IX-C 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. We have studied output characteristics of OFET devices based on newly synthesized organic compounds with novel device structures.

IX-C-1 Preparation of Organic Light-Emitting Field-Effect Transistors with Asymmetric Electrodes

SAKANOUE, Tomo[1]; FUJIWARA, Eiichi; YAMADA, Ryo; TADA, Hirokazu
(*[1]SOKENDAI)*

[*Chem. Lett.* **34**, 494–495 (2005)]

Light-emitting field-effect transistors (LEFET) based on poly [2-methoxy-5-(2-ethylhexoxy)-1,4-phenylenevinylene](MEH-PPV) were prepared with asymmetric electrodes of a Au/Cr source and an Al drain on a SiO_2 gate insulator (600 nm) through twice of photolithography and lift-off techniques (see Figure 1). The light emission was observed when the gate voltages increased above –40 V at the drain voltage of –100 V. The luminous efficiency of the devices was significantly improved comparing to those with conventional electrodes of Au/Cr.

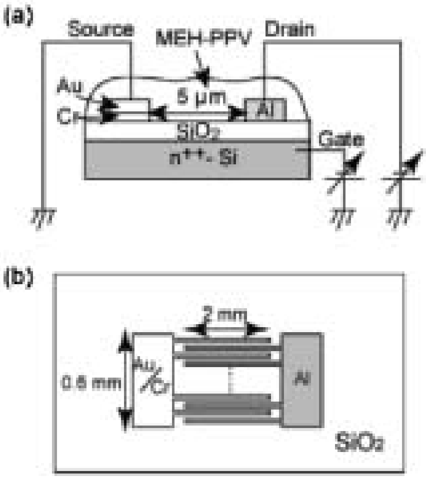


Figure 1. Schematic views of the LEFET with asymmetric Au/Cr–Al electordes. (a) Side view of the device. (b) Top view of the FET substrate.

IX-C-2 Field-Effect Transistors Based on Single-Crystalline Wires of Bis-(1, 2, 5-Thiadiazolo)-*p*-Quinobis(1, 3-Dithiole)

FUJIWARA, Eiichi; TAKADA, Masaki[1]; YAMASHITA, Yoshiro[2]; TADA, Hirokazu
(*[1]SOKENDAI; [2]Tokyo Inst. Tech.)*

[*Jpn. J. Appl. Phys.* **44**, L82–L84 (2005)]

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. Figure 1 shows the temperature dependence of carrier mobility in the range from 5 K to 330 K. The tunnel transport was found to be dominant at $T < 30$ K. Thermally activated hopping behavior was observed in the temperature range from 30 K to 200 K. The mobility decreased with increasing temperature at $T > 200$ K, indicating that phonon scattering governs carrier transport in single-crystalline wires.

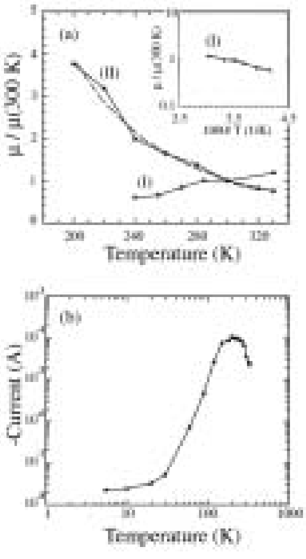


Figure 1. (a) Temperature dependences of the field-effect mobilities of densely packed grains (I) and crystalline wires (II). Each curve is normalized by the mobility at 300 K. Dashed line shows the T^{-x} fitting curve for $x = 3$. Inset shows Arrenius's plot of curve (I). (b)Temperature dependence of the drain current of BTQBT wires. The drain and gatevoltages were –50 V and –30 V, respectively.

IX-D Molecular Assemblies on Silicon Surfaces *via* Silicon–Carbon Covalent Bonds

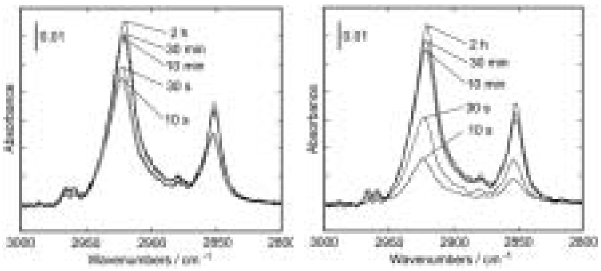
Preparation of molecular assemblies on inorganic semiconductors such as silicon and germanium has received a growing interest because of their potential application to stable regist for nano-patterning. We have prepared organic monolayers on silicon by wet process and studied film structures with IR.

IX-D-1 Characterization of Molecular Assemblies on Silicon Surfaces by Attenuated Total Reflectance Infrared Spectroscopy

ARA, Masato[1]; YAMADA, Ryo; TADA, Hirokazu
([1]SOKENDAI)

[*Thin Solid Films* in press]

Alkyl monolayers anchored to Si(111) were prepared in diluted and neat 1-alkene by thermal reaction. Monolayers prepared were investigated by attenuated total reflectance infrared spectroscopy. It was found that alkyl chains in the monolayers anchored to Si(111) had an all-trans conformation. The rate of reaction between 1-alkene and hydrogen-terminated silicon remarkably depended on the concentration of 1-alkene as shown in Figure 1. However, monolayers prepared in diluted 1-alkene were identical with that prepared in neat 1-alkene.



(a) (b)

Figure 1. ATR spectra of C12 monolayers prepared in neat 1-dodecene (a) and those prepared in diluted 1-dodecene (b) with a p-polarized configuration, respectively. Reaction was carried out for 10 s, 30 s, 10 min, 30 min, and 2 h.

IX-E Low Temperature Scanning Tunneling Microscopy and Spectroscopy of Organic Molecules on Metal Surfaces

The electronic structure of molecules adsorbed by metal surfaces is of growing interest in the field not only of surface science but also of molecular-scale electronic devices. Scanning tunneling microscopy and spectroscopy are useful to investigate molecular arrangements and electronic structure with atomic resolution. We have prepared epitaxial films of phathalocyanine molecules on clean metal surfaces and studies there structures by scanning tunneling microscopy and spectroscopy at low temperature.

IX-E-1 Scanning Tunneling Microscopy and Spectroscopy of Phthalocyanine Molecules on Metal Surfaces

TAKADA, Masaki[1]; TADA, Hirokazu
([1]SOKENDAI)

[*Jpn. J. Appl. Phys.* **44**, 5332–5335 (2005)]

We studied the electronic structure of cobalt-phthalocyanine (CoPc) molecules on Au(111) and Cu (100) surfaces by scanning tunneling microscopy and spectroscopy at 5 K. In the differential conductance (dI/dV) spectra as shown in Figure 1, there were some peaks related to the highest occupied molecular orbital (HOMO), the lowest unoccupied MO (LUMO) and the d-orbitals of the Co atom. CoPc molecules on the Cu (100) surface had new electronic states between the peaks related to HOMO and LUMO, while those on the Au(111) surface did not show additional peaks. A dI/dV image indicated that the new states were generated by the hybridization between the LUMO of molecules and the electronic states of the Cu(100) surface.

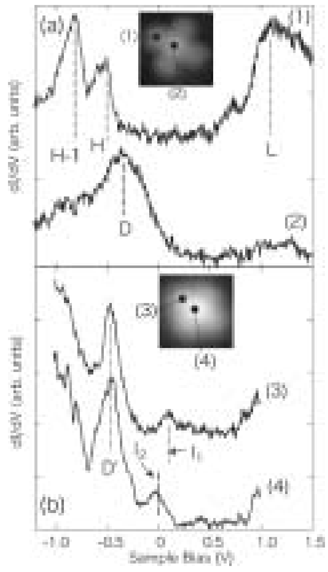


Figure 1. (a) *dI*/*dV* spectra of a single CoPc molecule on Au(111) surface at 5 K. (b) *dI*/*dV* spectra of a single CoPc molecule on Cu(100) surface at 5 K. Spectra (1)–(4) were measured at indicated spots on the inset images.

IX-F Ratchet Motions of a Droplet Caused by Electrochemical Reaction of Monolayers

Control of droplet motions on small spaces is of growing interest since it leads to non-mechanical pumping systems in micro-fluidic devices. By introducing asymmetric characteristics to the surface, the droplet moves because of the imbalance of surface tensions. We found that electrochemical reactions of monolayers were used to dynamically control the surface property and the motion of the droplet.

IX-F-1 Electrochemically Generated Wetting Gradient and Its Application for the Transport of Droplets

YAMADA, Ryo; TADA, Hirokazu

[*Langmuir* **21**, 4254–4256 (2005)]

The reversible transportation of droplets was realized by spatiotemporal control of the wetting gradient. The surface wetting was reversibly regulated by using electrochemical reactions of the ferrocenyl (Fc) alkanethiol monolayer and application of the in-plane bias voltage to the substrate as shown in Figure 1. The back-and-forth motion of the wetting boundary, where the surface changed from wetting to repulsive, sequentially caused a droplet unidirectional spreading and shrinking on the surface. These unidirectional motions resulted in the net transport of the droplet in inchworm-like manner as shown in Figure 2. The droplet moved backward when the direction of the in-plane bias voltage was reversed.

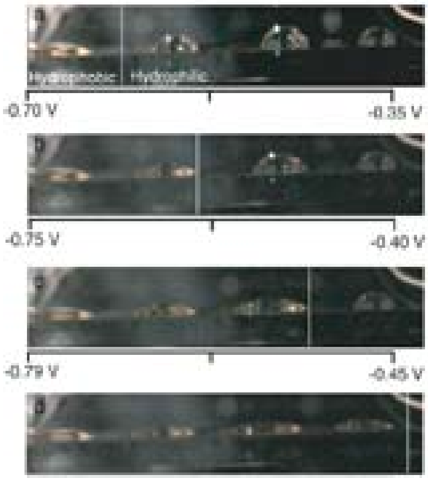


Figure 1. Photographs of nitrobenzene droplets. V_{bias} was fixed at 0.35 V and E_{offset} was shifted (a–d). Line in the photograph represents the position of the wetting boundary estimated from the shape of the droplets. Note that the current peak for Fc^+/Fc reaction was observed at *ca.* –0.5 V in cyclic voltammogram.

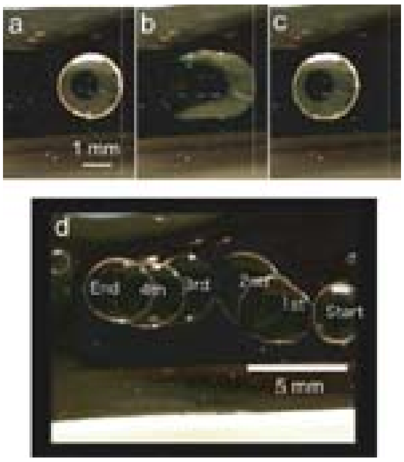


Figure 2. Photographs of inchworm motion of the droplet in the solution. E_{BIAS} = 0.5 V. E_{offset} = –300 mV (a), –340 mV (b) and –300 mV (c). (d) Trace of the multi-step inchworm motions of the droplet. Six photographs were superimposed.

IX-F-2 Transport of a Droplet by Directional Deformations with Asymmetric Electrode

YAMADA, Ryo; TADA, Hirokazu

Ratchet motions of a droplet were realized by the repeated deformations of it on an asymmetric V-shaped electrode. The surface wetting of the electrode was reversibly regulated by electrochemical reactions of the ferrocenyl-alkanehiol monolayer. When the surface was changed from repulsive to wetting, the contact line of the droplet facing to the wider side advanced while the other side was almost pinned. The contact line facing to the narrower side retracted when the surface was changed from wetting to repulsive. The directional deformations of the droplet resulted in a net transport of it.

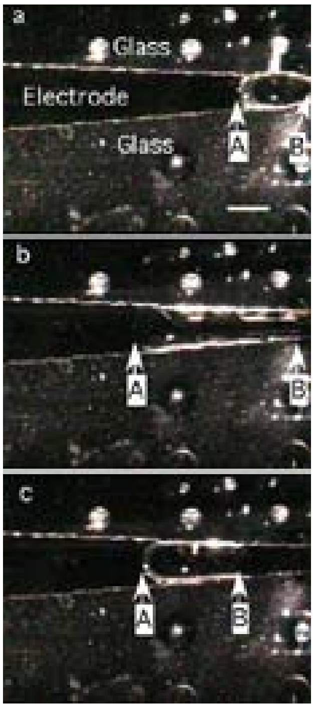


Figure 1. Directional deformations of the nitrobenzene droplet. The length of the scale bar in (a) is 3 mm. When the surface was changed from repulsive to wetting (a–b), the left side of the droplet (A) spread. When the surface was back to repulsive (bc), the right side of the droplet (B) shrank. These directional deformations resulted in a net transport of the droplet.