Epitaxial Growth of Conductive Charge-transfer Complex in the Organized Molecular Film on Fluorinated Copolymer as Template

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Epitaxial growth of organized molecular films of alkylammonium-Au bis(1, 3-dithiole-2-thione-4, 5-dithiolate) ((dmit)₂) charge-transfer complex on fluorinated copolymer as template estimated by in-plane X-ray diffraction (XRD). In the single crystal, didodecylammonium-Au(dmit)₂ molecules packed triclinic lattice. From the in-plane XRD measurement of multilayers on hydrogenated solids, alkyl-chains of this complex also formed triclinic system. The orthorhombic packing of this complex film formed on fluorinated crystalline polymer as substrate. This structural transition is induced by crystal structure of fluorinated copolymer as template. On the other hand, disordered molecular arrangement in these two-dimensional films formed on the amorphous fluorinated copolymer.

Key words: alkylammonium-metal(dmit)₂; epitaxial growth; organized molecular film; molecular arrangement; intermolecular interaction

1. INTRODUCTION

The air−water interface is often used to direct assembly processes, and a careful understanding of these processes is now possible largely as a result of surface-sensitive characterization methods.1 Traditional Langmuir monolayers can form two-dimensional molecular crystals1,2 or can selectively bind molecules or ions from the subphase to produce multicomponent assemblies.1,3 They are also used to induce the heterogeneous nucleation of three-dimensional crystals, where chemical or stereochemical features of the monolayer can direct the morphology, orientation, or chemical identity of the product crystals.4 Langmuir−Blodgett (LB) films can be obtained by transferring the Langmuir monolayers onto the solid substrate. This method is called the LB method, in which the number of layers and their sequence can be controlled at the molecular level.1,3 On the basis of these features, molecular conductor with stacked structure of functional groups, two-dimensional assemblies of alkylammonium-metal(dmit)₂, have also been fabricated as a part of LB films. Pullen, et al reviewed widely coordination chemistry of dmit.6 Cassoux also reviewed recent works work superconductive properties of metal(dmit)₂ and their derivatives.7 The LB films of dialkylammonium-Au(dmit)₂ salts exhibited a high lateral conductivity of 40 - 100 S/cm at room temperature after electrochemical oxidation or I₂ doping, and had metallic temperature dependence of the conductivity.8,9 Furthermore, the ac magnetic susceptibility and resistance suggested the existence of a superconducting phase below 4 K.10 Bryce and Petty reported electrical conductivity of LB films for charge-transfer complexes containing metal(dmit)₂.11 In addition, Miura, et al reported the three-dimensional crystal structure of (C₁₈H₃₇)₂N(CH₃)₂-Au(dmit)₂ molecule as end-on arrangement of (dmit)₂ unit.12 Structural formation of organized molecules is based on the intermolecular interaction on each molecule, and almost all molecular functionalities bring about their resultant structural formation. Epitaxial growth of two-dimensional film molecules from crystalline template is effective method of structural control at sub-nanometer scales.12,13 On the other hand, TTF (Tetrathiafulvalene)-TCNQ(Tetracyanoquinodimethane) and metal(dmit)₂ complexes indicated to the metallic conductivity are well-known to exhibit the various conductive properties such as semiconductor, metal, and superconductor.14,15 In a previous study, we have investigated molecular arrangement of organized molecular films of several alkylammonium-metal(dmit)₂ complexes and relationships between their arrangements and conductive properties.15,16 From the results of this research, molecular arrangement in the two-dimensional films is formed by competition of van der Waals interaction between alkyl chains and π–π interaction between metal(dmit)₂ units.16 Further, it is found that increase of stacking areas between metal(dmit)₂ groups enhance conductive properties.16,17 Namely, control of two-dimensional arrangement of functional groups is extremely important to bring about a superior conductivities. In the present work, transition of molecular arrangement in the two-dimensional films is carried out by using the
2. EXPERIMENTAL

2.1 Materials

The synthesis of alkylammonium-Au(dmit)$_2$, whose procedure is the same as that mentioned in the previous studies, is carried out. The monolayers of the alkylammonium-Au(dmit)$_2$ were spread from the acetonitrile/benzene (50/50, v/v) mixed solutions (approximately $10^{-4}$ M) onto distilled water (approximately 18 M$\Omega$ cm). The surface pressure-area ($\pi$–A) isotherms for the monolayers were measured by a FFACE film balance (Kyowa Kaimen Co.) at 17 °C. This alkylammonium-Au(dmit)$_2$ formed extremely condensed monolayers on the water surface. These monolayers were transferred onto glass substrates at 17 °C by the horizontal lifting methods from their monolayer on the water surface. These monolayers were characterized with a Rint2200V instrument for different geometrical arrangements (Bruker AXS, MXP-BX, Cu$\alpha$ radiation, 40 kV, 40 mA, an instrument specially made to order) equipped with a parabolic graded multilayer mirror. The a few layer level resolution of this in-plane XRD apparatus was realized by applying the X-rays at an incident angle of 0.2° and by slow scanning at 0.05°/50 s. The structural characteristics of the copolymers in bulk and the estimation of the two-dimensional lattice of the films was determined by analysis using an X-ray diffractometer for different geometrical arrangements (in-plane spacings; $d_1$=4.8 Å, $d_2$=4.5 Å, $d_3$=3.9 Å, stacking distance of Au(dmit)$_2$; 7.9 Å, two-dimensional layer spacing of Au(dmit)$_2$; 14.0 Å). In this case, this organized molecular film is formed on the monolayer of ferric stearate (III) as hydrophilic treatment of glass substrate. The ferric stearate packed hexagonally with 4.2 Å in-plane lattice spacing in their monolayer on glass. On the other hand, same complex film was produced on the water surface also pack the triclinic system (in-plane spacings; $d_1$=4.8 Å, $d_2$=4.5 Å, $d_3$=3.9 Å, stacking distance of Au(dmit)$_2$; 7.9 Å, two-dimensional layer spacing of Au(dmit)$_2$; 14.0 Å). In this case, this organized molecular film is formed on the monolayer of ferric stearate (III) as hydrophilic treatment of glass substrate. The ferric stearate packed hexagonally with 4.2 Å in-plane lattice spacing in their monolayer on glass.

2.2 Characterization

The structural characteristics of the copolymers in bulk and the estimation of the layer structures in organized molecular films were characterized with a Rint2200V diffractometer (RIGAKU Co.; in the case of the organized molecular films, this measurement method was used as the out-of plane X-ray diffraction method). Ni-filtered Cu$\alpha$ radiation (wavelength $\lambda$ = 0.154 nm) was generated at 40 kV and 30 mA. In the 0-2θ mode, the samples were scanned by a step-scanning method with a step width of 0.05° and intervals of 4 s for the diffraction angle 2θ in the range of 2–35°. The diffracted X-ray beam was monochromatized by a pyrographite monochromator and monitored by a scintillation counter. The in-plane spacing of the two-dimensional lattice of the films was determined by analysis using an X-ray diffractometer for different geometrical arrangements (Bruker AXS, MXP-BX, Cu$\alpha$ radiation, 40 kV, 40 mA, an instrument specially made to order) equipped with a parabolic graded multilayer mirror. The a few layer level resolution of this in-plane XRD apparatus was realized by applying the X-rays at an incident angle of 0.2° and by slow scanning at 0.05°/50 s.

3. RESULTS AND DISCUSSION

Figure 1 shows schematic packing models of didodecylammonium-Au(dmit)$_2$ (2C10-Au(dmit)$_2$), which indicate excellent conductive properties, in the single crystal. This single crystal re-crystallized from acetonitrile/benzene (50/50, v/v) mixed solution. X-ray crystallographic analysis was performed by Rigaku Saturn 724 diffractometer (rotating anode, 50 kV, 300 mA). The 2C10-Au(dmit)$_2$ complex form the triclinic packing ($a$=7.8 Å, $b$=19.7 Å, $c$=25.7 Å, $\alpha$=95°, $\beta$=92°, $\gamma$=91°) with relative low symmetric nature.

On the other hand, 2C10-Au(dmit)$_2$ complexes form the stable Langmuir monolayer on the water surface at room temperature. From the analysis of in-plane XRD profile in Fig. 2 (a), long-alkyl chain of 2C10-Au(dmit)$_2$ molecules in the two-dimensional films transferred by horizontal lifting method from their monolayer on the water surface also pack the triclinic system (in-plane spacings; $d_1$=4.8 Å, $d_2$=4.5 Å, $d_3$=3.9 Å, stacking distance of Au(dmit)$_2$; 7.9 Å, two-dimensional layer spacing of Au(dmit)$_2$; 14.0 Å). In this case, this organized molecular film is formed on the monolayer of ferric stearate (III) as hydrophilic treatment of glass substrate. The ferric stearate packed hexagonally with 4.2 Å in-plane lattice spacing in their monolayer on glass. On the other hand, same complex film on poly(tetrafluoroethylene-co-perfluoroethyl vinyl ether) (PFA) as a substrate clearly change in their profile (fig. 2(b)). In this case, peaks at relative lower angle side are developed, which mean the formation of two-dimensional lattice with larger lattice constant. Surprisingly, there are no peaks in the profile of two-dimensional films of 2C10-Au(dmit)$_2$ on amorphous fluorinated copolymer as substrate (Fig. 2(c)). This is drastic change. From these results, it seems that molecular arrangement of film molecules is greatly influenced by structure of substrate.

Figure 3 shows analysis of in-plane XRD profile in Fig. 2(b) and schematic models for molecular arrangement of 2C10-Au(dmit)$_2$ on crystalline perfluorinated substrate. Recently, authors modified previous reported lattice constant and crystal system of perfluorinated copolymers such as PTFE, PFA, and FEP.
These perfluorinated crystalline copolymers packed orthorhombically with the lattice constant; \(a=9.58\ \text{Å},\ \beta=5.54\ \text{Å},\ c=16.9\ \text{Å}\). The actual lattice constant is similar to our proposed one of this profile can exist on the orthorhombic lattice reciprocal lattice to the Fig. 2(b), reflections of part. From the results of analysis by the (Fig. 3 (a), about the epitaxial growth of 2C10-Au(dmit)\(_2\) molecular arrangement in the film plane bring lattice. It seems that these transition of adaptation of the analytical result by reciprocal tilted angle of 52° (Fig. 3(c)) in the case of align along the \(a\)-axis of substrate molecules with tilted angle of 52° (Fig. 3(c)) in the case of adaptation of the analytical result by reciprocal lattice. It seems that these transition of molecular arrangement in the film plane bring about the epitaxial growth of 2C10-Au(dmit)\(_2\) molecules induced by crystal structure of Teflon copolymer. Generally, fluorinated compounds indicate weak interaction to the hydrogenated molecules. In many case, these materials occur the phase separation in mixed system. Hence, it is appropriate that this structural transition is only caused by epitaxy from the crystal structure of substrate. Essentially, in the case of three-dimensional crystal and two-dimensional molecular films on hydrogenated substrate, 2C10-Au(dmit)\(_2\) molecules form the packing system with relative low symmetric nature. It is suggested that the epitaxial growth method from the crystalline substrate with high regularity is a useful technique to attain the control of arrangement and resultant enhancement of functionality such as molecular conductivity. On the other hand, achievement of disordering structure of molecules is induced by film formation on amorphous substrate in this case. It is important to consider selection of substrate in the case of functional molecular films.

As mentioned above, it is possible to control the molecular arrangement in organized molecular films of alkylammonium-metal(dmit)\(_2\) complexes as molecular conductor by the epitaxial growth from the substrate as a template.

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REFERENCES