

Porous Organic TFTs for the Applications on Real-Time and Sensitive Gas Sensors

Hsiao-Wen Zan, Ming-Zhi Dai, Ting-Yu Hsu, Hung-Cheng Lin, Hsin-Fei Meng, and Yuh-Shyong Yang

Abstract—A pentacene-based organic thin-film transistor (OTFT) with a porous active layer is demonstrated for the first time. The porous OTFT exhibits a fast, sensitive, and reversible response to ammonia gas with a detection limit as 500 ppb, whereas the OTFT without porous structure has a slow response and a poor recovery behavior. The sensing mechanism dominated by the dissociation of hydroxyl groups of the polymer dielectric layer is raised and discussed. The proposed device is the first OTFT-based ammonia sensor with reversible response and high sensitivity in low parts-per-million range. It is promising for the development of a diagnostic breath analysis system.

Index Terms—Ammonia, gas sensor, pentacene, porous, thin-film transistor (TFT).

I. INTRODUCTION

VAPOR sensors based on organic thin-film transistors (OTFTs) have been developed by many groups [1]–[3]. Compared with vapor sensors based on inorganic field-effect transistors (FETs) [4], [5], OTFTs are suitable for low cost, flexible, large-area, and single-use throwaway electronics operated at room temperature. When an organic semiconductor is known to suffer from the reliability issue when exposed to air, developing a disposable organic-based sensor avoids the reliability issues and meets the preference for biomedical applications. The sensing selectivity can be established by using an OTFT sensor array with various organic materials to form a sensing map [1] or by synthesizing specific functional groups to react with target gaseous molecules [2]. Vapor sensing in OTFTs relies on the charge transferring in the channel region. The diffusion of gaseous molecules through the grain boundaries of the organic active layer into the channel region is critical. Increasing the grain-boundary density was proposed to improve the sensing

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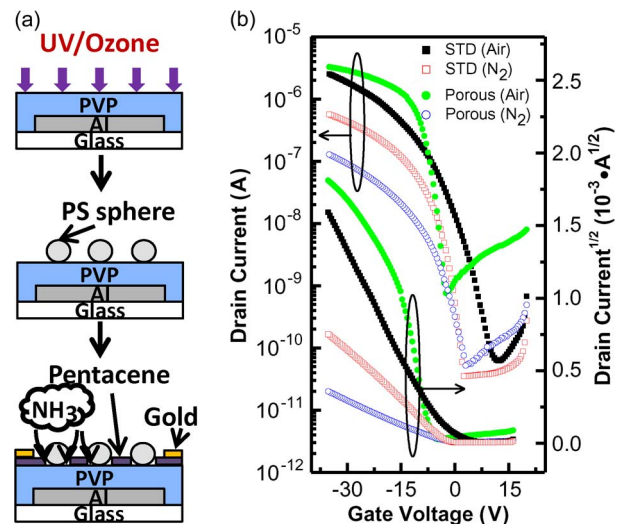


Fig. 1. (a) Process flow and schematic structures of the porous transistor. (b) Transfer characteristics of STD and porous OTFTs measured in atmosphere and N₂ conditions. Drain bias is -5 V (color online).

response [6]. In Si-based FETs, the porous structure is used to greatly improve the reaction between gaseous molecules and porous gate [5]. In OTFTs, the porous structure has never been proposed. In this letter, a simple method is proposed to fabricate a porous active layer in the OTFT. A large channel sidewall area is produced to directly contact with the analyte. A large, fast, and reversible sensing response is achieved. Low-concentration ammonia (NH₃) is the analyte in this letter. The detection limit of the proposed porous OTFT is 500 ppb, which is better than the reported NH₃ detection limit (10 ppm) by using a conventional OTFT [3]. Low-concentration (50–2000 ppb) NH₃ detection is important for the development of a diagnostic breath analysis system. The breath NH₃ concentration is higher in patients with liver diseases or disturbed urea balance (~ 0.7 ppm) than that in a normal person (< 0.3 ppm) [7], [8]. At present, only the optical system can detect low-concentration NH₃ [7], [9]. A portable, cheap, and disposable solid-state NH₃ sensor with low detection limit is in need.

II. EXPERIMENT

To realize the porous structure, the process of spontaneous patterning of higher order nanostructures is used [10]. The process flow is shown in Fig. 1(a). First, a 50-nm-thick aluminum gate electrode was evaporated through a shadow mask on to a glass substrate. A commonly used cross-linkable poly(4-vinyl phenol) (PVP) obtained from Aldrich with a

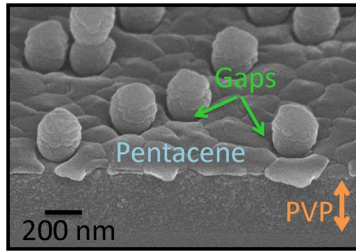


Fig. 2. SEM image of the active region in the porous OTFT (color online).

molecular weight about 20 000 was used as the polymer dielectric material. Poly(melamine-co-formaldehyde) (PMF) was used as the cross-linking agent. PVP with 8 wt.% was dissolved in propylene glycol monomethyl ether acetate with PMF, whereas the PVP-and-PMF weight ratio was 11 : 4. The mixed solution was then spun on substrate at 1200 r/min for 1 min. After annealing on the hot plate at 200 °C for 1 h, a 420-nm-thick PVP gate dielectric was formed. Then, the substrate was exposed to ultraviolet/ozone treatment for 5 s to increase the surface polarity of the PVP layer. Some samples, named as the porous OTFT, were immersed in ethanol solution with 8 wt.% positively charged polystyrene (PS) spheres. The PS spheres with a diameter of 200 nm are adsorbed on the PVP surface to serve as the shadow mask. Samples with PS spheres are then sequentially transferred to a beaker with ethanol and to a beaker with boiling isopropanol (isopropyl alcohol) solution to remove excess PS spheres. Then, samples are blown dry by a unidirectional nitrogen flow. The positively charged PS spheres become neutral in the drying process. A 50-nm-thick pentacene (purity, 99.99%; Aldrich) is evaporated onto the samples with a deposition rate at 1 Å/s. A 100-nm-thick gold is deposited through a shadow mask to complete the source/drain contacts. Because a complete removal of PS spheres usually damages the pentacene film, in this letter, the PS spheres are left on the active layer without affecting the device operation. Samples without PS spheres are served as the standard (STD) samples. For all devices, the channel width and length are 1000 and 200 μm , respectively. Various NH_3 concentrations are obtained by uniformly mixing various amounts of NH_3 (from a cylinder that contains 100-ppm NH_3) with high-purity nitrogen (N_2) into a 20-cm-long U-shape tube. The amount of N_2 is controlled by a mass-flow controller. The amount of 100-ppm NH_3 is controlled by an electrical syringe pump. The U-shape tube with mixed gas is connected to a microfluid measuring system made by Teflon (polytetrafluoroethylene; width = 1 cm, length = 3.5 cm, and height = 0.1 cm). The gas pressure is 1 atm.

III. RESULTS AND DISCUSSION

A scanning electron microscope (SEM) image of the porous active layer is shown in Fig. 2. Because the diameter of the PS spheres is 200 nm, the 50-nm-thick pentacene film is not able to fully cover the spheres. Gaps with a width around 10–30 nm between the PS spheres and the 50-nm-thick pentacene film are clearly observed. These gaps enable a large area of the sidewall of the pentacene film to directly contact with the analyte. The

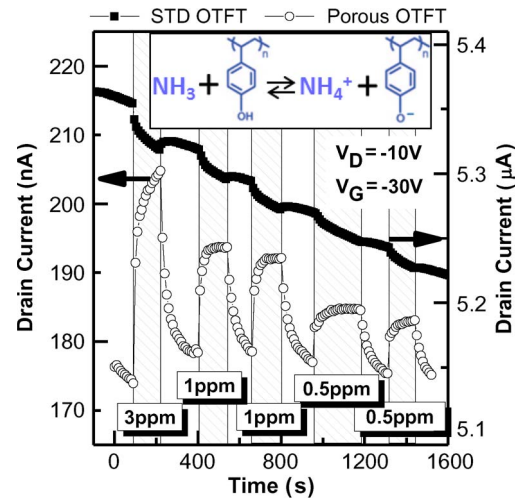


Fig. 3. Drain-current response of the STD and porous OTFTs to various NH_3 concentrations. (Inset) Chemical reaction equation of the $-\text{OH}$ functional group in PVP and NH_3 (color online).

transfer characteristics of porous and STD OTFTs measured in air are compared in Fig. 1(b). The threshold voltage, the field-effect mobility, the subthreshold swing, and the on/off current ratio for porous OTFTs are -5 V, $0.77 \text{ cm}^2/(\text{V} \cdot \text{s})$, 2.2 V/dec , and 4×10^3 . Those for STD devices are -15 V, $0.52 \text{ cm}^2/(\text{V} \cdot \text{s})$, 6.25 V/dec , and 4×10^4 . For OTFTs with PVP dielectric, it is reported that the hydroxyl ($-\text{OH}$) groups in the PVP film dissociate into negative-charged molecules when reacting with water molecules [7]. The negative-charged molecules enhance the accumulation of holes in the channel and hence increase the carrier mobility, as well as the drain current I_{DS} . For the porous OTFT, a large portion of the PVP layer contacts with air through the gaps. A large amount of the $-\text{OH}$ groups dissociate into negative-charged molecules, and as a result, the mobility in the porous OTFT is larger than that in the STD OTFT. When devices are in a dry environment with pure N_2 , their transfer characteristics are shown by the hollow symbols in Fig. 1(b). The field-effect mobilities of the STD and porous OTFTs drop to be 0.125 and $0.03 \text{ cm}^2/(\text{V} \cdot \text{s})$, respectively.

The ammonia sensing responses of the STD and porous OTFTs are compared by plotting the drain current as a function of time exposed to different ambient conditions in Fig. 3. Due to the bias stress effect, the STD device exhibits a decreased drain current with increasing measuring time in the pure N_2 environment [11]. When the STD OTFT is exposed to NH_3 , a current drop is observed. When NH_3 is removed, the current increase is smaller than the current drop, indicating an incomplete recovery. The sensing mechanism may be dominated by the formation of acceptor-like deep states, which is a slow reaction. The porous OTFT, on the contrary, exhibits a fast and reversible current increase when exposed to NH_3 with concentrations ranged from 0.5 to 3 ppm. The current increase indicates a new sensing mechanism. The absolute current variation ratios (the absolute current variation over the initial current value, i.e., $|\Delta I/I_0|$) for the STD and porous OTFTs are plotted as a function of NH_3 concentration in Fig. 4(a). $|\Delta I/I_0|$ of the porous OTFT exhibits a linear relationship with the NH_3 concentration.

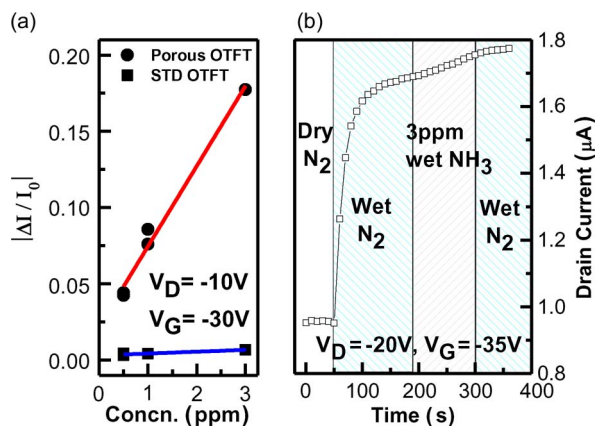


Fig. 4. (a) Absolute current variation ratio (the absolute current variation over the initial current value) as a function of NH_3 concentration. (b) Drain-current variation of the porous OTFT when exposed to 3-ppm NH_3 in wet N_2 conditions (RH \sim 80%) (color online).

The sensing mechanism of the porous OTFT is proposed to be dependent on the dissociation of $-\text{OH}$ groups in the PVP film when reacting with ammonia molecules [12]–[14]. The chemical reaction equation is shown in the inset of Fig. 3. In a dry environment, $-\text{OH}$ groups in the PVP film are mostly neutral. When samples are exposed to ammonia, $-\text{OH}$ groups in the PVP film react with ammonia to form negatively charged molecules. If samples are in a wet environment, $-\text{OH}$ groups are dissociated by reacting with water molecules [12]–[14], and devices lose their response to ammonia molecules. The drain current of the porous OTFT is plotted as a function of time when exposed to a wet environment with or without ammonia, as shown in Fig. 4(b). When 3-ppm ammonia is added into the wet environment (the gray region), the porous OTFT has almost no response to ammonia. For future applications, the control of a dry testing environment is required, or a water-repelling treatment on devices may be developed to suppress the moisture effect.

IV. CONCLUSION

In this letter, a simple and low-cost method has been proposed to fabricate the first porous OTFT to serve as a sensitive

and fast response ammonia sensor. Compared with the STD device, the porous structure significantly improves the sensing behavior. The results open a new route to develop OTFTs as sensitive gaseous sensors.

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