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Organic Field-Effect Transistor with Organic Acceptors for Ammonia Gas Sensor

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Abstract

Noninvasive ammonia gas sensor based on the C_8-BTBT organic field-effect transistors (OFET) with organic acceptors (F_4-TCNQ) was fabricated in this study. The gas sensor can be driven under small threshold voltage with 0 gate voltage. Owing to the charge transfer of the strong acceptor F_4-TCNQ layer, over 8 times sensitivity at 0.5 ppm ammonia was observed in the organic acceptors treated OFET. The high sensitivity of organic acceptors treated OFET can be applied to monitor the liver cirrhosis patients.

1. Introduction

Organic field-effect transistors (OFETs) have great potential for gas sensor application due to their low processing cost, ease of large area fabrications, flexibility on substrates, and high sensitivity [1-4]. In particular, the high sensibility of the target molecules at low concentration is a requirement for the breath diagnostic system. Ammonia in breath is a typical symptom of the severe hepatitis, liver cirrhosis, or hepatic carcinoma patients. They have higher concentration of ammonia (0.745 ppm) than that of a normal person (0.278 ppm) [5]. In this study, we fabricated a new ammonia gas sensor based on organic field-effect transistors (OFET) prepared by 2,7-dioctyl [1] benzothieno[3,2-*b*] [1] benzothiophene (C_8-BTBT) and surface treated with organic acceptor layer, 2,3,5,6- tetrafluoro-7,7,8,8-tetra-cyanoquinodimethane (F_4-TCNQ), as shown in Fig. 1. The acceptor layer modified OFET is targeting the detection of low concentration (0.5 ppm) ammonia gas. C_8-BTBT possesses high air stability due to its high ionization potential [6]. It, however, has the drawback of a relatively high threshold gate voltage. Many different approaches have been reported to reduce threshold gate voltage, such as carrier doping by F_4-TCNQ [7]. The threshold voltage can be tuned due to the charge transfer from the C_8-BTBT active layer to the organic acceptor F_4-TCNQ layer [8].

2. Experiments

The device structure is shown in Fig. 2. The solution-crystallized method was performed to prepare C_8-BTBT thin film as active layer based on the reported reference [9]. The supporting piece was placed on an inclined substrate with angle of 10-20 degree. A droplet of 0.1 wt% of C_8-BTBT in heptane solution was sustained at the edge of the support piece. The crystalline domain grows in the direction of channels through the slow solvent evaporation at room temperature. The support piece was removed after solvent evaporation. The sample was placed in vacuum oven for 4 hours at 40℃ in order to remove the residual solvent completely. 50 nm thick of gold was thermally evaporated as source and drain conductors under the vacuum of 5.0×10^{-6} Torr via the shadow mask. The channel length (l) and width (w) are 2000 and 100 nm, respectively. 1-nm-thick of F_4-TCNQ acceptor layer is thermally evaporated on the C_8-BTBT OFET. Electric properties of OFET were measured by Keithley 2636 semiconductor analyzer. NH_3 concentration was controlled in the chamber by adjusting mass flow controller. General procedure for measuring the electric properties of OFET is placed under various NH_3 gas concentrations at 760 Torr with relative humidity at 40±2%.

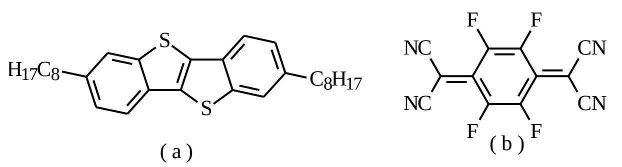

Fig. 1 Molecular structure of (a) C_8-BTBT and (b) F_4-TCNQ

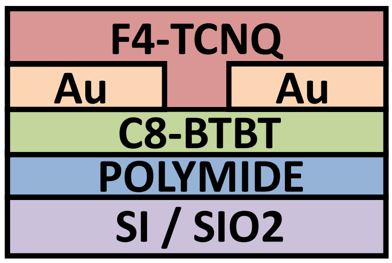

Fig. 2 The schematic device structure of the OFET

3. Results and Discussion

The I_D current increases slightly with lower V_{th} after the F_4-TCNQ layer was thermally evaporated, as shown in Fig. 3 and 4. The charge transfer between the acceptor layer (F_4-TCNQ) and the active layer (C_8-BTBT) was suggested in the literature [10]. The strong electron-withdrawing groups in the chemical structure of acceptor layer have the major influence in the carrier concentration of the active layer and its threshold voltage. The threshold voltage was adjusted slightly above 0 V for further study. The electric properties of untreated OFET under 0.5, 1.0, and 2.0 ppm

NH_3 gas concentration were shown in Fig. 3. The small I_D current decrease may be attributed to the ammonia interacting with C_8-BTBT. The positive charges (holes) of the active layer are reduced when exposed to ammonia, permitted less current flowing through in C_8-BTBT. The threshold voltage of the OFET was also reduced [11].

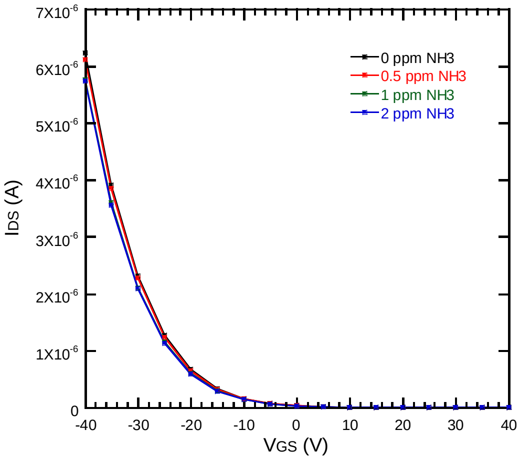

Fig. 3 Electric properties of OFET under 0.5, 1 and 2ppm NH_3 gas concentration.

On the other hand, the surface treated acceptor layer OFET received larger decrease in I_D current and larger V_{th} shift when exposed to ammonia than the untreated OFET. The dual gate mechanism may be applied to explain the result [12]. The ammonia gas served as donor providing the lone pair electrons as a virtual gate when the acceptor layer serves as a dielectric layer. As a result, the change of the charge distribution in the acceptor layer will reduce the holes accumulation at OFET channels. Hence, the significant I_D current decrease and V_{th} shift were observed when increasing ammonia gas concentration.

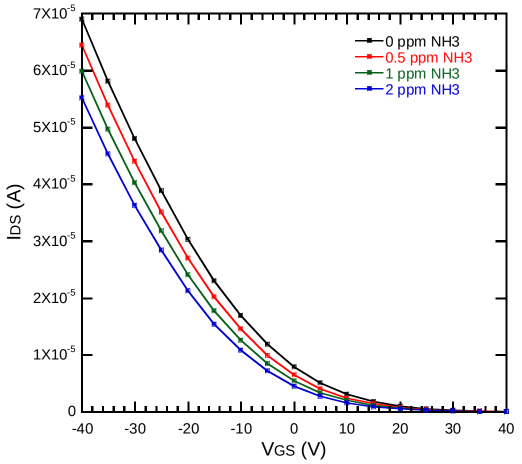

Fig. 4 Electric properties of OFET with a 1nm-thick F_4-TCNQ acceptor layer under 0.5, 1 and 2ppm NH_3 gas concentration.

To quantify the ammonia sensing behavior of OFET, the ratio of the currents measured in the NH_3 gas environments can be expressed the sensing behavior OFET. The sensitivity is defined as shown in Eq. (1):

$$Sensitivity \equiv \frac{I_{D(NH_3)} - I_{D(base)}}{I_{D(base)}} \times 100\% \quad (1)$$

The positive and negative values represent the donor-enriching or donor-trapping effects on the applied devices. Table 1 summarized the sensitivity results on the acceptor layer (F_4-TCNQ) treated and untreated OEFTs at the selected gate voltage in atmospheric pressure with relative humidity 40±2%.

Table 1 The sensitivity of C_8-BTBT OFET treated and untreated with acceptor (F_4-TCNQ) layer

	0.5 ppm	1.0 ppm	2.0 ppm
Untreated (V_G = 0 V)	-2.22%	-10.71%	-16.71%
Untreated (V_G = -40 V)	-1.86%	-7.54%	-7.92%
Treated(V_G = 0 V)	-18.18%	-31.24%	-42.72%
Treated (V_G = -40 V)	-6.64%	-13.22%	-20.11%

The negative value indicated that the ammonia interacted with the OFET surface causing the holes reduction (i.e. hole trapping) in the active layer (C_8-BTBT). The acceptor layer (F_4-TCNQ) is further enhanced the holes reduction. As a result, the F_4-TCNQ treated OFET has over 8 times sensitivity at 0.5 ppm than untreated OFET with 0 gate voltage.

4. Conclusions

In this study, a low concentration ammonia OFET gas detector has been fabricated. Compared with the untreated OFET, the acceptor layer modified OFET has significantly improved the ammonia sensing behavior. The results open a non-invasive way to monitor the liver cirrhosis patients.

Acknowledgements

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