurements of the same material indicate that the thickness of the OTS is $24 \pm 2 \text{ Å}$, and the layer consists of $65 \pm 1 \text{ vol } \%$ crystalline material with the remainder being void.

This NR model is consistent with our previous model of the OTS coating, which was proposed based on ellipsometry results and FTIR data reported elsewhere. That is, the same model is applicable to *two* techniques. The fact that neutron

TABLE II. Fit parameters used to model the OTS as a monolayer. Neutron properties of materials used in this study were taken from the literature (Ref. 13).

SLD of the ambient medium, 10^{-6} Å^{-2}	Air SLD=0.00	D ₂ O SLD=6.35	H ₂ O/D ₂ O SLD=4.00	H ₂ O/D ₂ O SLD=2.07
Thickness, $\text{Å} \pm 2$	25	25	22	23
SLD of OTS layer, 10^{-6} Å^{-2}	-0.24	2.00	1.20	0.50
Vol % crystalline	65	65	64	65
OTS $\chi^2, 10^5$	0.9	0.8	0.8	0.6

FIG. 5. AFM topographical (left) and phase contrast (right) images of one of the OTS-coated wafers.

model fits four different contrasts of the ambient may suggest that it is a trustworthy representation of the interfacial structure. However, both ellipsometry and neutron reflection are model-dependent techniques and do not analyze the surface directly. The models assume uniform planar layers with sharp interfaces without roughness. This is a sensible way to model these data because both techniques are sensitive to specular reflected radiation only and do not measure diffuse reflectivities. Therefore, information about roughness larger than the wavelength of the radiation is lost. Also, reflectivity of neutrons decreases rapidly with the increase of momentum transfer thus reducing the sensitivity of the technique to measure very thin layers. In modeling ellipsometric data the coupling between the thickness and the refractive index for very thin layers makes it impossible to determine a unique solution for both thickness and index and so more complicated models with roughness are not justified. Besides, illuminated sample spots are large in both methods so that the detectors collect signal from a large area of the sample resulting in an averaging of all microscopic imperfection.

To test the validity of such modeling, a technique that directly measures the surface structure on the nanometer level, AFM, was employed to analyze the OTS films.

C. AFM measurements of OTS on thin Si substrates

AFM measurements were performed on silicon wafers which were coated *simultaneously* with silicon blocks used for NR measurements. SE analysis of blocks and wafers gives the identical spectra within errors. Therefore, it is possible to compare AFM findings from wafers with the NR results from blocks. The samples were studied using AFM in the tapping mode when the cantilever was excited into resonance oscillation with a piezoelectric crystal. The changes in oscillation amplitude were used as a feedback signal to measure topographic variations of the sample. Figure 5 (left) and

(right) show topographical and phase-contrast images of a 300 nm×300 nm area of the sample coated with OTS. In phase imaging AFM, the phase lag of the cantilever oscillation and the signal sent to the cantilever's piezo driver are simultaneously recorded. This lag is sensitive to variations in material properties such as adhesion and viscoelasticity.^{16,17} The simultaneous use of both modes in the real time scan provides not only topographical mapping but also information on variations in adhesion, friction, viscoelasticity and, perhaps, other properties. Section analysis for the image shown in Fig. 5 (left) is presented in Fig. 6.

Close study of the images in Fig. 5 reveals that the “hardest” regions seen in the phase contrast image correspond to the lowest regions seen in the height image. This result suggests that these are areas where the substrate is bare. The substrate surface can thus be used as a reference point in measuring the film thickness. Figure 6 shows the elevation of the features along a section line and demonstrate that the thickness of the OTS layer is significantly larger than a single monolayer of 25 Å. Clearly, the film consists of domains with thicknesses of 2, 3 and, sometimes 4 monolay-

FIG. 6. Section analysis of the AFM image shown in Fig. 5 (left).

TABLE III. Parameters based on AFM findings used to fit NR data from the OTS film.

Contrast of solution	SLD=0.0×10 ⁻⁶ Å ⁻²		SLD=6.350×10 ⁻⁶ Å ⁻²		SLD=4.00×10 ⁻⁶ Å ⁻²		SLD=2.070×10 ⁻⁶ Å ⁻²	
	Thickness, ±2 Å	SLD ×10 ⁻⁶ Å ⁻²	Thickness, ±2 Å	SLD ×10 ⁻⁶ Å ⁻²	Thickness, ±2 Å	SLD ×10 ⁻⁶ Å ⁻²	Thickness, ±2 Å	SLD ×10 ⁻⁶ Å ⁻²
Layer1	10 Å	-0.32	10 Å	0.32	10 Å	0.07	8 Å	-0.12
Layer2	15 Å	-0.18	17 Å	3.00	17 Å	1.90	17 Å	0.90
Layer3	25 Å	-0.10	25 Å	5.60	25 Å	3.60	25 Å	1.70
χ ² , 10 ⁵	1.0		0.9		1.1		0.7	

ers. From the height measurements of the sample in five different areas, the average thickness was found to be 55 ± 5 Å with a mean surface roughness of 23 Å. This average thickness of the OTS layer is significantly larger than a single monolayer thickness of 25 Å and corresponds to more than a bilayer thickness. The mean surface roughness is calculated by:³²

$$R_{\text{mean}} = \frac{1}{\text{Area}} \int \int_{\text{Area}} |h(x,y)| dx dy,$$

where $h(x,y)$ is the image height in the X - Y plane defined so that the mean value of $h(x,y)$ is zero.

From phase mode images, in which the bare substrate corresponds to the darkest regions, it is found that the total OTS coverage of the surface is about 90%. The remaining 10% of the surface corresponds to pinholes between approximately 20 and 50 Å in diameter in which the silicon substrate is bare. At 50 Å height, the OTS coverage is about 40%.

In light of these findings, the previous modeling of neutron reflectivity and ellipsometry data, which used a model based on a uniform layer, must be revisited and a more complex model assumed.

D. Refined modeling of OTS layer using combined data from SE, NR, and AFM

From quantitative analysis of a complex AFM image as in Fig. 5 it is clear that a more complicated model is needed to account for the OTS structure at the surface. The next logical step is to employ a two-layer model with surface roughness in order to separate the effect of regions with different OTS coverage.

Fitting the same ellipsometric data shown in Fig. 3 but now using a two-layer model results in a good fit with an MSE of 5.1, which is just slightly larger than the MSE of 4.7 obtained from a single layer model. MSE was calculated for the same number of variable parameters. The thicknesses in the bilayer were set and a fitting procedure was used to determine the void fraction. The first layer of the best fit model is 25 Å thick and consists of 90 vol % of liquid-like OTS and 10% voids (i.e., pinholes); the second layer is the same thickness and contains 60 vol % OTS, in contrast to the 40 vol % estimated from AFM images. Comparing the quality of fit using this model with the previous one using a single-layer model, it is clear that ellipsometry is virtually insensitive to the very low coverage at about 75 Å unless the refractive index profile of the whole interfacial region is known from other measurements.

This two-layer model accounts for the average thickness of the film of 50 Å. However, it is not possible to fit neutron reflectivity profiles for all contrasts of ambient liquid with this model. Therefore, with the average total thickness of the OTS film as a constraint in modeling, a three-layer model is employed in order to define the structural composition of the OTS layer close to the silicon oxide surface more accurately. The first layer of the two-layer model is split into two layers. Also surface roughness using a density Gaussian distribution is introduced in order to account for the mean surface roughness of 23 Å.

Fitting the same neutron reflectivity profiles shown in Fig. 4 but employing a three-layer model, with the AFM findings as a starting point to fit the data, results in a good fit with standard deviations similar to the previously calculated for a single layer model fit (Table II). Parameters were systematically varied in the three-layer model to determine the range of acceptable values. In the best fit model that fits equally well for all four contrasts used in the NR experiments, the first layer of 10 ± 3 Å consists of 90 ± 10 vol % liquid-like OTS, the second layer of 17 ± 2 Å contains 50 ± 10 vol % OTS, and the third layer of 25 ± 3 Å contains 20 ± 5 vol % OTS. The structural parameters of this model are summarized in Table III. Surface roughness of 20 ± 2 Å was added to each model at the interface between the top layer and the ambient medium.

We next determined if the physical model derived from our AFM and NR analysis could likewise be used to describe the SE data. We used the three-layer model employed in simulations for NR data and optical parameters of crystalline OTS as a starting point for the SE model. We systematically varied the thickness and OTS coverage to find the best fit to the data. The resulting model is consistent with the NR model within the range of uncertainty reported above. When the same ellipsometric data as in Fig. 3 are fitted with the refined model, the quality of the fit remains nearly the same (MSE=5.2) as obtained with the bilayer model. It is impossible to tell whether the OTS is in crystalline or liquid-like form within the accuracy of the model. Changing the refractive index from the crystalline to the liquid-like value introduces a change of about 3 Å in the total thickness of the layer and results in a fit of the same quality.

Surface roughness in a sample significantly decreases the sensitivity of NR to SLD profiles at solid interfaces. With surface roughness it becomes very difficult to fit neutron and ellipsometric data to a unique model. A single uniform layer is the simplest model of the interface, but it does not account

FIG. 7. Scattering length density profiles for one- and three-layer models with surface roughness used to fit neutron reflectivity at the scattering length density of $6.35 \times 10^{-6} \text{ \AA}^{-2}$ at the Si interface. (—) shows the single layer model; (---) shows the three-layer model with surface roughness. For comparison, a three-layer model profile without roughness is shown as —●—.

well for the real topological features of the interface found with AFM. Uniform layer models are a simple approximation of the interface, but they do not work well for the solid/air analysis because of the sharp steps between layers of different species. Sharp steps between adjacent species manifest themselves in well-defined interference patterns in neutron reflection simulated profiles, contrary to the observed *smooth* reflectivity curves. The introduction of roughness (for example, a Gaussian-like surface density profile for each layer in the model) seems to be a more appropriate way to model data because it smears the interference patterns and makes the modeled profiles smooth in agreement with what is experimentally observed. However, broadening of the distribution of species in the model inevitably leads to ambiguity, and, therefore, additional information is required to eliminate implausible models.

As an example of the effects of roughness, Fig. 7 shows the SLD profiles for a three-layer model with and without surface roughness. Although the differences between the SLD profiles appear at first to be relatively minor, the model without the roughness does not adequately describe the data. On the other hand, this roughness in the sample produces data that can be equally well described as a uniform monolayer using the profile illustrated in Fig. 7 and which was already applied to the data as shown in Fig. 4. In contrast, SE is not sensitive to roughness on this length scale.

IV. CONCLUDING REMARKS

We have shown that the same sets of neutron reflection and ellipsometric data from SALs on silicon can be fitted to different models of the surface structure. The models depend on additional assumptions introduced into the model, which are based on the findings by other techniques, such as IR and AFM. A combination of ellipsometry and neutron reflection methods does not provide enough information to describe the surface structure adequately, although additional information about hydrocarbon chain orientation of the OTS molecules could be obtained using IR ellipsometry.³³ Uniform single layer models are too simplistic and do not describe well the surface structure when tested against AFM results. The

roughness of the layers in the model is of paramount importance to the final conclusions about the structure. Direct investigations of the surface using AFM necessitate a complex model containing surface roughness. Ultimately, the complementary use of three techniques indicate an interface structure with a density that decreases with distance from the substrate and that on average exceeds the thickness of a single monolayer.

What are the important implications of this work? Because of possible ambiguities in the interpretation of the surface structure, great care must be taken in constructing a model for surface-modifying films, prior to any further utilization of these models, such as in building blocks in the modeling of the interfacial structure of more complex systems. Obtaining structural information using direct methods and comparing that structure against the model based on the reflectivity techniques' data is essential. If not, unrealistic claims will be made which, in turn, will multiply in subsequent analysis.

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