Headline Articles

Novel Method to Prepare Organosilane Monolayers on Solid Substrate

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A novel and convenient method to prepare organosilane monolayers was proposed. Pure water was put onto a cleaned silicon wafer and then a toluene solution of *n*-trichloro(octadecyl)silane (OTS) was spread on it. X-ray photoelectron spectroscopy and atomic force microscopic observation revealed that an OTS monolayer was successfully formed on the solid substrate after the water was evaporated. The static water contact angle of the silicon wafer covered with the OTS monolayer was 105°. Molecular aggregation states of the OTS monolayer were examined by electron diffraction, Fourier transform infrared spectroscopic, X-ray reflectivity, and grazing incidence X-ray diffraction measurements. The prepared OTS monolayer was in a two-dimensional hexagonal crystalline state at 293 K and alkyl chains of the OTS molecules were oriented normal to the surface. Also, the alkyl chains in the monolayer were highly ordered, although the experimental procedure for the monolayer preparation was quite simple. The development of this novel method to prepare a low energy surface will contribute to the material science as well as having industrial applications.

In 1980 Sagiv first reported how to prepare an organosilane monolayer onto a solid substrate by immersing it into an organosilane solution, the so-called technique of chemisorption.[1] The specific feature of the organosilane monolayer is that there exists strong interactions between monolayer and substrate via the covalent bond, as well as among molecules. Hence, the organosilane monolayers are highly stable against various environmental attacks such as moisture, water, and even HCl aqueous solution. This intriguing stability has motivated many researchers to study formation mechanism, molecular aggregation states, and physical properties of the organosilane monolayers so that the monolayer with highly functionalized surface would be constructed.[2–7]

To improve molecular ordering of the organosilane monolayers onto solid substrates, the Langmuir–Blodgett (LB) method has been applied to prepare them.[8–18] Grazing incidence X-ray diffraction (GIXD) measurement revealed that the ordering of alkyl chains in the LB organosilane monolayer is a little better than that of the chemisorbed one.[16] The formation mechanism of the *n*-trichloro(octadecyl)silane monolayer, which is commonly termed as *n*-octadecyltrichlorosilane (OTS), by the LB technique has been published elsewhere.[17] In short, the OTS molecules two-dimensionally crystallize and polymerize right after one spreads a solution on the water subphase, even though the OTS molecules are not compressed mechanically. Upon compression, these crystalline domains are gathered and furthermore fused and/or recrystallized at the domain interfaces owing to the compressive strain or stress, resulting in the monolayer with fairly large monocrystallines.[19–21] Since the LB method includes a lot of time-consuming steps in its procedure, however, it might be unpractical to apply this method to prepare a low energy surface for industrial applications.

Thus, it has been long desired that such organosilane monolayers with high molecular ordering can be prepared by a more convenient method. As mentioned above, the OTS molecules can aggregate and crystallize spontaneously only by spreading its solution at the air/water interface. Postulating that this aggregation behavior is universal for the OTS, one may reasonably infer that the OTS monolayer can be prepared without using an expensive Langmuir trough. If that is the case, the OTS monolayer is supposed to be prepared by a quick, simple, and inexpensive way. Such an achievement in terms of making low energy surfaces will contribute intensively to the material science as well as having industrial applications.

In this study, water droplets are put onto a silicon wafer, and then toluene solution of the OTS is spread on it for the purpose of the simple preparation of the OTS monolayer onto the solid substrate. After the water evaporation, the obtained monolayer is structurally characterized in detail.

Experimental

Monolayer Preparation. *n*-Trichloro(octadecyl)silane (OTS, $CH_3(CH_2)_{17}SiCl_3$, Shin-Etsu Chemical, Ltd., Co.) was used to prepare the monolayer. OTS was purified by vacuum distillation. A toluene solution of OTS was prepared with the concentration of 3×10^{-3} M. Toluene was refluxed with sodium for 6 h and then distilled because the trichlorosilyl group of OTS is sensitive to moisture. Figure 1 shows the schematic representation of the preparation process for the OTS monolayer. Water droplets with the total volume of 1.0 mL were put onto a silicon wafer with an area of 1.5×4.0 cm^2. The OTS toluene solution of 0.01 mL was subsequently spread in order to cover completely the water surface with the OTS molecules. The special care was taken for how much volume of the solution was spread, because an excess amount of the molecules might cause the monolayer to collapse and/or the multilayer to form. Also, an insufficient amount of the molecules would lead to the insufficient cover of the substrate. The OTS monolayer was finally obtained after water evaporation.

Monolayer Characterization. The monolayer formation was confirmed by X-ray photoelectron spectroscopy (XPS) in conjunction with atomic force microscopy (AFM). XPS (PHI 5800 ESCA system, Physical Electronics, Co., Ltd.) measurements were performed with a monochromatized AlK_α source at 14 kV and 24 mA. The emission angle of photoelectrons was set to be 45°. AFM (SPA 300, Seiko Instruments Inc.) was operated with the constant force mode under the ambient atmosphere at room temperature, using a 20×20 μm^2 scanner and a silicon nitride tip on a cantilever with the spring constant of 0.025 N m^{-1}. The normal force to the monolayer was kept as small as possible during the scan.

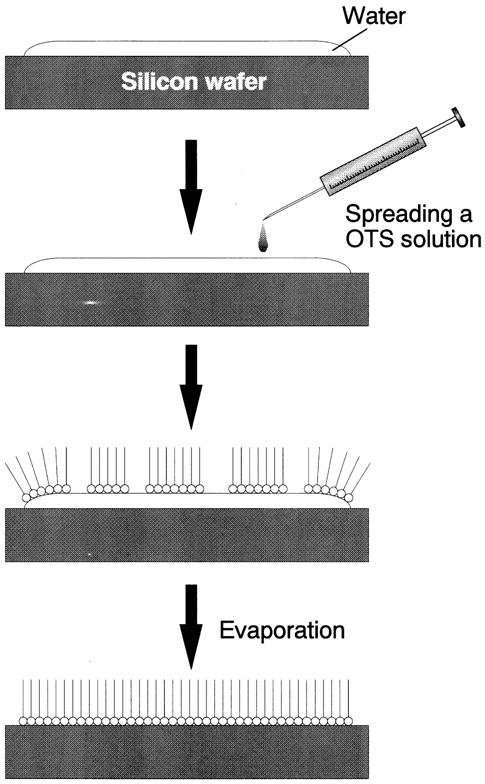

Fig. 1. Schematic representation of the novel preparation method for the OTS monolayer.

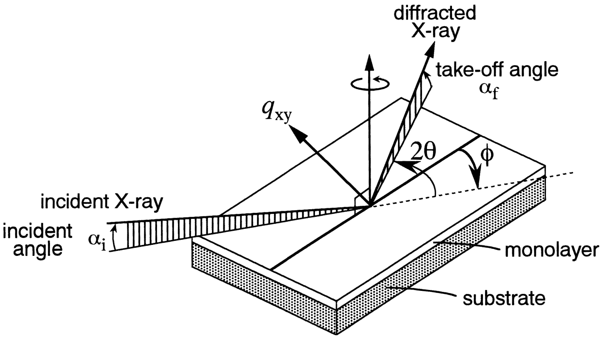

Fig. 2. Definition of various angles in GIXD configuration.

Molecular aggregation states of the OTS monolayer were investigated on the basis of electron diffraction (ED), Fourier transform infrared specrtoscopic (FT-IR), X-ray reflectivity, and grazing incidence X-ray diffraction (GIXD) measurements. ED patterns of the monolayer were obtained with a transmission electron microscope (Hitachi H-7000), which was operated at the acceleration voltage of 75 kV and the beam current of approximately 0.5 μA. The electron beam diameter was 2.5 μm. The substrates used for the ED measurements were collodion-covered TEM grids with an evaporated hydrophilic SiO_x layer.[19–21] The FT-IR spectra were recorded at the resolution of 2 cm^{-1} with a Nicolet Magna 860 which was equipped with a mercury–cadmium–tellurium (MCT) detector. A polarized beam struck the sample at the incident angles of 10° and 74° so as to examine the molecular orientation. As substrates for the FT-IR measurement, silicon wafers with both polished surfaces were used to reduce interference fringes in the spectra. To obtain the spectra with the high signal-to-noise ratio, 256 scans were collected. The monolayer thickness was evaluated by specular XR measurement. A monochromator was set next to the exit of the X-ray source (RU-300, Rigaku, Ltd., Co.). The sample was placed on the sample stage of a 3-axis goniometer. The reflected beam was detected by a scintillation counter after the beam passed through the slit. The molecular arrangement of the OTS monolayer was examined by GIXD measurement as well. The wave vector was defined as q_{xy} $\{= (4\pi/\lambda) \sin \theta$, where θ and λ were the angle and the wavelength of X-ray (CuK_α, $\lambda = 0.154$ nm), respectively. Also, the anisotropy of the molecular orientation in the OTS monolayer was evaluated by GIXD measurement at various directions of incident planes. Figure 2 illustrates the schematic representation of the various angles, α_i, α_5, θ and ϕ which define the reflection geometry. The ϕ was defined as the angle between the incident X-ray direction and the long axis of the silicon wafer substrate. The measurement was operated by a series of θ–2θ scans.

Results and Discussion

At first, an XPS measurement of the silicon wafer treated by the above-mentioned method was made to confirm whether an OTS monolayer was formed on it. Figure 3 shows survey scan spectrum of the treated silicon wafer at the emission angle of 45°. C_{1s}, O_{1s}, Si_{2s}, and Si_{2p} peaks were clearly observed at the binding energy of 285, 533, 151, and 100 eV, respectively, in the spectrum. In contrast, no Cl_{2p} peak, which can be assigned to the Si–Cl bond of original OTS molecules, was detected at all. Hence, it seems most likely that the hydrolysis reaction of the OTS molecules had completely proceeded. That is, it can be envisaged that the desired OTS monolayer was formed on

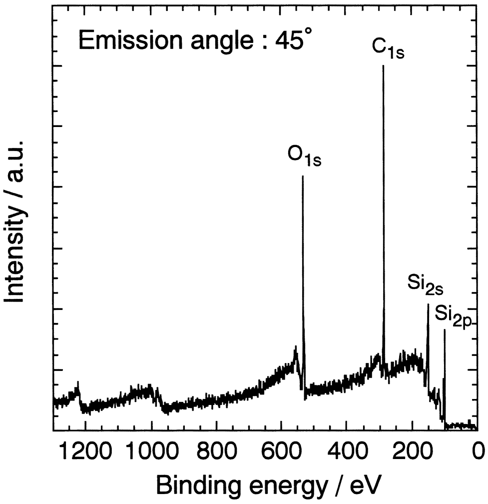

Fig. 3. XPS survey scan spectrum of the treated silicon wafer at the emission angle of 45°.

the silicon wafer substrate.

To ensure the formation of the OTS monolayer on the silicon wafer, AFM observation of the treated silicon wafer was carried out. Figure 4 shows the typical AFM image, and indicates that most of the region was covered with the OTS molecules. The height difference between covered and uncovered regions was approximately 2.3 nm, which is comparable to the OTS molecular length in all trans conformation. This means that the brighter and darker areas correspond to the OTS monolayer and the bare Si wafer, respectively. Therefore, it seems reasonable to conclude that the OTS monolayer can be formed by the simple and convenient method proposed in this study. In the AFM image, some uncovered region was clearly seen, although such a region was less than 10% of the total surface area. Considering the fact that water molecules evaporate during the film formation process, the uncovered region might be a pathway for the water evaporation. The static water contact angle on the silicon wafer covered with the OTS monolayer was evaluated to be higher than 105°, which was slightly lower than that of the OTS monolayer prepared by the chemisorption, 111 ± 2°.[22] Hence, it can be claimed that this novel method is effective to prepare a hydrophobic surface.

We now turn to the molecular aggregation states of the obtained OTS monolayer. Figure 5 shows ED patterns of the OTS monolayer prepared at 293 K onto a hydrophilic SiO_x substrate. The ED pattern was dependent on where an observation area was, meaning that either (a) hexagonal arcs or (b) Debye ring was observed. The spacing of each ED pattern was 0.42 nm, and this magnitude was in perfect accordance with that of the (10) for the hexagonal crystalline OTS monolayer prepared by the LB method.[9,12] In the case of the LB OTS monolayer, the two-dimensional crystalline domains of the OTS with the size of a few micrometers were formed even at the zero surface pressure. Upon monolayer compression, these crystalline domains are mechanically gathered with the aid of a barrier, and then sintered at domain interfaces, resulting in fairly larger domains in hexagonal packing. Hence, only the ED pattern of hexagonal arcs was observed for the LB OTS monolayer at a higher surface pressure. On the contrary, in the case of the OTS monolayer prepared by the novel method at 293 K, either ED pattern of hexagonal arcs or Debye ring was observed, even though the mechanical compression was not applied. In the novel method, the apparent area of the air/water interface decreases with proceeding water evaporation. This process corresponds to the monolayer compression on the water subphase, as shown in Fig. 1. Hence, it is plausible that the water evaporation induces the sintering of one crystalline domain into another at the domain interfaces. Since the induced lateral compression by the water evaporation would be relatively weak in comparison with that of the LB method, the domain sintering is concurrently weak as well. As a result, the randomly oriented crystalline domains are formed, as shown in Fig. 5b.

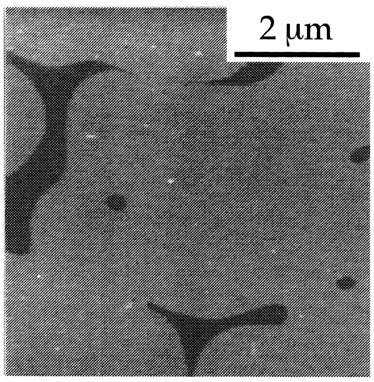

Fig. 4. AFM image of the treated silicon wafer.

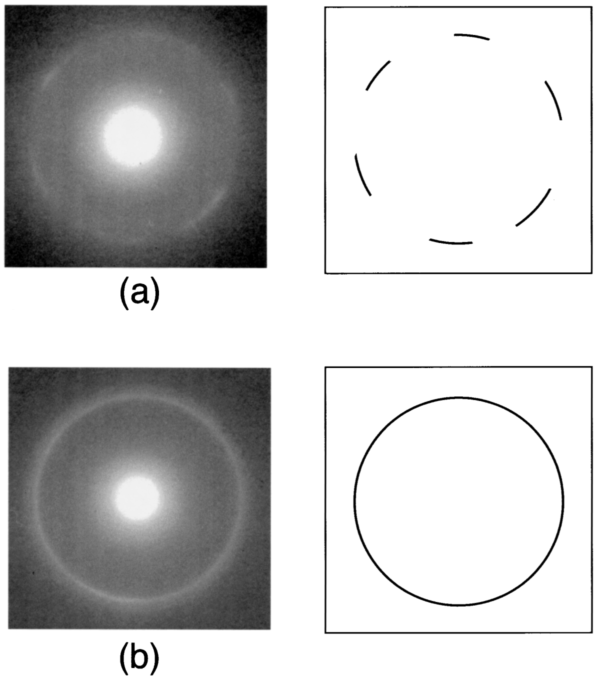

Fig. 5. ED patterns of the OTS monolayer at 293 K.

Figure 6 shows the transmission FT-IR spectra of the obtained OTS monolayer at the two IR incident angles of 10 and 74°. The measurement temperature was 293 K. The peaks observed at 2963, 2917, and 2849 cm^{-1} were assigned to the anti-

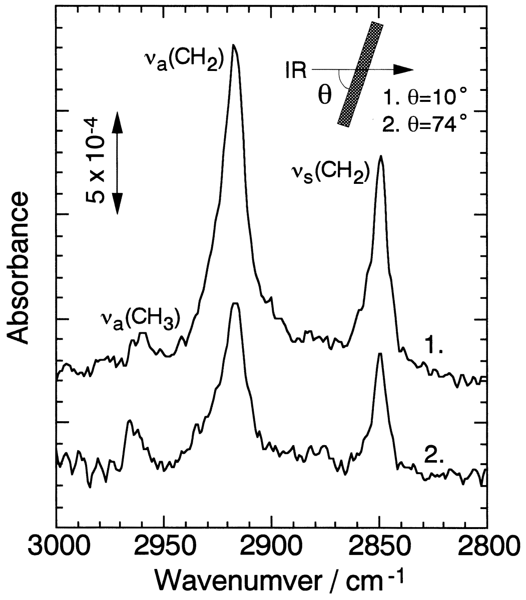

Fig. 6. Transmission FT-IR spectra in the range from 2800 to 3000 cm^{-1} for the OTS monolayer at 293 K. IR incident angles were set to be 10° or 74°.

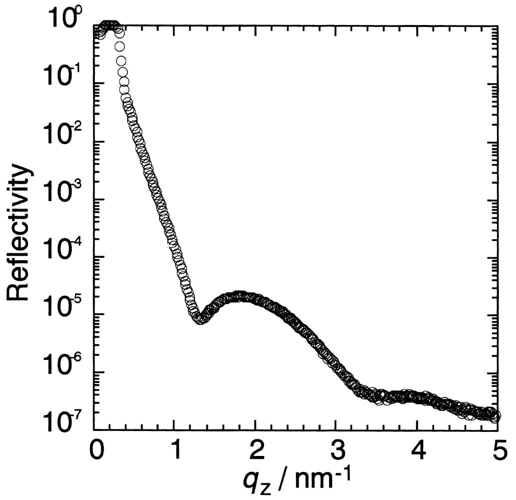

Fig. 7. Specular XR curve for the OTS monolayer at 293 K.

symmetric C–H stretching band of methyl group, $\nu_a(CH_3)$, the antisymmetric $\nu_a(CH_2)$, and symmetric $\nu_s(CH_2)$ C–H stretching bands of alkyl chains for the OTS molecules, respectively. In the cases of the *n*-alkane, fatty acid, and organosilane monolayers in a hexagonal crystalline state at 293 K, it has been reported that the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ bands are observed at 2917 and 2849 cm^{-1}, respectively.[12,19,21,23] Thus, Fig. 6 indicates that the OTS monolayer is in a hexagonal crystalline state at 293 K. The relative intensities of $I_{\nu_a}(CH_2)/I_{\nu_a}(CH_3)$ and $I_{\nu_s}(CH_2)/I_{\nu_a}(CH_3)$ at the incident angle of 10° were larger than those at 74°. Since the *p*-polarized beam was used for the FT-IR measurement, the electric field vector of the infrared beam was almost parallel to the monolayer surface at the incident angle of 10°. The angles of the transition moments of the $\nu_a(CH_2)$, $\nu_s(CH_2)$, and $\nu_a(CH_3)$ bands to the molecular axis are 90°, 90°, and 35°, respectively.[24] Therefore, the difference between relative intensities implies that the alkyl chains of the OTS molecules almost oriented normal to the surface in the monolayer.

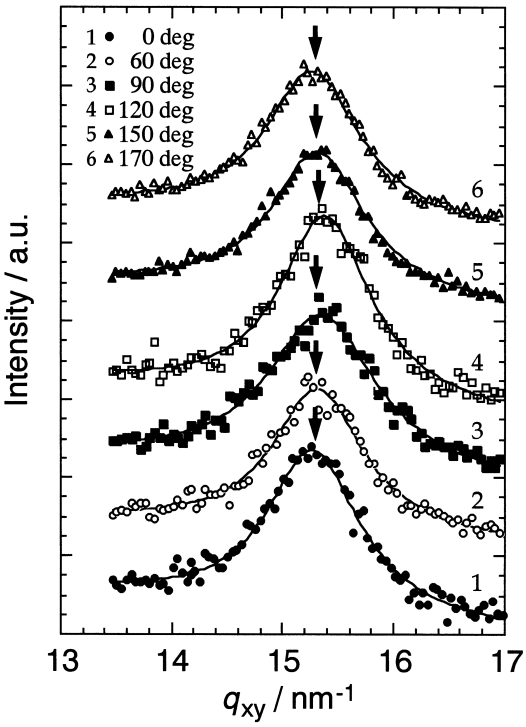

Fig. 8. GIXD profiles for the OTS monolayer at 293 K. Measurements were performed at various ϕs.

To strengthen this notion, the film thickness of the OTS monolayer was examined by XR measurement. Figure 7 shows the scattering vector dependence of X-ray reflectivity for the OTS monolayer prepared onto the silicon wafer at 293 K. The first minimum arises from a destructive interference between X-ray reflections from the top and bottom regions of the OTS monolayer. The magnitude of q_z for the first minimum in the XR curve was defined as $q_{z,\mathrm{min}}$. The film thickness calculated by $\pi/q_{z,\mathrm{min}}$ was 2.37 nm, which was a little smaller than that of the LB OTS monolayer with the molecular tilting of 9° to the surface normal, 2.34 nm.[16] Then, it seems likely that the film thickness of the monolayer corresponds well to the OTS molecular length in an all-*trans* state. That is, the OTS molecules in the monolayer prepared by the novel method oriented normal to the surface. This result was in excellent agreement with AFM and IR results.

Finally, we come to the molecular ordering of the OTS monolayer prepared by the novel method. Figure 8 shows GIXD profiles of the OTS monolayer at various ϕs at 293 K. Since the background of a silicon wafer substrate showed linear dependence in the *q*-range employed, the data were fitted by using a Lorentzian function on a linear background. Taking into account the ED results, it can be considered that peaks observed in Fig. 8 are assigned to the (10) reflection from the hexagonal lattice of the OTS monolayer. The (10) spacing calculated by the peak position, $q_{xy,\mathrm{max}} = 15.3$ nm^{-1}, was 0.412 nm. This value corresponds well to that of the LB OTS monolayer.[16] Also, the full width at half maximum (FWHM) of the (10) reflection peak for the OTS monolayer determined by the novel method was the same as that of the LB OTS monolayer. The peak position on the GIXD profile was independent of ϕ, as shown in Fig. 8. If the alkyl chains of the OTS molecules tilted in the monolayer, the peak position should depend on ϕ because of the apparent change of the spacing. Therefore, it seems reasonable to conclude that the alkyl chains of the OTS molecules in the monolayer prepared by this novel method orient normal to the monolayer surface.

Conclusion

The OTS monolayer was successfully prepared by the proposed novel and convenient method. The coverage ratio of the monolayer on the substrate was approximately 90%, and the treated substrate showed hydrophobic character. The obtained OTS monolayer was in a hexagonal crystalline state at 293 K, and its (10) spacing was calculated to be ca. 0.412 nm. The alkyl chains of the OTS molecules in the monolayer almost oriented normal to the surface.

Finally, we briefly compare the method proposed in this study with the LB and chemisorption techniques. In the case of the LB technique, it is possible to prepare an OTS monolayer with micro- and macro range orders. However, to obtain such a highly ordered monolayer, the compression condition must be carefully chosen.[17] On the other hand, in the cases of the proposed method and chemisorption technique, it is experimentally easy to cover a silicon wafer with the OTS molecules. In terms of the surface coverage, the chemisorption is superior to the proposed method, as deduced from the results of the water static contact angle. On the other hand, the molecular ordering in the OTS monolayer prepared in this study is somehow comparable to that in the LB OTS monolayer. This is not the case for the chemisorbed OTS monolayer. Hence, which method is appropriate should be strongly dependent on what the priorities for each purpose are.

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