Transactions of the Materials Research Society of Japan Vol.28 85-88 (2003)

Analysis of Aggregation States of Polymer Thin Films Based on Grazing Incidence X-ray Diffraction

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Grazing-incidence X-ray diffraction (GIXD) of organosilane monolayers and poly(3-hexylthiophene) was carried out. The in-plane structure of organosilane monolayers depended on the alkyl chain length and preparation method. With an increase in alkyl chain length($CH_3(CH_2)_{n-1}$) from n=18 to 20, the monolayers changed from the hexagonal phase to the rectangular phase. Also, it was revealed that the organosilane monolayers prepared by water-cast method formed order structure compared with those prepared by chemisorption. Poly(3-hexylthiophene) films were prepared onto various substrates and the degree of orientation of side-chain lamellae was studied by GIXD and conventional symmetrical reflection methods. The symmetrical reflection method suggested that the side-chain lamellae were highly oriented perpendicular to the surface of the films. On the other hand, GIXD implied that the lamellar orientation near the surface was disordered in comparison with the bulk.
Key words: Grazing incidence X-ray diffraction, organosilane monolayer, poly(3-hexylthiophene), in-plane structure

1. INTRODUCTION

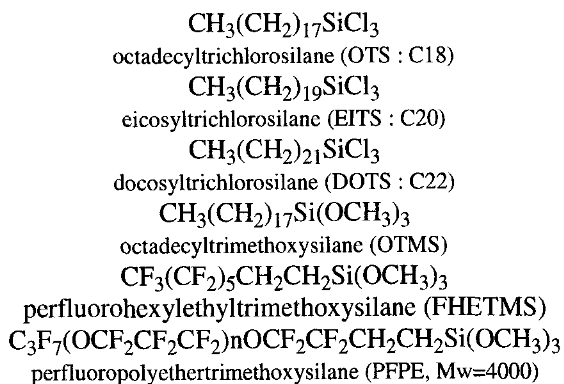
The aggregation structure of organic ultrathin films has received much attention because of their applications to electronic devices and surface functional nano-coatings. Since X-ray diffraction of an organic ultrathin film obtained by conventional and laboratory-scale X-ray source was weak in intensity, little investigation has been done on their structural analyses. Grazing incidence X-ray diffraction (GIXD) using evanescent X-rays has been applied for the analysis of in-plane molecular aggregation structure of organic ultrathin films.[1,2] In order to carry out precise structural analyses, it is necessary to utilize a highly monochromatic beam from the synchrotron radiation source as the incident X-rays. In this study, the molecular aggregation structures of poly(alkylthiophene) and organosilane monolayers were investigated by GIXD.

2. EXPERIMENTAL

2.1 Sample Preparation

Figure 1 shows the chemical structure of organosilanes and poly(3-hexyl thiophene). The octadecyltrichlorosilane (OTS, Chisso Co., Ltd.), eicosyltrichlorosilane (EITS, Shin-Etsu Chemical Co., Ltd.), docosyltrichlorosilane (DOTS, Shin-Etsu Chemical Co., Ltd.), octadecyltrimethoxysilane (OTMS, Gelest Co., Ltd.), perfluorohexylethyltrimethoxysilane (FHETMS, Fluorochem Co., Ltd.), perfluoropolyethertrimethoxysilane (PFPE, Mw=4,000, Daikin Industries Ltd.) were used for preparation of monolayer.

Figure 2 shows the schematic representation of preparation processes of organosilane monolayers. OTS,



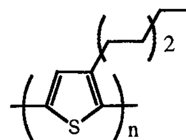


Figure 1 Chemical structures of organosilane compounds and poly(3-hexylthiophene).

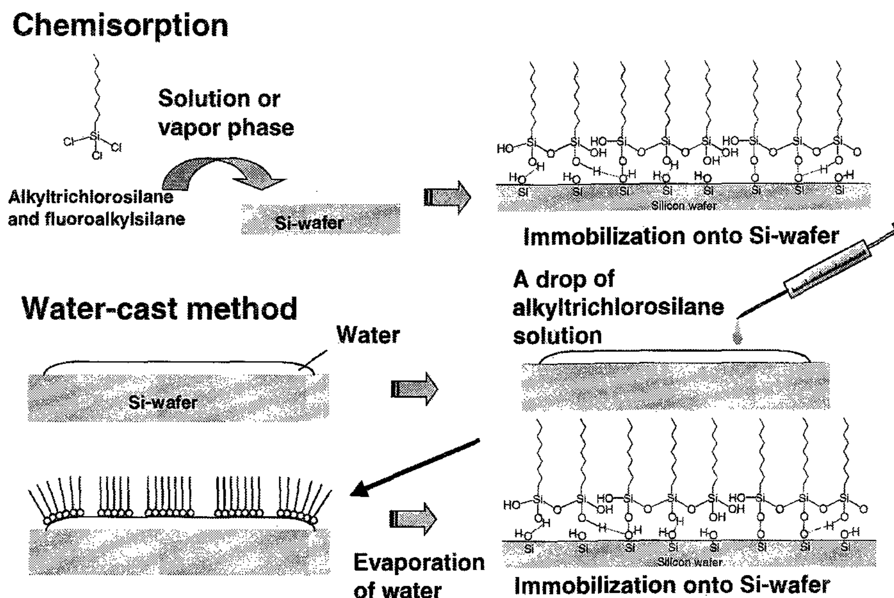


Figure 2 Schematic representation of the preparation of organosilane monolayers.

EITS, DOTS, OTMS, FHETMS were purified by vacuum distillation. PFPE was used without purification. Toluene was refluxed with calcium hydrate for 2h and distilled because organotrichlorosilane is sensitive to moisture. Bicyclohexyl was dried with molecular sieves. The substrates used in this study were Si-wafers cleaned by piranha solution and irradiation of vacuum ultraviolet ray (λ=172 nm) for 10 min under 15 mmHg.[3,4] OTS, EITS, and DOTS monolayers were prepared onto a substrates from their bicyclohexyl (Tokyo Kasei, Co., Ltd.) 5mM solutions by the chemisorption method under N_2 atmosphere at room temperature.[5] Samples were rinsed by successive bicyclohexyl, toluene and ethanol. A PFPE monolayer was prepared by the chemisorption method from its 0.2 % perfluorohexane (3M Co., Ltd.) solution in the same way. Perfluorohexane was used without further purification.

In order to prepare highly ordered monolayers, OTS, EITS and DOTS monolayers were prepared onto substrates by a water-cast method from their 5 mM toluene solutions.[6] Nano-pure water droplets with the total volume of ca. 0.8 mL were spread onto a cleaned Si-wafers with area of ca. 5 cm^2. The toluene solution with a volume of 5 μL was subsequently spread in order to cover completely the water surface with organosilane molecules. The organosilane monolayers were finally obtained after water evaporation at room temperature. OTMS and FHETMS monolayers were prepared by the chemical vapor adsorption method.[4,7,8] The substrates were placed together with a glass tube filled with 0.2 mL organosilane liquid into 65 mL Teflon™ container. The container was sealed with a cup and stainless container. Then the container was placed in an oven maintained at 423 K (OTMS monolayer) and 373 K (FHETMS monolayer) for 2 h. The samples were rinsed with ethanol and dried in vacuo.

In order to investigate the effects of surface free energy of substrates on chain-packing structure of polymer thin films, poly(3-hexylthiophene) (P3HT, Sigma-Aldrich Co., Ltd.) with head-to-head regioregularity of 98.5% and Mw=87k was spin-coated on Si substrates treated with various organosilanes. P3HT thin films with a thickness of ca.100nm were prepared onto the substrate by spin-coating from their chloroform solution. The sample was annealed at 473K for 30min.

2.2 Symmetrical Reflection Method

X-ray diffraction measurements were carried out by using a Rigaku RINT2500 with CuK_α X-ray source in the symmetrical reflection geometry.

2.3 GIXD

The GIXD measurements were carried out at a BL13XU beam line of SPring-8 using incident X-rays with the wavelength, λ of 0.123 or 0.128 nm. In GIXD measurements, strong diffraction was observed for ultrathin films when the incident angle (α_i) to the sample was below a critical angle (α_c).[5] In this condition, X-rays undergo the total external reflection and penetrate into the sample as evanescent waves. The α_c of organosilane was ca. 0.15°. Therefore, in order to analyze the near-surface structure of organic ultrathin films, GIXD measurements were carried out at α_i=0.10°. Diffraction from the sample was detected in the in-plane direction by a scintillation counter. Moreover, a sample cell with polyimide windows was attached to a sample stage. Helium gas was passed through the cell during the GIXD measurement to prevent the sample from its oxidation. The background-corrected GIXD profiles were analyzed by using a curve-fitting method with the Lorentzian function. All measurements were carried out at room temperature.

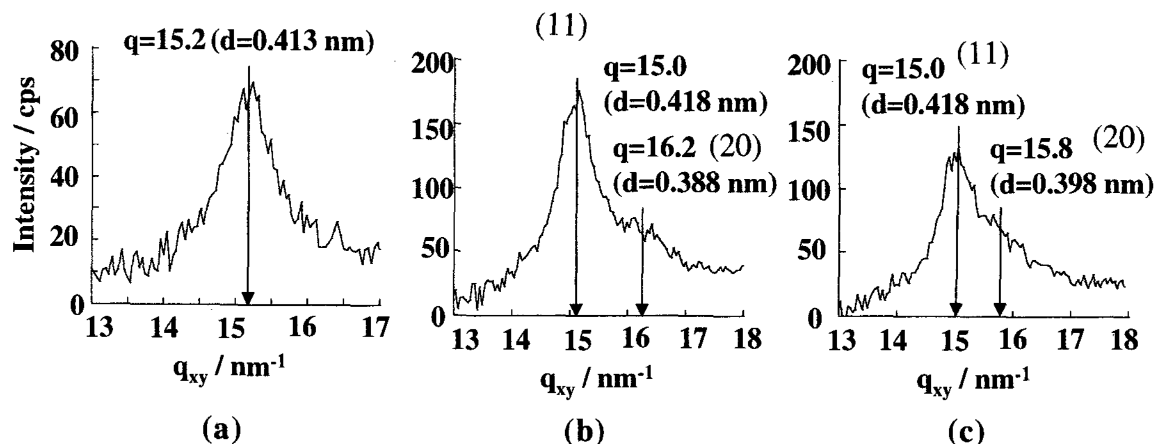


Figure 3 GIXD data for the (a)OTS-C18, (b)EITS-C20 and (c)DOTS-C22 monolayers prepared onto the silicon wafer substrate by water-cast method.

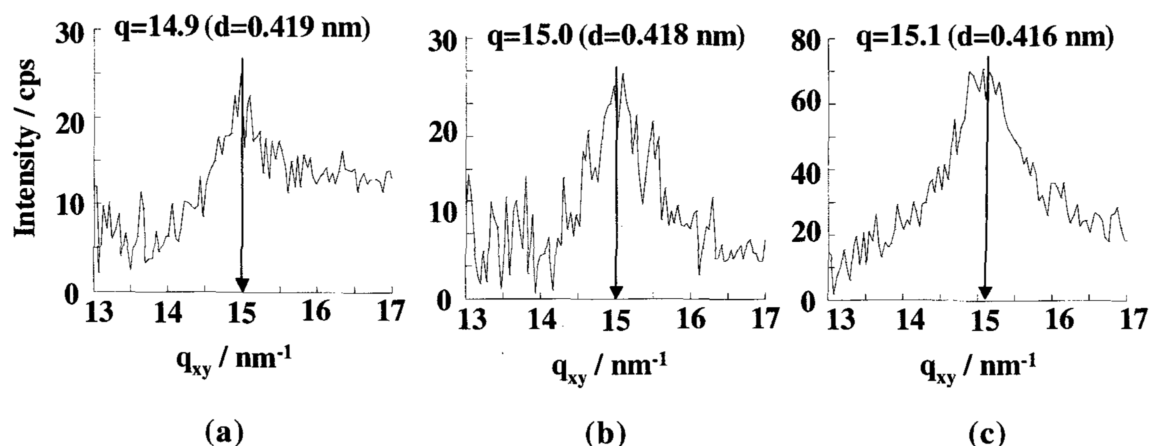


Figure 4 GIXD data for the (a)OTS-C18, (b)EITS-C20 and (c)DOTS-C22 monolayers prepared onto the silicon wafer substrate by chemisorption method.

3.RESULTS AND DISCUSSION

3.1 Oraganosilane Monolayers

Figure 3 shows GIXD profiles for the OTS-C18(a), EITS-C20(b), and DOTS-C22(c) monolayers prepared onto Si-wafer substrates by the water-cast method. In our previous report, ED and GIXD measurements revealed that the (10) spacing of the hexagonal lattice of the OTS-C18 monolayer was ca. 0.42 nm.[5,9,10] Taking into account the result obtained by the ED measurements, it can be considered that the peaks observed in Figure 3(a) is assigned to the (10) reflection of the hexagonal crystal of the OTS-C18 monolayer. The peak of the hexagonal (10) reflection was observed at $q_{xy,max}$ = 15.1 ~ 15.3 nm^{-1}.

On the other hand, in Figure 3(b) and 3(c), a main peak and a shoulder were observed at $q_{xy,max}$ = 15.8 ~ 16.3 nm^{-1} and 15.0 nm^{-1}, respectively. Calculated (20) and (11) spacing of EITS-C20 and DOTS-C22 monolayer were ~0.42 nm and ~0.40nm. In our previous report, the authors revealed that the (20) and (11) spacings of the rectangular lattice of the OTS-C18 monolayer at 223 K were ca. 0.42 and 0.40 nm by the ED measurements, respectively.[10] Therefore, it is most likely that the peaks observed in Figure 3(b) and 3(c) can be assigned to the (20) and (11) reflection of the rectangular crystal of the EITS-C20 and DOTS-C22 monolayers. Thus, these results apparently indicate that the EITS-C20 and DOTS-C22 molecules in the monolayer state are more tightly packed one another at room temperature in comparison with the OTS-C18 molecules in that state.

Figure 4 shows GIXD data for the OTS-C18(a), EITS-C20(b), and DOTS-C22(c) monolayers prepared onto Si-wafer substrates by the chemisorption method. In Figure 4, peaks assigned to the (10) reflection of the hexagonal crystal were observed at $q_{xy,max}$ = 14.9 ~ 15.0 nm^{-1}. The $q_{xy,max}$ slightly shifted to the larger q range with increasing the length of alkyl chain. In our previous study, lateral force microscopy, Fourier transform-infrared spectroscopy, and ED revealed that the packing density of alkylsilane molecules in the monolayers depends on their chain length.[10] Thus, it seems reasonable to consider that decrease of the hexagonal (10) spacing of alkylsilane monolayer is due to the increase of *van der Waals* interaction among their long alkyl chains. However, no crystalline diffraction peaks was observed for the OTMS monolayer prepared by the chemical vapor adsorption method. Since deposition was made above the melting temperature of OTMS, the alkyl chain was immobilized on the Si-substrate in the disordered state.

3.2 P3HT thin films

Poly(alkylthiophene) is one of candidates of polymer

FET devices. The molecular alignment of the conducting polymer thin film might influence the charge carrier transport properties.[11] In order to investigate effects of surface free energy of substrates on chain-packing structure of polymer thin films, P3HT was spin-coated on Si substrates treated with various organosilanes. Figure 5 shows XRD ($2\theta/\theta$ symmetrical reflection method) (a) and in-plane GIXD profiles (b) of P3HT spin-coated films prepared on surface-treated Si-wafers. Each film was annealed at 473 K for 30 min. Rf, PFPE, and Rh indicate the Si-wafers whose surface was treated with FHETMS monolayer, PFPE film, and OTMS monolayer, respectively. SiOH indicates the native oxide Si-wafer. Annealing effect was observed as a sharpening of the diffraction peaks, an appearance of higher-order peaks and decrease in intensity of the amorphous scattering. In the case of symmetrical reflection method the strong (100) reflection (d = 1.60 nm) corresponding to the side-chain lamellar stacking distance is observed. Even though the surface free energy of the substrate changed from ca.12 to 73 mN m^{-1}, a difference was hardly observed among their XRD profiles. On the other hand, in-plane GIXD profiles exhibited the (010) reflection (d = 0.38 nm) corresponding to the π-π stacking of the thiophene ring as well as the (100) reflection. These GIXD profiles also implied that chain-packing structure of P3HT might be independent of the magnitude of surface free energy of the substrates. On the other hand, the comparison between symmetrical reflection and GIXD revealed that the orientation of side-chain lamellar is distorted at the near surface region.

4. CONCLUSION

GIXD was applied for the structural analysis of organosilane monaolayers and polyalkylthiophene thin films. It was revealed that the molecular-packing structure of alkyltrichlorosilane monolayers was strongly depended on the preparation method and alkyl chain length. GIXD was also applied for the surface structural analysis of P3HT thin films. It was revealed that there was no appreciable influence of substrate on the side chain orientation in the near-surface region.

Acknowledgement

The synchrotron radiation experiments were performed at SPring-8 with the approval of JASRI as Nanotechnology Support Project of The Ministry of Education, Culture, Sports, Science and Technology, 2002B5115-NS2-np and 2003A0606-ND1-np.

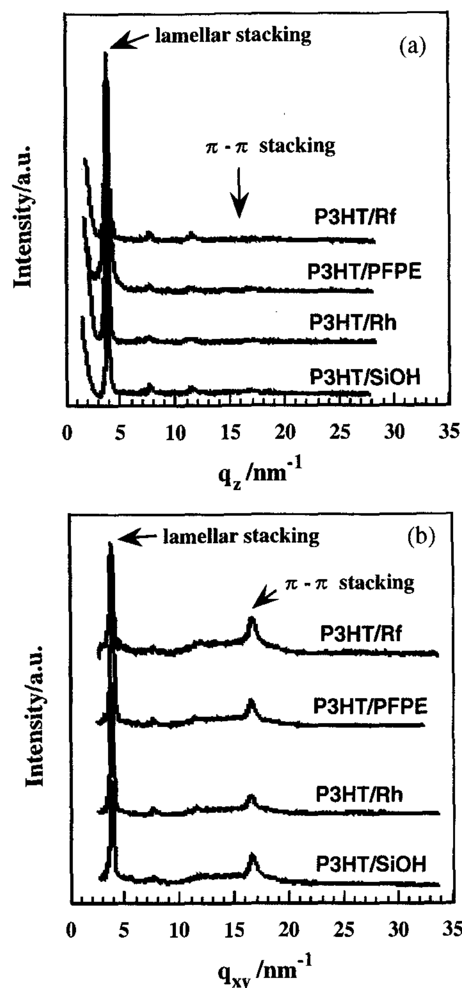


Figure 5 (a) XRD(symmetrical reflection method) and (b) GIXD profiles of P3HT spin-coated films on Si-wafer with different surface treatment.

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(Received July 21, 2003; Accepted August 21, 2003)