

VIII-D Field Effect Transistors with Organic Semiconductors

The mechanism of carrier transport in organic semiconductors and carrier injection from metal electrodes becomes the most important subject to be elucidated for the construction of high performance organic thin film devices. We have studied electrical properties of organic films using field effect transistors.

VIII-D-1 Electrical Characteristics of Phthalocyanine Films Prepared by Electrophoretic Deposition

TAKADA, Masaki¹; YOSHIOKA, Hirokazu²;
TADA, Hirokazu; MATSUSHIGE, Kazumi²
(¹GUAS; ²Kyoto Univ.)

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Electrical properties of phthalocyanine (Pc) films prepared by an electrochemical process were investigated using field effect transistors (FETs). Copper-Pc (CuPc) films were deposited electrophoretically on voltage-applied cathodic electrodes from trifluoroacetic acid/dichloromethane mixed solution containing protonated monomeric CuPc molecules. Optical absorption spectra showed that the CuPc films had α -type polymorphs. The grains grew with reaction time to close a gap between the FET electrodes. FET studies showed that CuPc films after annealing exhibited a *p*-type semiconducting behavior. Carrier mobility, conductivity and carrier density of the films were $1.4 \times 10^{-5} \text{ cm}^2/\text{Vs}$, $7.7 \times 10^{-7} \text{ S/cm}$ and $6.6 \times 10^{16} \text{ cm}^{-3}$, respectively. It is revealed that electrophoretic deposition is applicable for the preparation of active layers in organic electronic devices.

VIII-D-2 BTQBT (bis-(1,2,5-thiadiazolo)-*p*-Quinobis(1,3-dithiole)) Thin Films; A Promising Candidate for High Mobility Organic Transistors

TAKADA, Masaki¹; GRAAF, Harald;
YAMASHITA, Yoshiro²; TADA, Hirokazu
(¹GUAS, ²Tokyo Inst. Tech.)

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BTQBT (bis-(1,2,5-thiadiazolo)-*p*-quinobis(1,3-dithiole)) films have been prepared as active semiconducting layers of organic field effect transistors (FETs). BTQBT films showed a *p*-type semiconducting behavior. The hole mobility and on/off ratio of BTQBT films under ultrahigh vacuum conditions reached to $0.2 \text{ cm}^2/\text{Vs}$ and 10^8 , respectively, by optimization of the growth conditions. These values are in the same order as those of pentacene thin films, which indicates that BTQBT molecules have a great potential for active layers of organic electronic devices.

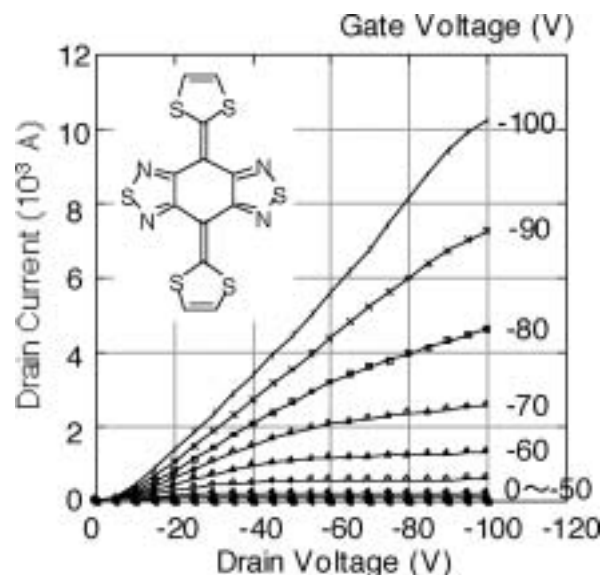


Figure 1. FET characteristics of BTQBT films measured in UHV.

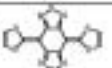
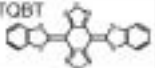
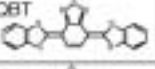
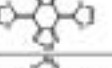


VIII-D-3 Field Effect Transistors of BTQBT and Its Derivatives

TAKADA, Masaki¹; YAMASHITA, Yoshiro²;
TADA, Hirokazu
(¹GUAS; ²Tokyo Inst. Tech.)

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We have prepared and characterized thin film field effect transistors (FETs) of bis-(1, 2, 5- thiadiazolo)-*p*-quinobis(1, 3-dithiole) (BTQBT) and its derivatives. Preparation and characterization of the films were carried out under ultrahigh vacuum condition. Most materials examined showed *p*-type semiconducting behaviors. Among *p*-type molecules, BTQBT films deposited at room temperature showed *p*-type semiconducting behaviors with mobility of $0.1 \text{ cm}^2/\text{Vs}$. The on/off drain current ratio was 10^7 . The mobility and on/off ratio reached to $0.2 \text{ cm}^2/\text{Vs}$ and 10^8 , respectively, by optimizing the film growth conditions. These performances are almost comparable to those of pentacene and polythiophene thin films, indicated that BTQBT molecule is a prominent semiconducting material as a high mobility thin film. It was also found that tetracyanoquinodimethane (TCNQ) derivative showed an *n*-type semiconducting behavior with an electron mobility of $8.9 \times 10^{-4} \text{ cm}^2/\text{Vs}$.

Table 1. Field Effect Mobilities of BTQBT and Its Derivatives.

	type	Mobility(cm ² /Vs)	On/off ratio
BTQBT 	p	1.0×10^{-1} (0.2 at 50°C)	10^7
DB-BTQBT 	p	4.6×10^{-4}	10^4
DB-TQBT 	p	1.6×10^{-5}	50
TQBT 	p	1.2×10^{-3}	3
BSQBT 	p	1.3×10^{-6}	10
BTDA-TCNQ 	n	8.9×10^{-4} Al electrodes	10^2

VIII-D-4 Preparation of Nanometer-Gap Electrodes for Field Effect Transistors by Electroplating

YAMADA, Ryo; TAKADA, Masaki¹; OISHI, Osamu; TADA, Hirokazu
(¹GUAS)

A pair of electrodes with a nanometer-scale spacing

was fabricated by electroplating of gold onto micrometer gap electrodes prepared through conventional photolithography. The electrodes were prepared on SiO₂ formed on a heavily doped Si substrate which serves as a gate electrode. Figure 1 shows a SEM micrograph of the electrode fabricated by this method. It was shown that the drain current changed as a function of a gate voltage when Ti-phthalocyanine thin film was deposited onto this electrode. Thus, the electrode made by this method can be used for the study of organic thin film field effect transistors.

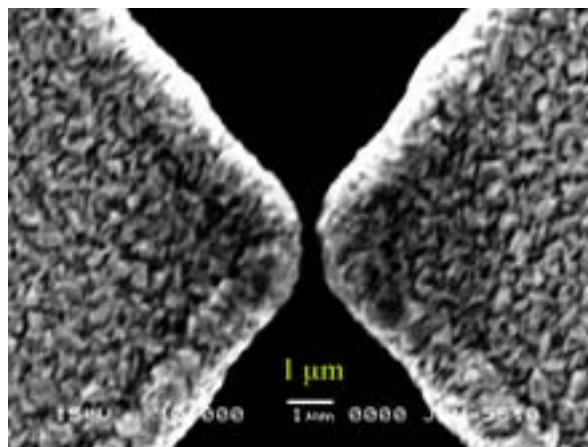


Figure 1. SEM Photograph of Nanometer Gap Electrodes.

VIII-E Preparation and Characterization of Highly Ordered Molecular Films on Silicon Bound with Si-C Covalent Bond

Self-assembled monolayers (SAMs) have received considerable attention because of their potential applications to molecular scale electronic devices. Covalently bond alkane SAMs formed by reaction between alkene and hydrogen terminated silicon are of increasing interest as nano-interface for molecular electronics devices fabricated on silicon microstructures. We have studied the growth manner and electronic structure of Si-C junction using scanning probe microscope such as STM (scanning tunneling microscope), AFM (atomic force microscope) and KFM (Kelvin force microscope).

VIII-E-1 Force Curve Measurement of Self-Assembled Organic Monolayers Bound Covalently on Silicon(111)

GRAAF, Harald; ARA, Masato¹; TADA, Hirokazu
(¹GUAS)

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Self-assembled monolayers of alkyl chains were prepared on silicon(111) surfaces. The surface was characterized by atomic force microscopy (AFM). Atomically flat terraces were observed in topographic images of the films with contact mode AFM, indicating the formation of highly ordered monolayers. Force curve measurements showed that the adhesion force between organic films and gold cantilever was much stronger comparing to the force on hydrogen terminated

surfaces.

VIII-E-2 Atomic Force Microscope Anodization of Si(111) Covered with Alkyl Monolayers

ARA, Masato¹; GRAAF, Harald; TADA, Hirokazu
(¹GUAS)

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Alkyl monolayers on Si were prepared through the reaction between 1-alkenes and hydrogen-terminated Si by heat treatment. The monolayers were characterized by atomic force microscopy (AFM), force curve and water contact angle measurements. It was found that surface properties were modified by the formation of highly ordered closely packed monolayers. The monolayers were anodized with a contact-mode AFM

by applying voltage between the conductive cantilever and surface under ambient conditions, which resulted in nanometer-scale oxidation of surfaces. After anodization, patterned areas were modified by removing the silicon oxide and terminating the surface of the grooves with hydrogen atoms by NH_4F etching, and by covering the etched surface with 1-octadecene molecules. The monolayers themselves showed high resistance to NH_4F etching and air oxidation.

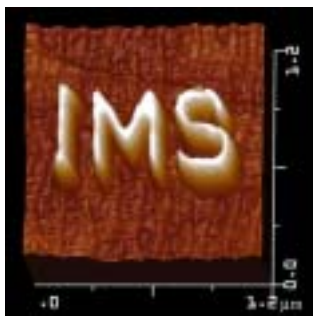


Figure 1. AFM anodization of Silicon Surfaces with AFM.

VIII-E-3 Nanopatterning of Alkyl Monolayers Covalently Bound to Si(111) with an Atomic Force Microscope

ARA, Masato¹; GRAAF, Harald; TADA, Hirokazu
(¹GUAS)

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Alkyl monolayers covalently bound to silicon were prepared through the reaction between 1-alkene molecules and hydrogen-terminated Si. The surfaces were anodized in nanometer scale with a contact-mode atomic force microscope (AFM) by applying positive bias voltage to the surface with respect to a conducting cantilever under ambient conditions. Following the anodization, patterned areas were selectively modified by chemical etching and coating with different molecules. The alkyl monolayers showed high resistance against chemical etching and protected Si surfaces from oxidation. AFM lithography of monolayers on Si was found to be useful for nanofabrication of organic/-inorganic interfaces based on the Si–C covalent bond.

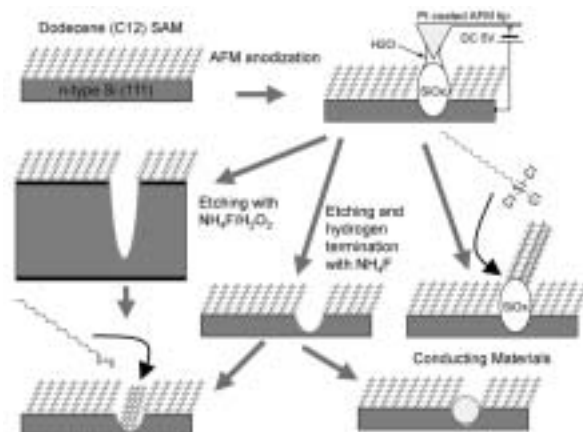


Figure 1. Nanopatterning of Silicon Surfaces with AFM.