VIII-E Field-Effect Transistors with Organic Semiconductors

Considerable attention has recently focused on organic field-effect transistors (OFET) because of their potential use in low-cost flexible electronic devices. In order to improve output characteristics, carrier transport in organic semiconductors is the most important subject to be elucidated.

VIII-E-1 Carrier Transport in Field-Effect Transistors Based on Single-Crystalline Wires of Bis-(1, 2, 5-thiadiazolo)-*p*-Quinobis(1, 3-dithiole) (BTQBT)

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We prepared single-crystalline wires of bis(1, 2, 5-thiadiazolo)-*p*-quinobis(1, 3-dithiole), whose ends were anchored to the drain and source electrodes of bottom-contact-type field-effect transistors. Figures 1 shows the SEM image of BTQBT wires grown on the substrates at 360 K. Molecular crystalline wires bridge the gaps between electrodes. It is noted that wires are anchored selectively to the electrodes and no aggregates exist on SiO_2 surface under appropriate growth conditions. Figure 2 shows the temperature dependence of the field-effect mobilities of the devices composed of nanowires and small grains in the temperature range from 5 K to 300 K. The tunnel transport and thermally activated hopping were found to be dominant at $T < 30$ K and 30 K $< T <$ 150 K, respectively, in both devices. While hopping behavior was still dominant in the device of small grains at $T >$ 150K, the mobility of wires varied as $T^{-1.3}$, indicating that phonon scattering governed carrier transport in single-crystalline wires.

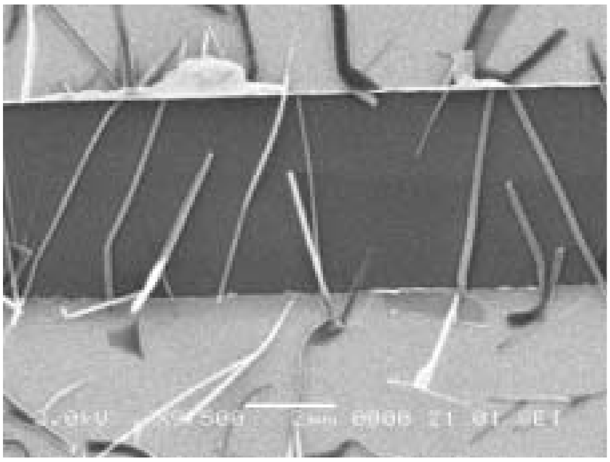

Figure 1. SEM image of BTQBT wires on FET electrodes with spacing of 5 μm.

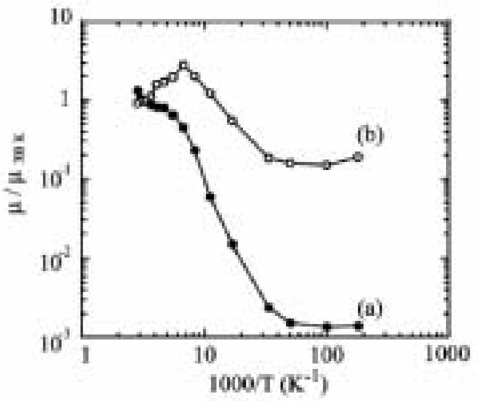

Figure 2. Temperature dependence of field-effect mobilities of small grains (a) and wires (b).

VIII-E-2 Field-Effect Transistors of F_{16}CuPc with Bottom- and Top-Contact Electrodes

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Output characteristics of organic field-effect transistors depend strongly upon device structures. We have prepared bottom- and top-contact FET devices based on hexadecafluoro-copperphthalocyanine (F_{16}CuPc) films and studied electrical properties. It was found that electron mobilities of the top contact FETs were higher than those of the bottom contact FETs probably due to the difference in electric field distribution. Electron mobility of top contact FETs increased with increasing grain size of $CuPcF_{16}$ films, but large grains cause lower mobility owing to poor contact at the interface between the electrodes and the organic film in the bottom contact FETs. The FET with thick $CuPcF_{16}$ films resulted in the higher mobility in the bottom contact FETs because of less influence of air. In top contact FET, however, the thicker film gave rise to the less drain current because of the increase of resistance between source electrode and accumulation layer.

VIII-F Molecular Assemblies on Silicon Surfaces *via* Silicon-Carbon Covalent Bonds

Preparation of molecular assemblies on inorganic semiconductors such as silicon and germanium has received a growing interest because of their potential application to stable regist for nano-patterning. We have prepared organic monolayers on silicon by wet process and studied film structures with IR and AFM.

VIII-F-1 Molecular Conformation of *n*-Alkyl Monolayers Covalently Bonded to Si(111) Probed by Infrared-Visible Sum-Frequency Spectroscopy

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Infrared-visible sum-frequency spectra of *n*-alkyl (C_nH_{2n+1}; n = 10–13, 18) monolayers anchored on the Si(111) surface through a Si–C covalent bond were measured for the C–H stretch region. Spectral shapes exhibited azimuthorientation dependence compatible with the C_{3v} symmetry of the substrate as shown in Figure 1, indicating that the monolayers were epitaxially constructed on the substrate. Three methyl bands dominated each spectrum, and two-weak methylene bands were identified. Two distinct intensity patterns of the methyl bands were observed depending on n as shown in Figure 2. The observed spectra were interpreted with reference to reported molecular models of the monolayer that consist of alkyl chains with an all-trans head part and a twisted stem.

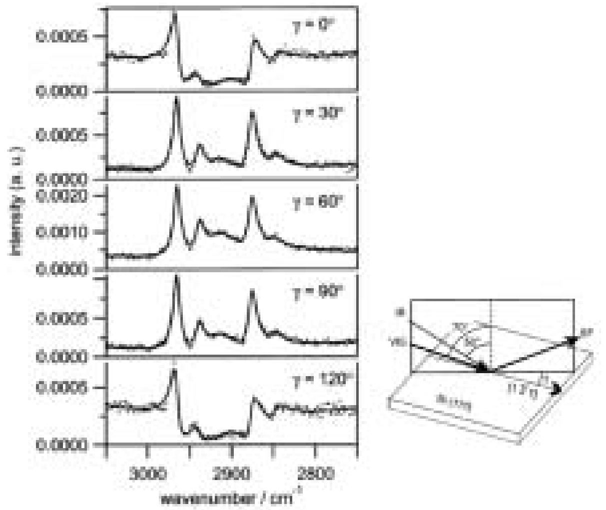

Figure 1. Azimuth dependence of SF spectra of tridecyl ($C_{13}H_{27}$) monolayer on Si(111). The spectra were measured at room temperature.

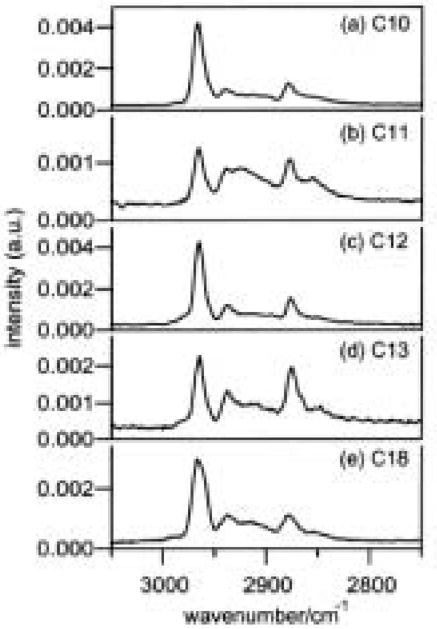

Figure 2. SF spectra of *n*-alkyl (C_nH_{2n+1}; n = 10–13, 18) monolayers on Si(111) measured at the azimuth $\gamma = 60°$.

VIII-F-2 Study on Phase Transition of Alkyl-Monolayers Anchored Covalently to Silicon by Temperature Dependent ATR-FT-IR

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The phase behavior of alkyl-monolayers formed on Si(111) surface was investigated by an attenuated total reflection Fourier transform infra-red spectroscopy from room temperature to 590 K (Figure 1). A continuous disordering process of the monolayer was indicated from the gradual peak shifts toward higher frequency in C–H stretching modes with small decrease in the peak intensities as temperature was increased to 440 K. The rapid decrease in peak intensity was observed above 440 K. The observed changes in the spectrum were reversible by 440 K while the peak intensity was decreased and peak position became higher when the substrate was cooled to room temperature after heated above 440 K, indicating the destruction of the monolayer above 440 K. The temperature limit for the reversible phase transition was much higher than that for alkanethiol monolayer on Au(111) surface (*ca.* 350K), showing that the monolayer formed by Si–C covalent bond was more stable than that of alkanethiols on Au(111) surface due to the stronger anchoring of the molecules to the substrate.

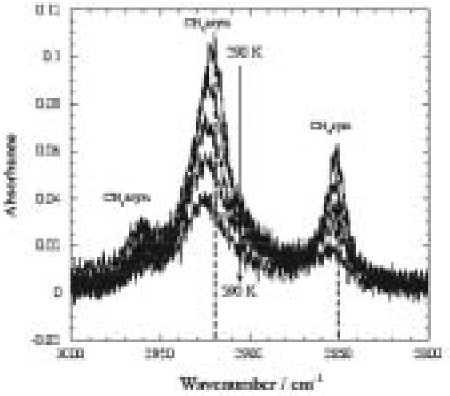

Figure 1. Temperature dependent ATR-FT-IR spectra in the C–H stretching region of octadecene-monolayer on Si(111) surface.

VIII-F-3 Friction Force Microscopy Using Silicon Cantilevers Covered with Organic Monolayers *via* Silicon-Carbon Covalent Bonds

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Cantilevers covered with hydrocarbon (CH) and fluorocarbon (CF) monolayers *via* Si–C covalent bonds were prepared and used for adhesion force measurements and friction force microscopy of the surface patterned also with CH and CF areas. The adhesion and friction forces on CF areas were larger than those on CH areas, especially using CF cantilevers as shown in Figure 1. Large polarizabilities of CF molecules compared to CH molecules are found to enhance the contrast in adhesion and friction images. The cantilevers covered with organic monolayers *via* covalent bonds are useful for chemical force microscopy with contact and noncontact mode atomic force microscopy in various atmospheres since the interface between molecules and cantilevers is thermally and chemically stable.

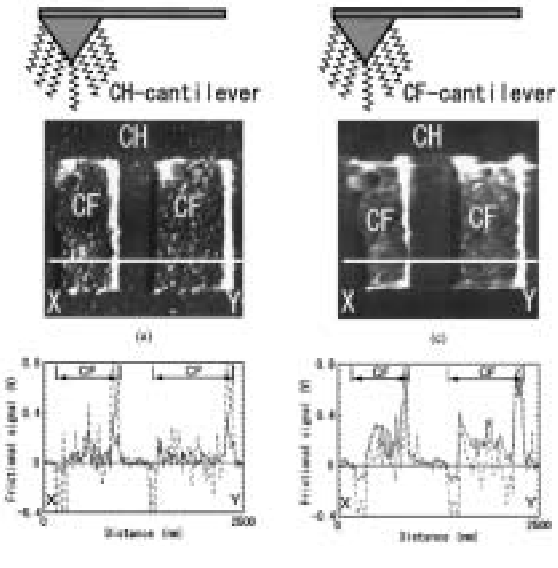

Figure 1. FFM images (a) and (c) (2.5 mm × 2.5 mm) and the friction profiles (b) and (d) of the patterned surface on Si(111) with a CH (a, b) and a CF cantilever (c, d). Spring constants of both cantilevers were 0.6 N/m. Typical loads applied were 30 nN. Solid curves and dashed curves were the profiles measured in air and *in vacuo*, respectively.