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The response characteristics of odor sensor based on organic thin-film transistor for environment malodor measurements

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Abstract

This paper studies the response characteristics of an odor sensor based on organic thin-film transistors (OTFTs) obtained from spin-coated poly-3-hexylthiophene (P3HT) on a thermally grown SiO_2/Si wafer. The response characteristics of the odor sensor based on OTFTs are measured for odor gases generated from liquid fumes of 2-mercaptoethanol and 3-methylindole, such as are typically emitted by pig slurry in ambient air conditions. The experiments show that the response characteristics of the OTFT, when exposed to the 2-mercaptoethanol and 3-methylindole gases, result in a threshold voltage shift, a change in drain current, and a change in mobility with the gate bias.

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This paper studies the response characteristics of an odor sensor based on organic thin-film transistors (OTFTs) obtained from spin-coated poly-3-hexylthiophene (P3HT) on a thermally grown SiO_2/Si wafer. The response characteristics of the odor sensor based on OTFTs are measured for odor gases generated from liquid fumes of 2-mercaptoethanol and 3-methylindole, such as are typically emitted by pig slurry in ambient air conditions. The experiments show that the response characteristics of the OTFT, when exposed to the 2-mercaptoethanol and 3-methylindole gases, result in a threshold voltage shift, a change in drain current, and a change in mobility with the gate bias.

1. Introduction

The treatment and disposal of waste generated by the practice of intensive livestock farming and industrial development has raised public awareness of malodors as environmental pollutants. Malodors emanating from pig slurries are an increasing source of environmental pollution, and many malodors with repugnant smells have very low human olfactory thresholds, and so are perceived as odor nuisances, even when their concentrations in the air are very low. These include volatile fatty acids, p-cresol, amines, sulfides, disulfides, mercaptans, and many heterocyclic compounds [1,2]. It has been reported that environmental odors greatly affect the physiological and psychological status of a human population. Thus, in order to detect environmental pollutants in terms of repugnant smell, the use of odor sensors for odor analysis has attracted a great deal of attention in recent years [3,4]. In particular, OTFT technology, a relatively new research area, produced the first working OTFTs fabricated from polythiophene over two decades ago [5]. OTFTs have been widely investigated for their use in such applications as flexible displays, smart cards, memory devices, and sensors, because they have the advantages of being lightweight, having a low-temperature process, requiring only low-power consumption at low operational voltages, and having good compatibility with various substrates [6,7]. An odor sensor, based on OTFTs, is currently of major interest in the development of applications for semiconductor manufacturing, medical diagnostics, agriculture, environmental remediation, and food science. Also, odor sensors based on OTFTs have been proposed as multi-parameter gas sensors. One argument in favor of using OTFTs as odor sensors is that by monitoring the changes in the bulk conductivity, the field-induced conductivity, the saturation-current (I_{SC}), the off current (I_{off}), the threshold voltage (V_{th}), the field-effect mobility (μ), and the sub-threshold slope (SS) they can offer more information about a particular analyte than can an equivalent chemiresistor [8]. Another advantage that OTFT sensors have over chemiresistors is the signal amplification inherent in transistor device structures, which produces gains in the sensitivity and in the signal-to-noise ratios [9]. The sensitivity of some OTFTs to a few gases has been noted in previous work; for example, Torsi et al. have shown that more information is available from a transistor sensor than from an equivalent chemiresistor sensor [10,11].

This paper studies the response characteristics of an odor sensor based on OTFTs obtained from spin-coated P3HT on a thermally grown SiO_2/Si wafer. Such odor sensors based on OTFTs respond to a direct interaction between the analyte gas molecules and the organic semiconductor layer, without the need of any additional sensing element. It is shown that an odor sensor based on P3HT OTFT can effectively monitor for chemicals associated with

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repugnant smells such as pig slurry, or pollutants such as body waste in a diaper, in ambient air conditions.

2. Experiment

The schematic illustration for the fabrication of bottom-gate top-contact OTFTs is shown in Fig. 1(a). The dielectric layer of OTFTs has been fabricated by thermally growing 100 nm of silicon dioxide (SiO_2) on top of a heavily p-doped silicon wafer to act as the gate contact. The P3HT active layer is spin-coated, at a spin rate of 5000 rpm/min, for 30 s on a thermally grown SiO_2/Si wafer. Here, a polymer binder from a solution of P3HT in toluene solvent is used. The spin-coated P3HT active layer is annealed using a hotplate at 110 °C for 10 min. The source-drain Au electrodes, of 150 nm thickness, are deposited on top of the spin-coated P3HT active layer through a shadow mask by the thermal evaporation method (DOV Co., Ltd) under a vacuum of 2×10^{-6} Torr at room temperature. The OTFT channel width/length have been fabricated to a size of 7.8 mm/100 μm. Finally, after deposition of the source-drain Au electrodes, the OTFTs are annealed using a hotplate at 110 °C for 10 min. The morphology of the spin-coated P3HT active layer has been analyzed using an atomic force microscope (AFM, XE-100 system). All the current–voltage (I–V) characteristics of the OTFTs have been measured using the semiconductor characterization system (Keithley SCS-4200) in a dark box at room temperature. As shown in Fig. 1(a), simple bottom-gated, top-contacting OTFTs are fabricated using P3HT thin films. This structure has generally been used for OTFTs because it provides much better performance than a bottom-contacting structure [12,13]. Fig. 1(b)–(d) shows the chemical structure of P3HT (Sigma–Aldrich Co., used as OTFT active layer), 2-mercaptoethanol (Sigma–Aldrich Co., 1 mol, used as analyte gas), and 3-methylindole (Sigma–Aldrich Co., 1 mol, used as analyte gas), respectively.

3. Results and discussion

Fig. 2 gives an AFM image of the surface morphology of the P3HT film deposited on a thermally grown SiO_2/Si wafer using the spin-coating method. The spin-coated P3HT film is approximately 500 nm thick, and is not patterned for this sensor. The AFM image shows that the large crystals of the organic film, with a surface roughness of 150 nm, grow directly on a thermally grown SiO_2/Si wafer. The surface of the spin-coated P3HT active layer is both homogeneous and smooth. Generally, the sensing performance of organic semiconductor sensors can be influenced by various factors, such as the composition of the film, the organic semiconductor (OSC) molecular structures, the degree of crystallization, the surface morphology, and the grain boundaries. The electrical performances of OTFTs are higher for large grain sizes than for smaller grain sizes, but the magnitude of the response is higher for the smaller sized grains, suggesting that flexibility at the molecular level and porosity at the morphological level increase sensor response [10,11]. The response characteristics of the odor sensor based on OTFTs was measured for odor gases generated from liquid fume of 2-mercaptoethanol and 3-methylindole, such as are typically emitted by pig slurry, in ambient air conditions.

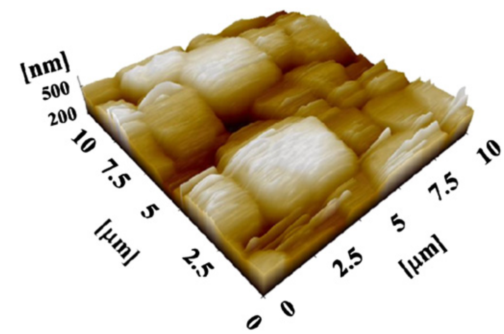

Fig. 2. An AFM image for the surface morphology of the P3HT film deposited on a p-type Si wafer by the spin-coating method.

Fig. 3(a) shows the drain current (I_{DS}) versus the drain voltage (V_{DS}) curves of the OTFT-based sensor exposed without the analyte gas, exposed to 2-mercaptoethanol gas, and exposed to 3-methylindole gas, respectively. When the OTFT sensor is exposed to 2-mercaptoethanol gas, the drain current decreases relative to the drain current of the standard OTFT sensor, but when it is exposed to 3-methylindole gas, conversely, the drain current increases. Here, the variations in drain-source current can be explained by a change in the carrier transfer, due to the adsorption of odor molecules on the active layer or on sites between grain boundaries of the P3HT thin film. The presence of polar molecules is known to change the rate of charge transportation in organic materials by decreasing the amount of energetic disorder through charge–dipole interactions [14,15].

Fig. 3(b) shows the transfer characteristics ($\log_{10}(-I_{DS})$ versus V_G) of the OTFT-based sensor exposed without the analyte gas, exposed to 2-mercaptoethanol gas, and exposed to 3-methylindole gas. The curves show the transfer characteristics in the saturation regime at a V_{DS} of −40 V; the gate voltage (V_G) is swept from 5 V

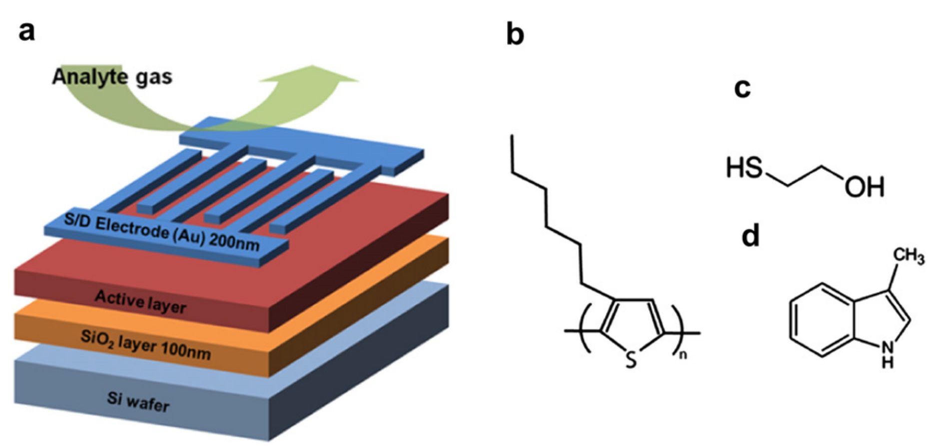

Fig. 1. (a) Cross section of an OTFT odor sensor on a thermally grown SiO_2/Si wafer, and, chemical structures of polymer binders (b) poly-3-hexylthiophene (P3HT) used as an organic active layer, (c) 2-mercaptoethanol used as analyte gas, and (d) 3-methylindole used as analyte gas.

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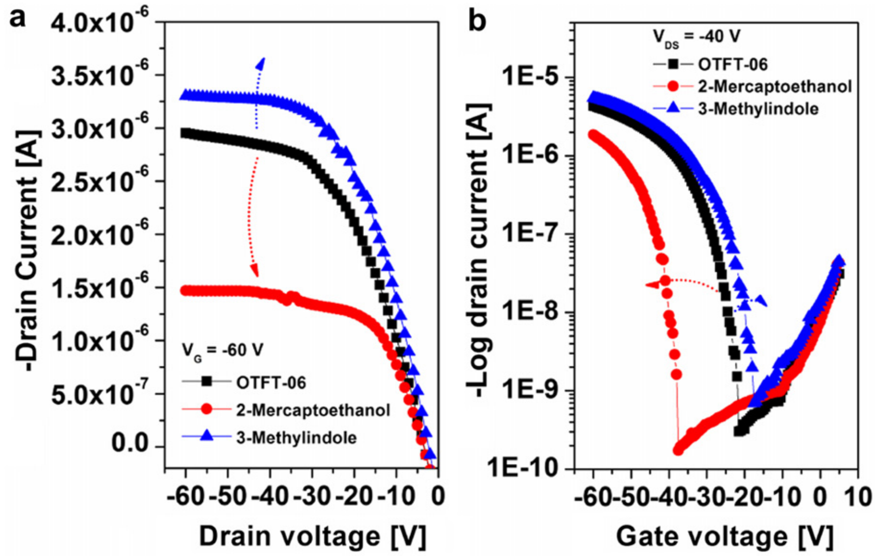

Fig. 3. (a) The drain current (I_{DS})–drain voltage (V_{DS}) curves of OTFT-based sensor exposed without analyte gas, exposed to 2-mercaptoethanol gas, and exposed to 3-methylindole gas. (b) Transfer characteristics ($\log_{10}(-I_{DS})$ versus V_G) of OTFT-based sensor exposed without analyte gas, exposed to 2-mercaptoethanol gas, and exposed to 3-methylindole gas.

to −60 V, with a −5 V step size. These curves exhibit the typical p-type transistor behavior in the accumulation mode, since the gate electrode is biased negatively with respect to the grounded source electrode. Here, several parameters of the OTFTs, when exposed to analyte gases, can be greatly influenced by the interaction of the OTFTs active layer with the analyte gases. These parameters can be seen to result in a change of the drain-source current, which, in the saturated regime, is given by plotting the $-\sqrt{I_{DS}}$ versus V_G and fitting the data to the following equation [16]:

$$I_{DS} = \frac{W\mu C_i}{2L}(V_G - V_{th})^2 \quad (1)$$

where C_i (3.45×10^{-8} F cm^{-2}) is the capacitance of the dielectric layer, $W = 7.8$ mm, $L = 100$ μm, and V_{th} is the threshold voltage. Additionally, $I_{on/off}$ and SS are determined from the $\log_{10}(-I_{DS})$ versus V_G curves of Fig. 3(b). With respect to the electrical characteristics of standard OTFTs, fitting the curve with Eq. (1) gives a saturation field-effect mobility (μ) of 2×10^{-2} cm^2 V^{-1} s^{-1}, SS of 0.34 V/dec, $I_{on/off}$ of 0.83×10^4, and V_{th} of −27 V from the curve of Fig. 3(b).

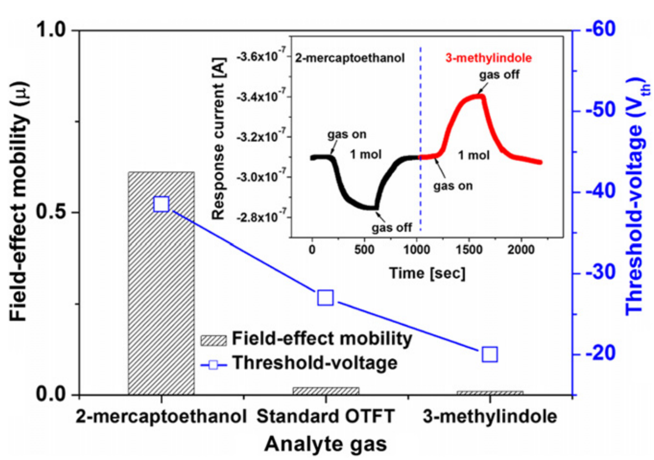

Fig. 4. The variation in field-effect mobility and threshold voltage of OTFT sensor during exposure to odor gas. The inset shows the time-response characteristics.

Fig. 4 shows the variations in the field-effect mobility and threshold voltage of OTFT sensor during exposure to 2-mercaptoethanol and 3-methylindole at concentrations of 1 mol. The inset image of Fig. 4(a) shows the change in the drain current as a function of time when exposed to 2-mercaptoethanol and 3-methylindole in concentration of 1 mol. The response characteristics of the time dependence were measured at a gate voltage of 0 V and a drain voltage of −1 V. Sensor recovery was obtained by degassing for 600 s in an air environment. The OTFT sensor showed fast response characteristics and was able to recover completely to the original baseline when the OTFT sensor was removed from the odor gas. For a comparison of the electrical characteristics when the OTFT-based sensor is exposed to 2-mercaptoethanol gas and 3-methylindole gas, parameters for all the proposed devices are summarized in Table 1, in which it can be seen that the V_{th} of the OTFT sensor when exposed to 3-methylindole shifts in a negative direction in comparison with the V_{th} of the standard OTFT sensor without exposure to the analyte gases; however, the response characteristics of the OTFT sensor when exposed to 3-methylindole gas is shifted in a positive direction. Other parameters, such as the on/off current ratio and the sub-threshold slope, are not significantly changed. The shift direction in the threshold voltage is the result of the different interactions that can possibly take place between the organic semiconductor layer and the analyte gas molecules. Negative shifts in the threshold voltage are generally observed for dipolar molecules, such as methanol, acetone and methylene chloride, which interact with p-type organic semiconductors through Van-der-Waals interactions [4,17–19]. Polar molecules behave as acceptor-like deep trap states for the charge carriers moving at the interface between the organic

Table 1
Comparison of the electrical characteristics for the field-effect motilities in the saturation regime, the threshold voltages, the on/off current ratios, and the sub-threshold swings, when the OTFT-based odor sensor is exposed to no analyte gases, 2-mercaptoethanol gas and 3-methylindole gas, respectively.

Odor gases	V_{th} (V)	μ (cm^2/Vs)	$I_{on/off}$	SS (V/decade)
Standard OTFT (air)	−27	0.02	0.83×10^4	0.34
2-Mercaptoethanol (1 mol)	−38.5	0.61	0.11×10^4	0.52
3-Methylindole (1 mol)	−20	0.01	0.08×10^4	1.10

semiconductor layer and the insulator. The positive threshold voltage shifts are caused by the increase in hole charge density for non-dipolar molecules, such as nitrogen dioxide and oxygen [20]. Therefore, a shift in the threshold voltage is related to the change of work function at the interface between the organic semiconductor layer and the insulator, induced by the adsorption of the polar molecules and non-polar molecules [21]. The shift in threshold voltage can be estimated according to the Poisson equation, the result of which is given by [22]:

$$\Delta V_{\mathrm{th}} = -N\mu_I/\varepsilon \quad (2)$$

where N is the density of the adsorption site, μ_I is the number of dipole moments, and ε is the permittivity of the organic layer.

4. Conclusions

This paper has described the response characteristics of an odor sensor based on OTFTs obtained from spin-coated P3HT on a thermally grown SiO_2/Si wafer. It has been shown that OTFT odor sensors, incorporating such active materials, have a sufficient response for use in electronic nose devices, and can respond to a range of analytes, including 2-mercaptoethanol and 3-methylindole gases. These sensors provide a direct interaction between the impinging gas molecules and the organic semiconductor layer, without the need for any additional sensor elements. From these results, it can be seen that the drain current, when exposed to 3-methylindole, is increased in comparison to the drain current of the standard OTFT, but the drain current is decreased when the device is exposed to 2-mercaptoethanol. Also, it can be seen that the 2-mercaptoethanol and 3-methylindole gases result in a threshold voltage shift and a change in mobility with gate bias. It has been shown that an odor sensor, based on P3HT TFT, can effectively monitor for repugnant smells, such as pig slurry, or pollutants such as body waste in a diaper, in ambient air conditions. Such results are expected to be useful in a number of applications, including food processing, environmental remediation, agriculture, and medical diagnostics.

Acknowledgments

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