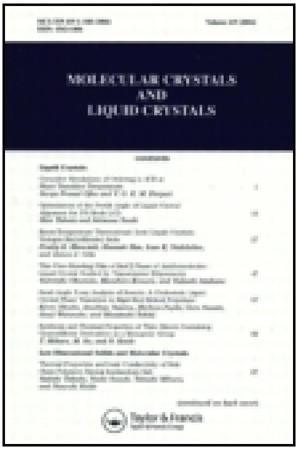

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Effects of Growth Conditions on Structure of Organosilane Monolayers on SiO_2 Substrates

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The effect of substrate temperatures on the structure of self-assembled monolayers (SAs) of organosilane $(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$ *on* SiO_2 *substrates were investigated by X-ray reflectometry and water contact angle measurements.* $(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$ *SAMs were fabricated by a chemical vapor deposition process for two hours, and the substrate temperature was varied between 80 and 170°C. The angular dependence of the specular X-ray reflectivity was measured, and thickness, density, surface roughness and interface roughness of SAMs were determined by fitting the observed curves to model calculations. It was clarified that the thickness, density and water contact angles of SAMs increased lineally with increasing temperature, and saturated at temperatures higher than 140°C.*

Keywords: growth condition; organosilane monolayers; X-ray reflectivity

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INTRODUCTION

It is well known that organosilane compounds $(CH_3)(CH_2)_nSi(OC_2H_5)_3$ ($n = 8$–18) adsorb onto SiO_2 substrates with covalent bonds and aggregate into stable self-assemble monolayers (SAMs). These methyl group terminated films and their derivatives are used in a wide field of applications, such as bio- and chemical sensing, wetting control, nanopatterning and organic electronic devices. Recently, we have found that organosilane SAMs inject charge carriers into organic thin film transistors and the carrier densities can be controlled by changing the kinds of SAMs molecules [1]. For further developments of the use of SAMs, investigation of the growth mechanism and characterization of SAMs are demanded.

X-ray reflection is a powerful technique to determine the thickness and density for SAMs on SiO_2 substrates, in sharp contrast to gold-thiol SAMs, where the detection of X-ray reflection from thin films is practically very difficult due to the large background from gold substrates. The angular dependence of the specular reflectivity of a thin film gives rise to the subsidiary maxima of the reflection curve. In an X-ray reflectivity curve, these maxima are caused by the interference of the waves reflected from the upper and lower interfaces of the layers. Characterization of those properties of the thin film can be performed by computer simulation and parameter fitting theoretically [2]. In this study, the effect of substrate temperatures on the structure of organosilane $(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$ SAMs on SiO_2 substrates were investigated by X-ray reflectometry. The thickness, density, surface roughness and interface roughness of SAMs were determined by fitting the observed curves to model calculations. The obtained data was compared with the data of water contact angle measurements on SAMs.

EXPERIMENTAL

Organosilane $(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$ SAMs were fabricated by a chemical vapor deposition process [3]. Silicon wafers having a 300 nm insulating layer of thermally grown silicon dioxide on the top were used as the substrate. Before forming the SAMs, the SiO_2 surface underwent a hydrophilic treatment by irradiating with ultraviolet light. The substrate temperature was maintained at designed temperature between 80 and 170°C and kept for two hours. For the macroscopic characterization, the water contact angle was measured by putting 1 μl of water droplets on the SAMs surface.

The angular dependence of the specular X-ray reflectivity was measured using a high-resolution X-ray diffractometer (ATX-G, Rigaku

Co.). X-rays with wavelength $\lambda = 0.15405\,\mathrm{nm}$ (Cu $K_{\alpha 1}$) are generated from Cu rotating anode (50 kV, 300 mA), collimated by parabolic multilayer mirror and monochromated by channel cut Ge (220) asymmetric monochromator. The coherent component of the reflected X-ray beam measured in θ-2θ scans yield the electron density profile in the direction normal to the sample surface because the scattering vector is perpendicular to the sample surface in the experimental geometry.

ANALYSIS OF X-RAY REFLECTIVITY

The X-ray reflectivity from a multilayered (organic monolayer/SiO_2/Si substrate) system is evaluated using the coherent scattering approximation developed by Parratt [4]. The attenuation of scattered intensity due to the rough interfaces is calculated using the approach by Vidal and Vincent [5] and deBore [6]. The incoherent component of scattered X-rays caused by roughness is calculated by the perturbation theory using the distorted-wave Born approximation [7], taking into consideration only the primary scattering processes. The details of this approach have been described in a literature written by Holy *et al.* [8].

For X-rays the index of refraction is conventionally written as $n = 1 - \delta - i\beta$, where

$$\delta = \frac{r_e \lambda^2}{2\pi} \rho N_0 \frac{\sum_{i=1}^{n} X_i (Z_i + f_i')}{\sum_{i=1}^{n} X_i M_i} \tag{1}$$

$$\beta = \frac{r_e \lambda^2}{2\pi} \rho N_0 \frac{\sum_{i=1}^{n} X_i f_i''}{\sum_{i=1}^{n} X_i M_i} \tag{2}$$

Here, r_e is the classical electron radius, λ the X-ray wavelength, ρ the mass density, N_0 Avogadro's number, Z_i, M_i, and X_i are atomic number, atomic weight and the molar fraction of the ith atom, respectively. f_i is the atomic scattering factor of the real and imaginary components, f' and f''. The calculated model spectra using the recursion formula were converted to the X-ray reflectivity data by the nonlinear least squares method. Each layer was described by four parameters δ, β, thickness (d) and roughness (σ) as described below.

The X-ray reflectivity is defined as $|r_{12}|^2 = I/I_0$, where I_0 and I are intensities of incident and scattered X-rays, respectively. In the multilayered system, the r is given by the following formula,

$$r_{j,j+1} = \frac{r_{j+1,j+2} + F_{j,j+1}}{r_{j+1,j+2} \times F_{j,j+1} + 1} \alpha_j^4 \tag{3}$$

where

$$F_{j,j+1} = \frac{g_j - g_{j+1}}{g_j + g_{j+1}} \exp\left(-\frac{8\pi^2 g_j g_{j+1} \sigma_{j+1}^2}{\lambda^2}\right) \tag{4}$$

$$\alpha_j = \exp\left(-\frac{i\pi g_j d_j}{\lambda}\right) \tag{5}$$

$$g_j = \sqrt{n_j^2 - \cos^2\theta} \tag{6}$$

here, θ is the incident angle of X-rays. Hence, we could obtain the simulation curves of X-ray reflectivity data by parameters of ρ, d, and σ.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of X-ray reflectivity curves against incident angle θ for the SAMs ($(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$)-$SiO_2$-(300 nm)-Si substrate system. The best-fit curves to the experimental data were overwritten on the experimental data. Compared with the substrate without SAMs (the curve denoted as "Untreated" in Fig. 1), quicker delays in reflectivity followed by an intensity minimum or a kink were clearly observed for the SAMs treated samples, indicating that a very thin layer is formed on top of the SiO_2 surface. Fitting the observed curves to model calculation was performed, following the procedure described above, where we assumed that the sample consists of SAMs, SiO_2 layers and a Si substrate. Calculated curves fit nicely to the observed reflectivity for all samples as shown in Figure 1. The obtained thickness, density, surface roughness and interface roughness of $(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$ SAMs are listed in Table 1. There was no correlation in between the substrate temperature and the obtained roughness, and the values were around 2–3 Å. As to the thickness and the density, however, clear dependences on the substrate temperatures were found.

Figure 2 shows the temperature dependence of the thickness and the density of $(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$ SAMs. As shown in this figure, the thickness of SAMs lineally increased with substrate temperatures below 140°C. On the other hand, in the temperature range higher than 140°C, the thickness did not increase with substrate temperature, and the value $\sim$13 Å kept to be constant. Because the molecular length of all-trans C18 alkyl group is 21.4 Å, the obtained thickness of SAMs is considerably small. Furthermore, the reported value of octadecylsilane SAMs prepared from solution was 23.7 Å [9]. This difference in the

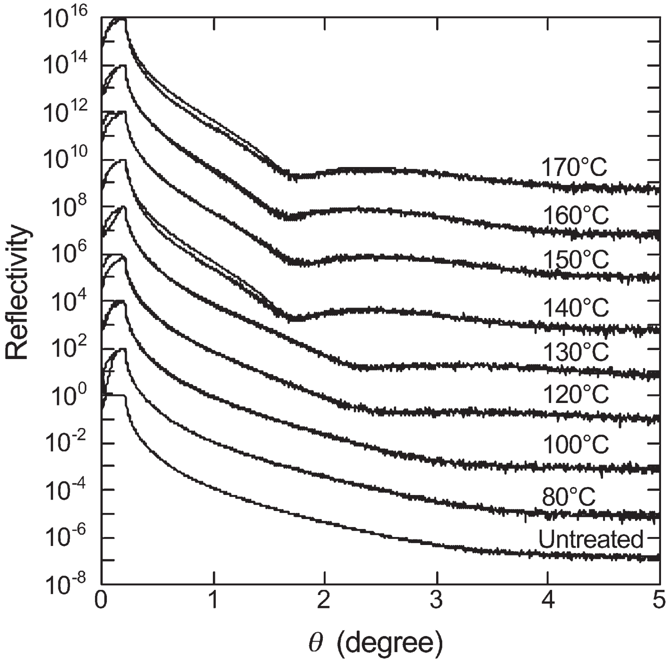

FIGURE 1 Temperature dependence of X-ray reflectivity curves against incident angle θ for the SAMs-SiO_2-(300 nm)-Si substrate system. The best-fit curves to the experimental data were overwritten on the experimental data.

thickness may be attributed to the disordering in the alkyl-chains of SAMs. The temperature dependence of density of SAMs is also shown in Figure 2. The density of SAMs also lineally increased with substrate

TABLE 1 Determined Parameters of Organosilane $(CH_3)(CH_2)_{17}Si(OC_2H_5)_3$ SAMs

Substrate temperature (°C)	Thickness (Å)	Density (g/cm^3)	Surface roughness (Å)	Interface roughness (Å)
80	5.1	0.57	2.7	2.1
100	6.6	0.63	2.4	2.1
120	8.6	0.68	2.0	2.3
130	9.3	0.65	1.9	3.0
140	12.9	0.87	2.9	3.8
150	12.7	0.85	2.4	2.9
160	13.5	0.86	2.9	2.9
170	12.5	0.90	2.0	4.5

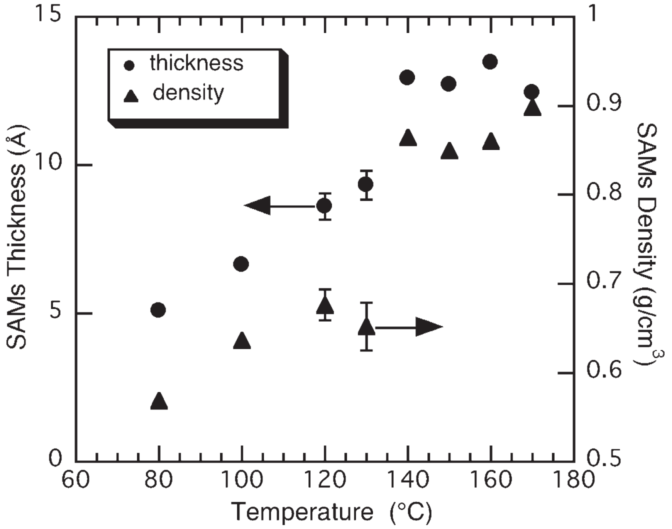

FIGURE 2 Temperature dependence of thickness and density of $(CH_3)(CH_2)_{17}$ $Si(OC_2H_5)_3$ SAMs.

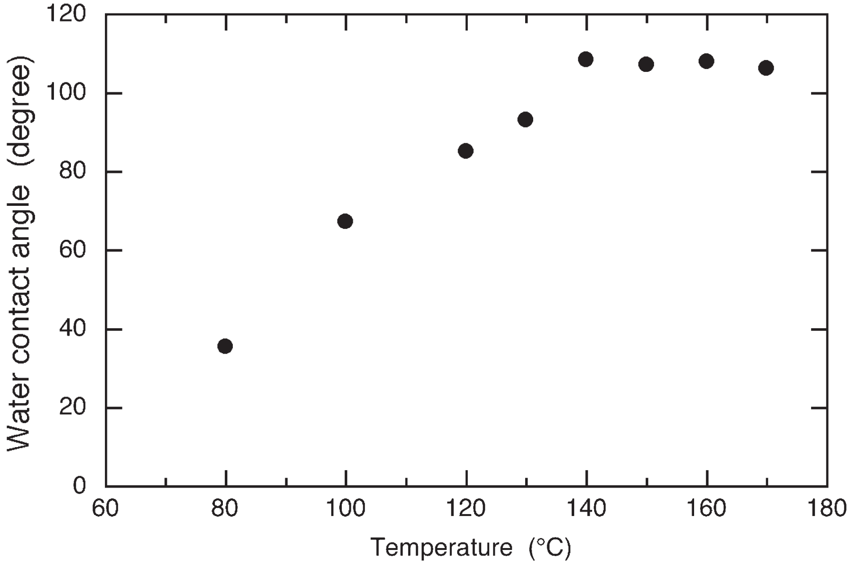

FIGURE 3 Temperature dependence of water contact angle of $(CH_3)(CH_2)_{17}$ $Si(OC_2H_5)_3$ SAMs.

temperatures below 140°C. In the temperature range higher than 140°C, the density was saturated against substrate temperature, and did not increase with temperature. The saturated value of density is about 0.9 g/cm^3, which is about 10% smaller than that of closely packed polyethylene. This notable smallness in densities suggests the disordering in the alkyl chains in SAMs.

Figure 3 shows the corresponding water contact angles measured on the same samples as used in the X-ray reflectivity measurements. The temperature dependence of water contact angles showed the same tendency as that observed in Figure 2. Namely, these also are lineally increased with substrate temperature below 140°C, and saturated above 140°C. The maximum value was around 110°C, which agree well with the reported value [3]. This suggests that methyl terminated group fully cover the surface of SAMs that formed above 140°C. From these facts, it was concluded that the structure of the SAMs was affected by the substrate temperature, and it saturate at above 140°C. The density and the thickness were considerably small in comparison with that of crystalline state even if SAMs were saturated. In the saturated structure, the SAMs surface seems to be covered by methyl group.

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