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Gas Sensor Integrates with a Vertical Polymer Space-Charge-Limited Transistor

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1. Introduction

Organic semiconductor materials (OSMs) have been investigated and applied to thin-film transistors because of the low-cost and large-area fabrication on flexible substrates. The gas-sensing ability of OSMs is an unique property that allows the integration of vapor sensors with organic thin-film transistors (OTFTs), which has been extensively studied recently. However, high operation voltage (> 10 V) is usually required in these OTFT-based gas sensor. Sensitivity is also limited because the gas molecules mostly interact with bulk area (the exposing area) rather than channel area (buried under bulk region). In this report, we suggest that the proposed porous vertical space-charge-limited transistor (SCLT) integrates a gas sensor and a switching transistor in one single device.

The SCLT exhibits a high on/off current ratio (>10000) at a low operation voltage (< 2 V) in our previously reports. The operational mechanism of the vertical polymer SCLT is similar to the solid-state vacuum tube triode.[1] The hole current from the bottom (emitter) to the top (collector) of the bottom-injection SCLT is modulated by the metal-grid, which forms the base terminal of the vertical channel. The bias of the metal-grid controls the potential profile in the vertical channel and hence switches the on and off states of SCLT.

The current flows in the bulk region of the vertical channel. Exposing the vertical channel to gas molecules creates a significant interaction between channel and gas molecules and hence a high gas sensitivity. In sensor array technology, to save the operational power and to improve the signal-to-noise ratio, the pixel circuit is composed of one sensor and one switching transistor. Our proposed device can serve as a pixel circuitry by itself, facilitating the development of low-power sensor array technology.

2. Device Fabrication

The fabrication and the scanning electron microscope (SEM) image of SCLT sensor are shown in Fig. 1, we prepared an indium tin oxide (ITO) glass substrate as the emitter (E). Cross-linkable poly(4-vinyl phenol) (PVP) (8 wt.%) (Mw approx. 20000, Aldrich) and cross-linking agent poly(melamine-co-formaldehyde) (PMF) were dissolved in propylene glycol monomethyl ether acetate (PGMEA) with a PVP:PMF mass ratio of 11 : 4. The solution was then spun onto ITO at 1600 rpm for 40 s and annealed at 200°C for 1 hour to form a 200 nm-thick organic dielectric layer. A 1.5 wt.% P3HT (RR > 98.5%, Rieke Metals Inc.) solution dissolved in chlorobenzene was then spun onto PVP to form a 20 nm thick layer. The substrate was spin-rinsed with toluene to increase the P3HT surface polarity. The substrate was then immersed into a solution of 100 nm-diameter negatively charged polystyrene (PS) balls. After the PS balls had adhered to the P3HT surface, 40 nm-thick Al metal was deposited onto the prepared PVP substrate by thermal evaporation, to serve as the base (B). We used Scotch tape (3M) to remove the PS balls and reveal the metal-grid base. O_2 plasma at 100 W was applied to etch the bare PVP for 8 min, to form vertical channels. A 400 nm-thick P3HT active layer was spun onto the substrate, and was annealed at 200°C for 10 min. The substrate was immersed into a solution of 100 nm-diameter PS balls again. Once the balls had adhered to the P3HT surface, a 40 nm-thick Al layer was deposited by thermal evaporation. The PS balls were then removed by tape to form a collector (C) electrode with high-density nano-meter pores. The test gas easily interacted with the active layer via the nano-meter pores.

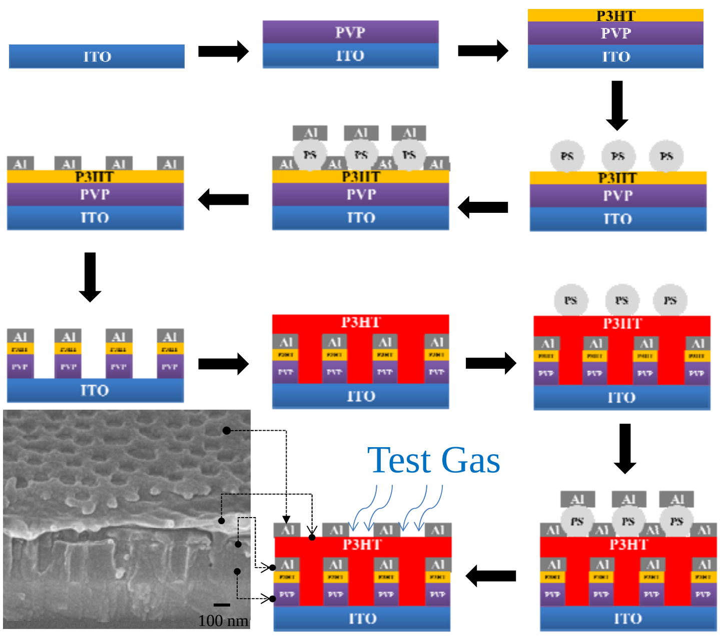

Fig.1 The fabrication and the SEM image of the SCLT sensor.

3. Results and Discussion

The transfer characteristics, the collector current density (J_{CE}) as a function of the base voltage (V_{BE}), of the SCLT with porous collector (porous SCLT) are shown in Fig. 2. With collector bias (V_{CE}) as -2.4 V, porous SCLT exhibits an on/off current ratio as 4750 and a switching swing as 140 mV/dec.

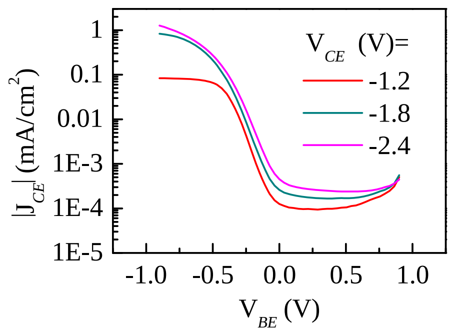

Fig. 2 The transfer characteristics of the porous SCLT.

The porous SCLT was placed in a micro-fluid sensing chamber containing an atmosphere of high purity (99.9999%) nitrogen gas. We used an electrical syringe pump system to inject the test gas (NH_3, 99.9999% pure) into a tube to mix with the N_2. The gas mixture then entered the micro-fluid system. The amount of N_2 was controlled by a mass-flow controller, and specific concentrations of ammonia (NH_3) were obtained by adjusting the injection speed of the syringe pump.

The real-time NH_3 sensing response of the porous SCLT is shown in Fig. 3. In Fig. 3(a), the detectable concentration is 30 ppb. For P3HT OTFT with a conventional bottom-gate structure, the detection limit to ammonia gas is larger than 1 ppm.[2] The high sensitivity to ammonia achieved in this work enables the development of non-invasive breath ammonia analysis for monitoring dysfunction of the human body.[3] For such applications, a portable and real-time ammonia sensor with a detection limit of 50 ppb is critical, but is still challenging. Our results may facilitate the development of low-cost point-of-care technology. Fig. 3(b) shows the repeat sensing operation at the specific concentration, and presents a stable sensing performance of the porous SCLT under the same NH_3 concentration.

Since the proposed sensor is embedded in a vertical transistor, it is therefore important to evaluate the switching properties of the transistor under NH_3 sensing. The switching function of the porous SCLT under NH_3 sensing is shown in Fig. 4. The porous SCLT exhibits a significant current drop under NH_3 sensing (the shaded areas). During NH_3 sensing, a good on/off switching property is still obtained when switching V_{BE} between -0.9 V (on state) and 0.9 V (off state). This result suggests that the proposed porous SCLT integrates a NH_3 sensor and a switching transistor in one single device.

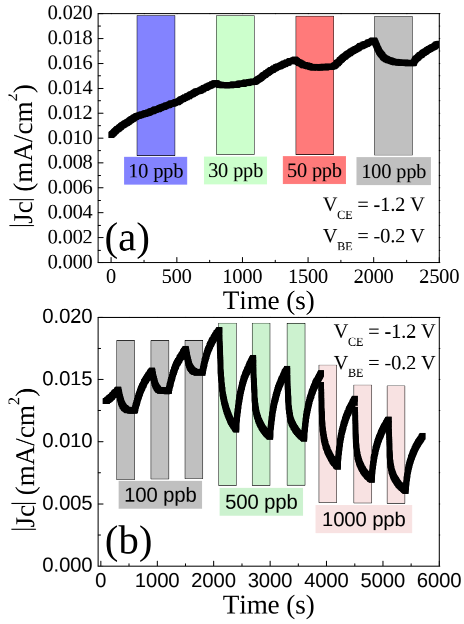

Fig. 3 The real-time sensing response of porous SCLT under (a) various NH_3 gas from 10 ppb to 100 ppb, (b) the repeat sensing operation within 100 ppb, 500 ppb and 1000 ppb.

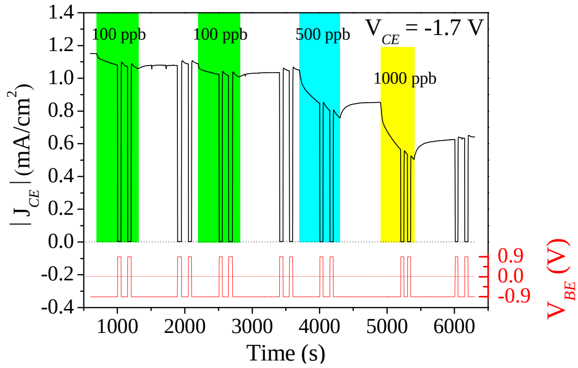

Fig. 4 The real-time sensing switching function of porous SCLT under NH_3 gas at V_{CE} = -1.7 V.

4. Conclusions

We proposed a low-power sensitive gas sensor embedded in a vertical polymer transistor, SCLT. In sensor array technology, to save the operational power and to improve the signal-to-noise ratio, the pixel circuit is composed of one sensor and one switching transistor. Our proposed device can serve as a pixel circuitry by itself, facilitating the development of low-power sensor array technology.

References:

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