



## Special Feature: Sensors

Research Report

### Gas Sensors Based on Organic Field-effect Transistors: Improving the Gas Selectivity by Using a Variety of Organic Materials

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**■ABSTRACT■** Organic field-effect transistors (OFETs) fabricated on chemically modified dielectric layers are proposed as high-selectivity gas sensors. Since conventional SnO<sub>2</sub> sensors have a similar response to different reducing gases, more selective gas sensors are desired. The sensitivity and selectivity of OFET-based gas sensors can be finely tuned by using various organic materials. It was found that an OFET's humidity sensitivity can be changed by introducing chemically modified SiO<sub>2</sub> dielectric layers. There is a good correlation between the sensitivity to humidity and the surface free energy of the dielectric layers. Our data suggest that surfaces with a low surface free energy have a low humidity adsorption probability. Therefore, the corresponding OFETs display low sensitivity to humidity. Furthermore, OFETs fabricated on a surface with a high ratio of dispersive to polar components of the surface free energy have a high selectivity between ethanol and humidity. This finding suggests that a high selectivity can be achieved by introducing a variety of chemically modified dielectric layers in order to change the components of the surface free energy.

**■KEYWORDS■** Organic, Semiconductor, Gas, Sensor, Selectivity

#### 1. Introduction

Organic field-effect transistors (OFETs) have attracted considerable attention for applications beyond flat-panel displays and radio-frequency tags.<sup>(1)</sup> Specifically, the use of OFETs in gas sensors has attracted recent interest.<sup>(2,3)</sup> Tin oxide (SnO<sub>2</sub>) has been widely used in gas sensor applications due to its capability of detecting a variety of toxic and flammable gases such as carbon monoxide, hydrogen, and hydrocarbons. The SnO<sub>2</sub> grains maintain a high resistance under atmospheric conditions due to adsorbed oxygen molecules, and the resistance decreases when a reducing gas molecule reacts with the adsorbed oxygen. Since basic SnO<sub>2</sub> sensors have a similar response to a variety of reducing gases, sensors with a higher selectivity are desired. The selectivity of a sensor can be somewhat modified or even improved by changing its surface characteristics.<sup>(4)</sup> One of the most common ways to modify sensor surface characteristics is to introduce additives. Many studies have shown the effects of different additives on the morphology and properties of tin oxide. Noble metals are usually added to adjust or optimize the SnO<sub>2</sub> sensing properties. Irrespective of these efforts,

selectivity remains an issue with SnO<sub>2</sub> sensors.

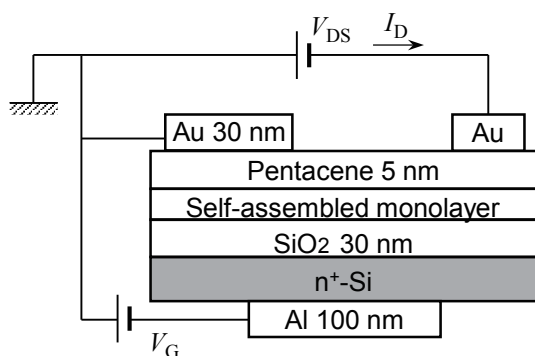
On the other hand, OFET-based chemical gas sensors are also beginning to attract interest, because their chemical and physical properties can be finely tuned using a variety of organic materials. Fingerprint identification of 16 gases by OFETs made of 11 organic semiconductor materials was reported.<sup>(5)</sup> A variety of organic semiconductor materials can influence the gas sensitivity of OFETs.

In this work, instead of modifying the organic semiconductor itself, we modified the surfaces of the dielectric layers to vary the OFET gas sensitivity and selectivity. OFETs were fabricated on chemically modified silicon dioxide (SiO<sub>2</sub>) dielectric layers, which have often been used to improve carrier mobility.<sup>(6)</sup> We measured changes in the carrier mobility or drain current of the fabricated OFETs after exposure to humidity or ethanol. The relationship between the sensitivity to humidity and the surface free energy of the dielectric layers is discussed. Furthermore, we discuss the relationship between the selectivity for ethanol vs. humidity and the ratio of dispersive to polar components of the surface free energy.

## 2. Experimental Methods

The fabricated OFETs had a bottom-gate, top-contact structure, as shown in **Fig. 1**. The substrate was an n-type Si wafer ( $< 0.02 \Omega\text{cm}$ ), which was heavily doped with antimony and covered with a 30-nm-thick layer of thermally grown  $\text{SiO}_2$  as a gate dielectric layer.  $\text{SiO}_2$  was selected as the dielectric because of its high breakdown voltage, low defect concentration, and ease of chemical modification. Before the deposition of the pentacene channel layer, the surface of the  $\text{SiO}_2/\text{Si}$  substrate was chemically modified. First, we treated the  $\text{SiO}_2/\text{Si}$  substrate with an ultraviolet ozone ( $\text{UV}/\text{O}_3$ ) cleaner (Nippon Laser and Electronic Laboratory NL-UV253) for 20 min to create OH groups for the subsequent silylation reaction. The  $\text{SiO}_2/\text{Si}$  substrate was then placed in a Teflon pressure cooker along with a cup of 0.1 ml silylation agent, and the cooker was sealed with a cap. The cooker was placed in an oven at  $100^\circ\text{C}$  for 1 h in order to form a self-assembled monolayer on the dielectric surface. Silylation was performed using octadecyltrimethoxysilane (OTS), hexamethyldisilazane (HMDS), and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane (FTS), as shown in **Fig. 2**. A 5-nm-thick active layer of pentacene was then deposited on the substrate by vacuum evaporation at a rate of  $0.1 \text{ nm/min}$  under a pressure of  $1 \times 10^{-5} \text{ Pa}$ . The OFET fabrication was completed by evaporating a 30-nm-thick gold layer through a shadow mask to form the source and drain contacts, and by forming a 100-nm-thick aluminum layer on the back side of the wafer as a gate contact. The channel length and width were 100 and  $6000 \mu\text{m}$ , respectively.

The fabricated OFETs were characterized using a Keithley 2612 dual-channel System Source Meter



**Fig. 1** Schematic structure of OFETs fabricated in this study.

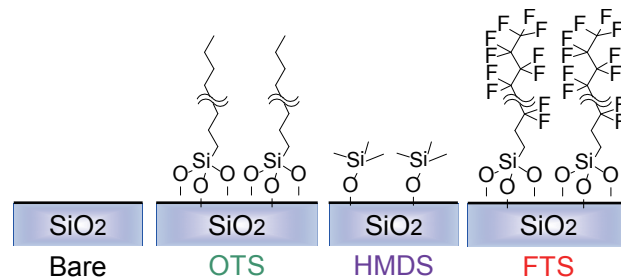
instrument. The drain current or mobility responses of the OFETs were measured. The mobility was evaluated based on the drain current measured at  $V_G = -5 \text{ V}$  and  $-4 \text{ V}$ , and  $V_{DS} = -5 \text{ V}$ . In order to enhance the baseline stability,  $V_G$  was pulse-modulated at a repetition frequency of 1 Hz and a duty ratio of 10%, and the direct current offset voltage was  $0 \text{ V}$ .<sup>(7)</sup> The mobility of the fabricated OFETs was calculated using the following equation for metal-oxide-semiconductor field-effect transistors in the saturation region:

$$I_D = (\mu WC/2L) (V_G - V_T)^2 \quad (1)$$

Here,  $I_D$  is the saturated drain current,  $\mu$  is the mobility,  $V_G$  is the gate voltage, and  $V_T$  is the threshold voltage.  $L$ ,  $W$ , and  $C$  are the channel length, channel width, and capacitance of the gate insulator, respectively. The OFETs were held in a flow-through cell and exposed to controlled concentrations of humidity. The humidity was varied between 2000 and 10000 ppm using two streams of dry air with a combined flux of  $5 \text{ L/min}$ . One stream was passed through tandem water bubblers and then mixed with the other stream, and the resulting mixed stream was then introduced into the cell.

The static contact angles of the chemically modified  $\text{SiO}_2$  dielectric layers were measured using a contact-angle meter (Kyowa Interface Science Drop Master 500) with a  $1 \mu\text{L}$  droplet. The surface free energies and their components were determined from the static contact angles of deionized pure water and n-hexadecane, which were determined using the Kaelble-Uy method.<sup>(8)</sup> In this method, the surface free energies are divided into their polar and dispersive components.

The surface morphologies of pentacene were measured using atomic force microscopy (AFM; Veeco Dimension V). The AFM measurements were



**Fig. 2** Schematic of chemically modified dielectric layers investigated in this study.

performed in tapping mode in air at room temperature.

### 3. Results and Discussion

#### 3.1 Sensitivity

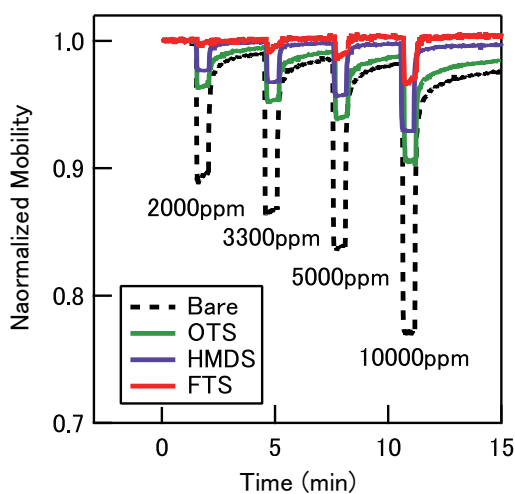
**Figure 3** shows the mobility responses of OFETs fabricated on chemically modified SiO<sub>2</sub> dielectric layers. After the mobility reached a stable value under a stream of dry air, the OFETs were exposed to alternating streams of dry and wet air. As shown in Fig. 3, the presence of humidity decreased the carrier mobility of all OFETs. The changes in mobility under various levels of humidity are shown in **Fig. 4**. Compared to an OFET fabricated on bare SiO<sub>2</sub> without silylation, the carrier mobilities in OFETs fabricated on OTS- and HMDS-modified dielectric layers decreased to a lesser extent in the presence of humidity. The OFET fabricated on an FTS-modified dielectric layer decreased the least. We found that chemically modified dielectric layers change the OFET's sensitivity to humidity.

Chemically modified dielectric layers could influence device sensitivity in many different manners. One possibility is that the chemical modification changes the adsorption probabilities of H<sub>2</sub>O molecules on the dielectric layer's surface. **Figure 5** shows a schematic diagram of the effect of chemically modified dielectric layers. Owing to the polycrystalline morphology

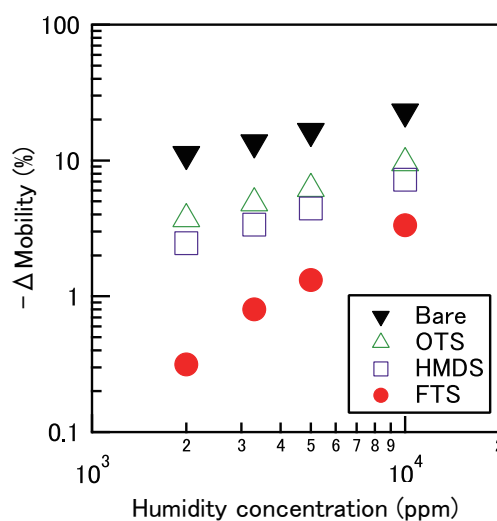
of organic semiconductor layers such as pentacene, polar molecules such as H<sub>2</sub>O are expected to diffuse through the semiconductor layer onto the surface of the dielectric layer.<sup>(9)</sup> The presence of polar molecules is known to decrease the rate of charge transport in organic semiconductor layers, and this decrease is ascribed to an increase in the amount of energetic disorder owing to charge-dipole interactions.<sup>(10,11)</sup> As shown in Fig. 5(b), the low-surface-free-energy dielectric surface has a low adsorption probability for polar molecules. Therefore, the small change observed in the mobility of OFETs fabricated on low-surface-free-energy dielectric layers is probably due to the dielectric surface's low adsorption probability for H<sub>2</sub>O molecules.

To investigate the effect of humidity adsorption probability, the surfaces of the chemically modified SiO<sub>2</sub> dielectric layers were characterized by measuring the contact angles of water and n-hexadecane.

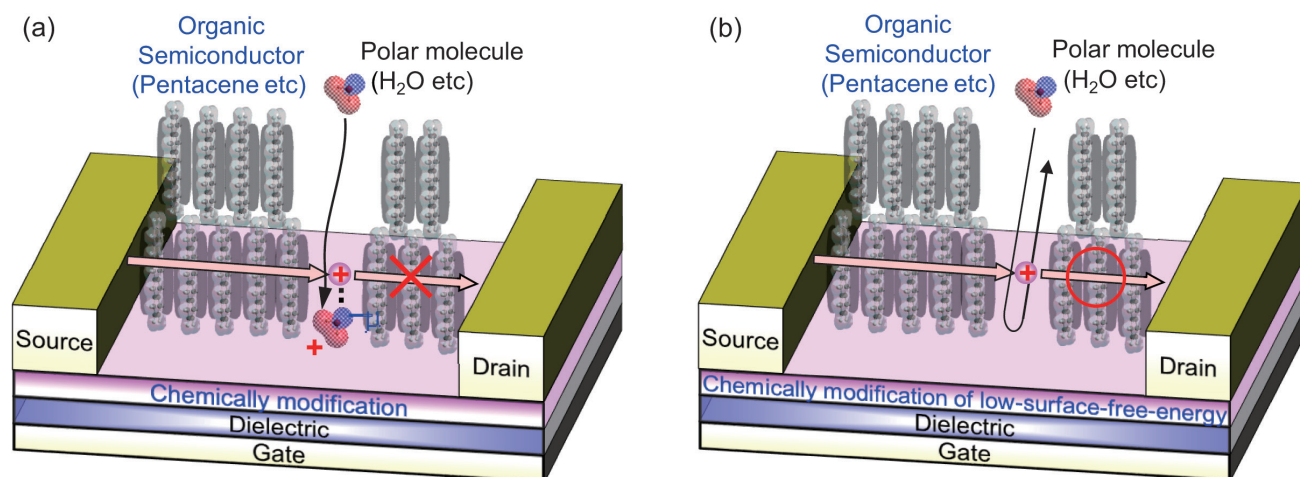
**Table 1** summarizes the static contact angles of water and n-hexadecane on the chemically modified dielectric layers and the surface free energy of the chemically modified SiO<sub>2</sub>. **Figure 6** shows the relationship between the sensitivity to humidity and the surface free energy of the dielectric layers. The sensitivity was defined as the change in carrier mobility at a humidity of 2000 ppm. The sensitivity to humidity is closely related to the surface free energy. Surfaces with low surface free energy, such as the FTS-, OTS-,



**Fig. 3** Mobility responses of OFETs fabricated on bare, OTS-, HMDS-, and FTS-modified SiO<sub>2</sub> dielectric layers. The OFETs were exposed to alternating streams of dry and wet air.



**Fig. 4** Changes in the mobility of OFETs fabricated on chemically modified dielectric layers under various humidity concentrations.



**Fig. 5** Schematic diagram of the effect of chemically modified dielectric layers. (a) Polar molecules are expected to diffuse through the organic semiconductor layer onto the surface of the dielectric layer. The presence of polar molecules decreases the rate of charge transport in organic semiconductor layers. (b) The low-surface-free-energy dielectric surface has a low adsorption probability of polar molecules.

and HMDS-modified surfaces, have a low humidity adsorption probability. As a result, OFETs fabricated on FTS-, OTS-, and HMDS-modified SiO<sub>2</sub> dielectric layers have a low sensitivity to humidity.

Another possibility is that the chemical modification changes the morphology of the pentacene thin film on the dielectric surface. **Figure 7** shows  $5 \times 5 \mu\text{m}^2$  AFM images of 5-nm-thick pentacene films deposited on chemically modified SiO<sub>2</sub> dielectric layers. The chemical modification changed the grain size of the pentacene. Furthermore, the mobility increased with increasing grain size in the pentacene films. However, the sensitivity had no relationship with grain size, even though the presence of a large number of grain

boundaries was expected to enhance the sensitivity to humidity.<sup>(12)</sup> For example, the OFET fabricated on an FTS-modified SiO<sub>2</sub> dielectric layer was only slightly sensitive to humidity, even though the grain sizes of the FTS-modified SiO<sub>2</sub> dielectric layer were markedly smaller than those of the other modified SiO<sub>2</sub> dielectric layers. The pentacene grain size had little effect on the sensitivity to humidity.

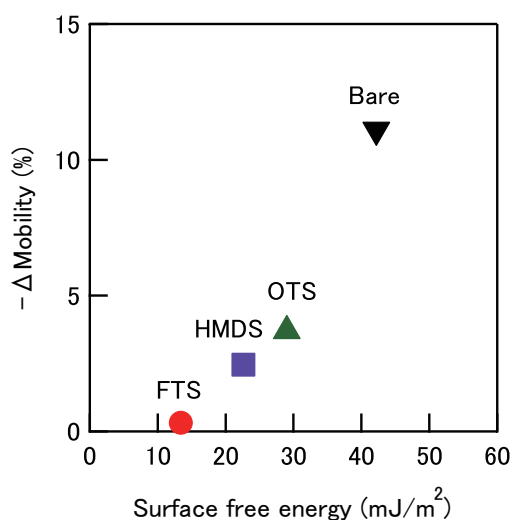
### 3.2 Selectivity

Both the sensitivity and the selectivity of OFET-based gas sensors can be finely tuned by introducing

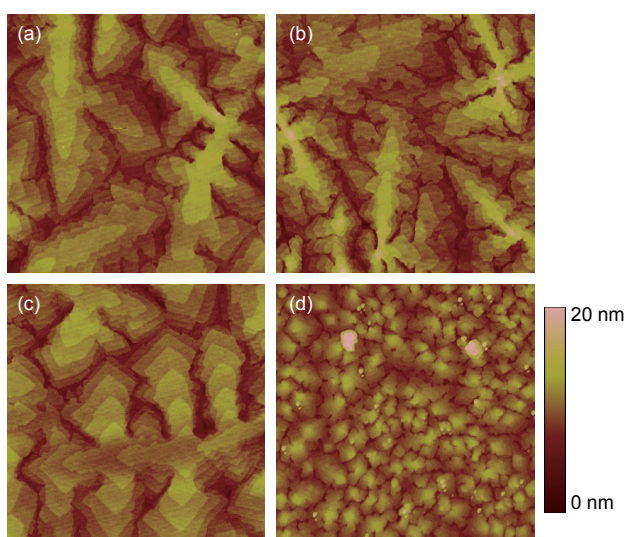
**Table 1** Static contact angles ( $\theta$ ) of water and n-hexadecane, and surface free energies and their components of chemically modified dielectric layers.

	Bare	OTS	HMDS	FTS
$\theta_{\text{water}} (^{\circ})$	$63.9 \pm 2.5$	$90.9 \pm 3.2$	$100.8 \pm 0.5$	$105.4 \pm 0.4$
$\theta_{\text{hexadecane}} (^{\circ})$	$17.5 \pm 1.0$	$12.5 \pm 2.9$	$40.3 \pm 0.4$	$75.0 \pm 1.2$
Surface free energy (mJ/m <sup>2</sup> )	42.2	29.0	22.6	13.4
Dispersive component (mJ/m <sup>2</sup> )	26.3	26.2	21.4	10.9
Polar component (mJ/m <sup>2</sup> )	15.9	2.8	1.2	2.5
Dispersive/Polar	1.61	9.36	17.8	4.4

chemically modified dielectric layers. **Figure 8** shows changes in the drain current ( $I_D$ ) of OFETs fabricated on chemically modified dielectric layers under various ethanol concentrations and humidities. In the case of ethanol, OFETs fabricated on HMDS-, OTS-, and FTS-modified  $\text{SiO}_2$  dielectric layers increased in sensitivity compared with bare  $\text{SiO}_2$ . In the case of humidity, OFETs fabricated on FTS-, OTS-, and



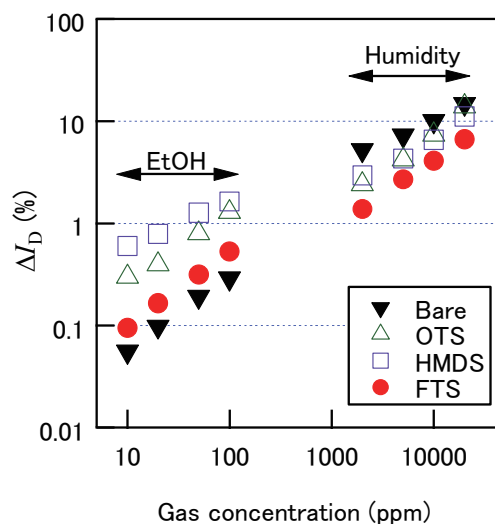
**Fig. 6** Relationships between changes in mobility by humidity and surface free energy of dielectric layers. The changes in mobility were recorded at 2000 ppm humidity.



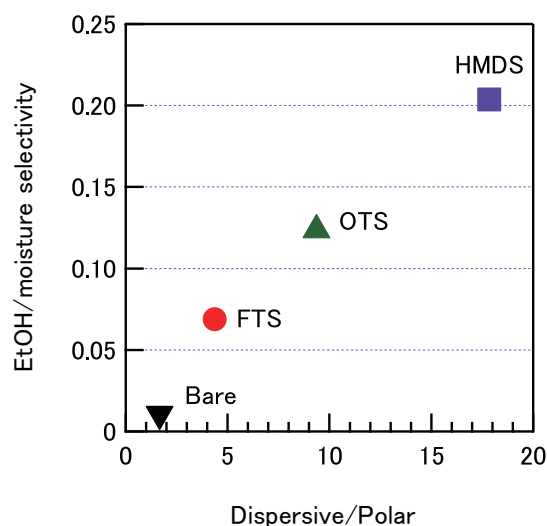
**Fig. 7**  $5 \times 5 \mu\text{m}^2$  AFM images of 5-nm-thick pentacene films deposited on (a) bare, (b) OTS-, (c) HMDS-, and (d) FTS-modified  $\text{SiO}_2$  dielectric layers.

HMDS-modified  $\text{SiO}_2$  dielectric layers decreased in sensitivity.

**Figure 9** shows the relationship between the selectivity for ethanol vs. humidity, which is defined by the ratio of the percentage changes in drain current at 10 ppm ethanol to 2000 ppm humidity, versus the ratio of dispersive to polar components of the surface



**Fig. 8** Changes in the drain current ( $I_D$ ) of OFETs fabricated on chemically modified dielectric layers under various ethanol or humidity concentrations.



**Fig. 9** Relationship between the selectivity of ethanol to humidity, which is the ratio of the percentage changes in drain current at 10 ppm ethanol to 2000 ppm humidity, and the ratio of dispersive to polar components of surface free energy of dielectric layers.

free energy of the dielectric layers. The selectivity for ethanol vs. humidity increased as the ratio of dispersive to polar components of the surface free energy of the dielectric layers increased. This was probably due to the nonpolar characteristics of ethanol, because the ethanol molecule contains both a polar C-O-H group and nonpolar C-H bonds. Although a surface with non-polar components repels both humidity and the polar C-O-H groups in ethanol, one with highly dispersive components attracts only the nonpolar C-H bonds in ethanol. Therefore, a high ratio of dispersive to polar components leads to a high selectivity for ethanol vs. humidity. This finding suggests that a high selectivity can be achieved by introducing a variety of chemically modified dielectric layers that change the components of the surface free energy.

#### 4. Conclusions

OFETs were fabricated on chemically modified SiO<sub>2</sub> dielectric layers. Changes in their mobility or drain current upon exposure to humidity and ethanol were measured. The carrier mobilities in OFETs fabricated on dielectric layers with a low surface free energy, such as FTS-, OTS-, and HMDS-modified dielectric layers, showed little change upon exposure to humidity. The selectivity for ethanol vs. humidity increased with increasing ratios of dispersive to polar components of the surface free energy of the dielectric surface. Our data suggest that the sensitivity and selectivity of OFET-based gas sensors can be finely tuned by the use of chemically modified dielectric layers.

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Figs. 1- 4 and 6- 7

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