Organic Electronics 15 (2014) 2769–2774

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Gas permeable silver nanowire electrode for realizing vertical type sensitive gas sensor

Ming-Yen Chuang [a], Hsiao-Wen Zan [a,*], Peichen Yu [a,*], Yi-Chun Lai [a], Hsin-Fei Meng [b]

[a] Department of Photonics and Institute of Electro-Optics, National Chiao Tung University, 1001 Ta Hsueh Rd., 300 HsinChu, Taiwan
[b] Institute of Physics, National Chiao Tung University, 1001 Ta Hsueh Rd., 300 HsinChu, Taiwan

ARTICLE INFO

Article history:
Received 14 April 2014
Received in revised form 24 July 2014
Accepted 5 August 2014
Available online 18 August 2014

Keywords:
Silver nanowire
Gas sensor
Vertical
Ammonia
P3HT

ABSTRACT

We successfully demonstrated a Poly (3-hexylthiophene) (P3HT) diode gas sensor with silver nanowires as a gas permeable top electrode. The silver nanowires dispersed in isopropyl alcohol (IPA) were used to form a top electrode by a simple drop-casting method. The meshes between nanowires enable gas molecules pass through the electrode and diffuse into the underlying organic sensing layer to dope or dedope the organic semiconductor. Here, the proposed sensor successfully detects ammonia down to 30 parts-per-billion (ppb), which is sensitive enough in many applications including breath ammonia monitoring as a point-of-care application.

1. Introduction

In recent years, solid state gas sensors have been a focus of research for their various applications, including breath analysis for disease monitoring, detection of humidity, air quality control, industrial process control, and hazardous gases detecting [1,2]. As a result, the demand to develop reliable solid-state gas sensor with low-cost process and high sensitivity is growing. Up to now, significant progress has been achieved to improve gas sensor performance. Incorporating various nanostructures into gas sensor is one of the powerful strategies to produce highly sensitive sensors by providing a high surface to volume ratio [3–6]. High surface to volume ratio enhances the interactions between sensing layer and the target gas, thus leads to an improved sensitivity. Among various kinds of nanostructure, nanowire structure is particularly attractive because nanowires can easily form a mesh structure to facilitate the current conduction. Zhang and co-workers demonstrated indium oxide (In_2O_3) nanowire devices for the detection of nitrogen dioxide (NO_2) down to parts-per-billion (ppb) levels [7]. Wang et al. also utilized polyaniline nanowires to form a resistive sensor with polymer nanoframework to successfully detect 0.5 ppm ammonia [8].

When most reported nanowire-based sensors utilize nanowire to serve as the active sensing layer, in this work, we introduce a different concept to utilize the metallic nanowire to realize a sensitive gas sensor. The metallic nanowire is used as a gas permeable top electrode to cover an organic sensing layer and form a vertical diode. The electrode with nanostructure allows gas molecules to penetrate the electrode and to interact with the charges in the underlying sensing diode. Previously, vertical type gas sensors with a porous top electrode were reported to exhibit very high sensitivity. A 10-ppb detection limit to nitric dioxide is realized by using vertical silicon nanowire sensor with a porous top electrode [9]. A detection limit lower than 20 ppb to ammonia is also successfully demonstrated by using vertical organic diode with a top porous electrode [10]. When vertical type gas sensor appears to deliver highly sensitive response, a low-cost reliable process to

* Corresponding authors.
E-mail addresses: hsiaowen@mail.nctu.edu.tw (H.-W. Zan), peichen.yu@gmail.com (P. Yu).

http://dx.doi.org/10.1016/j.orgel.2014.08.012
1566-1199/

fabricate the porous top electrode is still under developed. In previous reports, the porous electrode is formed by utilizing self-assemble nanospheres to serve as the hard mask during metal deposition. After metal deposition, the nanospheres are dissolved or removed by tap and the nanometer pores in metal layer are formed. The critical step is the packing of nanospheres before metal deposition. The nanosphere packing requires subtle process control.

Here, in this work, the gas permeable top electrode is formed by a one-step coating of metallic nanowires. The underlying organic sensing film does not need to have any structure and is formed by a spin coating method. In the proposed process, no lithography process is required. The proposed sensor with such an extremely simple process exhibits a detection limit lower than 30 ppb to ammonia, which is promising for future commercialization. It is also expected that, by replacing the material of the organic sensing layer, the proposed sensor can be extended to detect other kinds of gas molecules.

2. Experimental

The fabrication process was shown in Fig. 1. The indium tin oxide (ITO) patterned glass substrate was cleaned with O_2 plasma treatment after rinsed in deionized water. Then, a 200-nm-thick cross-linkable poly (4-vinyl phenol) (PVP) layer was spin-coated on ITO patterned glass substrate and annealed at 200 °C for 1 h. The PVP in active region was then removed by O_2 plasma etching to determine the active region as 1 mm^2, as shown in Fig. 1(c). Poly(3-hexylthiophene) (P3HT), a kind of p-type semiconductor, dissolved in chlorobenzene (2.5 wt%) was spin-coated and annealed at 200 °C for 10 min to form a 200-nm-thick sensing layer. Finally, the silver nanowires dispersed in isopropyl alcohol (IPA) were drop-casted on the P3HT with substrate heated at 60 °C. The silver nanowires are purchased from ECHUANG. The density of nanowires casted was controlled by the concentration of nanowires in IPA. Specifically, three concentrations (1.25 wt%, 0.625 wt%, and 0.3125 wt% of silver nanowires in IPA) are used to generate AgNWs with high, medium, and low densities. The intercrossed silver nanowires (AgNWs) act as a gas permeable top electrode and enable ammonia molecules to pass through the electrode and diffuse into P3HT sensing layer, as shown in Fig. 1(f).

To investigate the gas sensing response, the devices were mounted in a microfluid sensing chamber with electrical feed through and gas inlet/outlet. The pure nitrogen flow kept by a mass-flow controller was served as background ambience during the detection. An electrical syringe pump system was used to inject the ammonia into a tube where ammonia mixed with background nitrogen before entering the sensing chamber. The concentration of ammonia was controlled by adjusting the injection speed of the syringe pump. Keithley Source Meter (model 2400) was used to measure the current–voltage relationship of the sensor.

3. Results and discussion

The work function of silver nanowire is reported to be around 4.0–4.2 eV [11–13] and the highest-occupied molecular orbital (HOMO) of P3HT is about 5 eV, hence there may be a Schottky barrier between AgNW and P3HT. Accordingly, in the proposed sensor, the intertwined silver nanowires act as the cathode. Oxygen plasma treated ITO with a work function about 5 eV acts as the anode [14]. P3HT is sandwiched between ITO and AgNW to form a Schottky diode while an Ohmic contact can be obtained in the ITO/P3HT interface. The energy band diagram of the proposed sensor is shown in Fig. 2. The current as a function of applied voltage of the AgNW-covered P3HT diode is shown in Fig. 3(a). In forward bias condition, holes are injected from ITO into P3HT and are collected by AgNW electrode. In reversed bias condition, hole injection from AgNW into P3HT is limited and the current is low. The injection barrier may be due to the Schottky barrier between AgNW and P3HT [15]. The electric characteristics in Fig. 3(a) verify that silver nanowires are feasible to serve as the electrode in this work. As applying forward bias voltage, the current turns on within 1 V. The scanning electron microscope (SEM) images of the AgNW-covered P3HT

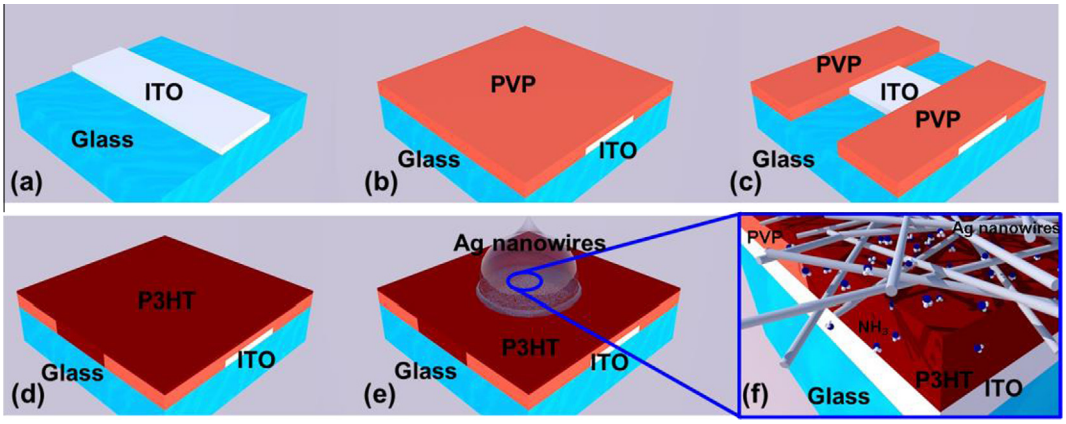

Fig. 1. Schematic illustration of process steps for fabricating the P3HT diode: (a) Glass substrate with patterned ITO. (b) Spin-coating PVP on substrate. (c) O_2 plasma etching to define active area. (d) Spin-coating P3HT. (e) Drop-casting Ag nanowires (AgNW). (f) Schematic illustration of NH_3 sensing.