Extended Abstracts of the 2015 International Conference on Solid State Devices and Materials, Sapporo, 2015, pp836-837

Vertical Nano-Junction Organic Diode as Sensitive Sensing Array

Ming-Yen Chuang[1], Jian-Nan Chen[2], Hsiao-Wen Zan[1]and Chia-Jung Lu[3]

[1] Institute of Electro-Optical Engineering, National Chiao Tung University,
1001, Ta Hsueh Road, Hsinchu, 300, Taiwan, ROC
Phone: (03)5712121 ext.31305 E-mail: hsiaowen@mail.nctu.edu.tw
[2] Institute of Electronics Engineering, National Tsing Hua University,
1001, Kuang Fu Road, Hsinchu, 300, Taiwan, ROC
[3]Department of chemistry, National Taiwan Normal University,
88, Ting Chow Road, Taipei, 11677, Taiwan, ROC

Abstract

We demonstrate an extremely sensitive ammonia gas sensor based on vertical organic diode to exhibit a 1-ppb detection limit. Using phenyl-C61-butyric acid methyl ester (PCBM) as the sensing layer, the nanoporous electrode enlarges the surface to volume ratio and hence realizes the ppb-regime sensitivity. The proposed vertical nano-junction (VNJ) organic diode is then investigated by changing the semiconducting materials (i.e. sensing material). In addition to a pure n-type or p-type sensing material, the blend of n/p organic semiconductor (PCBM/P3HT) is used to react with gas. Changing the n/p blending ratio from 0% to 100% delivers a tunable gas response to ammonia and nitric oxide, hence demonstrating a sensing map concept with good selectivity.

1. Introduction

In past decades, solid-state gas sensors draw much attention due to the low fabrication cost in mass production. Organic semiconducting material is particularly attractive because the wide range of material choice. The gas sensitivity in conventional organic-based resistors or transistors, however, is usually in parts-per-million (ppm) regime [1-3]. Improving the sensitivity to parts-per-billion (ppb) regime is hence an important issue if the gas sensor is used in environmental safety alert and in medical applications (i.e. breath analysis). In our previous work, we reported a sensitive ammonia gas sensor with a 50-ppb sensitivity to detect the breath ammonia of rats [4]. The vertical diode with nanometer junctions (VNJ) greatly enlarges the sensitivity.

Here in this work, we further improve the sensitivity to be 1-ppb by using PCBM as the sensing material. Furthermore, a tunable sensing response is achieve by blending n-type PCBM and p-type poly(3-hexylthiophene) (P3HT) as the sensing layer. VNJ-diode with five blended ratio is then used to detect ammonia (reducing gas) and nitric oxide (oxidizing gas). For nitric oxide, 100-ppb detection limit can be obtained by using pure PCBM VNJ diode. Using P3HT/PCBM ratio as 2:1, on the other hand, can almost fully eliminate the response to 1-ppm nitric oxide. The tunable sensing response can be used to form a sensing map to achieve good sensing selectivity.

2. Device Fabrication

As shown in Fig. 1, a PVP layer was spin-coated on the ITO patterned glass substrate followed by 200 ˚C annealing for 1 hour. Then, a thin P3HT layer as a surface modification layer was spin-coated on it followed by 200 ˚C annealing for 10 min. Polystyrene (PS) balls were coated on the P3HT before the deposition of top electrode (Al). Thus, PS balls served as a shadow mask. By removing them, a porous electrode formed. After O_2 plasma etching, the sensing material was spin-coated on the porous structure. In this work, P3HT and PCBM served as sensing materials. In order to enhance the injection of electrons into PCBM, polyethylene glycol (PEG, an electron transfer layer) was spin-coated before the coating of PCBM. The SEM image of the vertical porous structure was shown in Fig. 1(f).

To investigate the gas sensing response, the devices were mounted in a micro-fluid sensing chamber with electrical feed through and gas inlet/outlet. A flow of pure nitrogen served as background ambience.

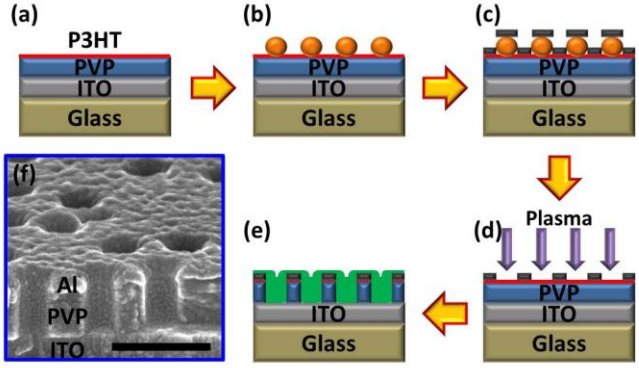

Fig. 1 The fabrication processes: (a) Spin-coating PVP and P3HT on ITO patterned glass substrate. (b) Coating PS balls. (c) Thermal deposition of Al. (d) Removing the PS balls followed by O_2 plasma etching. (e) Spin-coating the sensing layer. (f) The SEM image of vertical porous structure. The scale bar represent 500 nm.

3. Result and Discussion

We investigate the real-time ammonia sensing response (the ratio between the current difference and the initial current ($\Delta I/I_0$)) of PCBM and P3HT VNJ diodes as shown in Fig. 2 (a) and 2 (c), respectively. With pure nitrogen as the background ambience, the blue regions represent the injec-

tion of ammonia into the micro-fluid system with different ammonia concentrations. White regions indicate that the gas flow turns to be pure nitrogen. Under the exposure of ammonia, the current of PCBM VNJ diode increased while the current of P3HT VNJ diode dropped. Such an opposite response is well explained by a redox reaction [4-7]. The ammonia molecules act as reductants to reduce the conductivity of P3HT. For PCBM device, exposing to ammonia enhanced the electron concentration and the conductivity.

The redox reaction was also verified by using PCBM and P3HT VNJ diodes to detect nitric oxide, an oxidant gas. As shown in Fig. 2 (b) and (d), the orange regions represent the injection of nitric oxide into the micro-fluid system with different nitric oxide concentrations. The current of PCBM VNJ diode drops while the current of P3HT VNJ diode increases in the orange sensing regions. All the opposite response to reductant gas and oxidant gas and the opposite reaction between n-type and p-type diodes agree well with the redox reaction in previous reports [4-7]. The sensing reaction is reversible, implying that the redox reaction is mostly based on physical absorption instead of chemical bonding reaction. After studying the PCBM and P3HT sensor individually, we then consider the effect of the mixed n/p sensing layer.

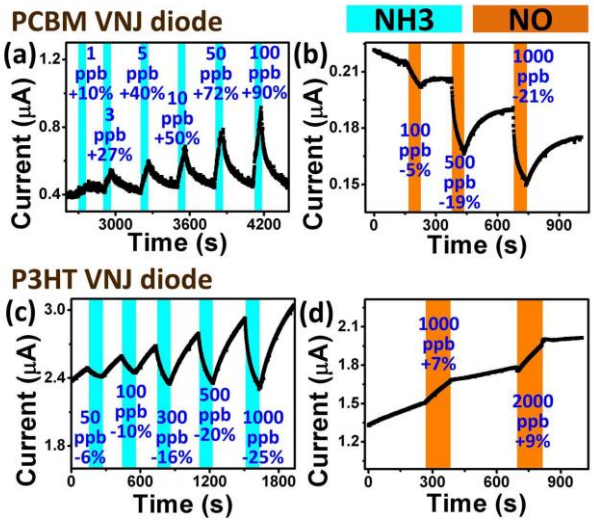

Fig. 2 The real-time current sensing of PCBM VNJ diode under exposure of (a) ammonia and (b) nitric oxide. The real-time current sensing of P3HT VNJ diode under exposure of (c) ammonia and (d) nitric oxide.

Fig. 3 (a) shows the response to ammonia and to nitric oxide of VNJ diodes with different PCBM ratio. For the detection of ammonia, the response decreases as increasing the blending ratio of PCBM. For example, the response to 500-ppb ammonia gradually decreases from -20%, -10%, to -6.5% as increasing the blending ratio of PCBM from 0%, 33%, to 50%. On the other hand, for the detection of nitric oxide, the response is almost eliminated when blending PCBM into P3HT. Specifically, when increasing the percentage of PCBM from 0% to 33%, the response to 1-ppm nitric oxide significantly drops from +7% to -0.7%, as shown in Fig. 3 (b). This result reveals that, in the blended sensing layer, the influence of reduction and oxidation reactions could be cancelled with each other. We hence can deliver a tunable response by modulating the blending ratio between n-type and p-type materials in VNJ diodes. Take the device with 33% blending ratio of PCBM for example (marked in Fig. 3 (a)). The device has almost no response to nitric oxide, but it still sensitive enough to ammonia. Hence, by tuning a proper ratio in the blended film, we may suppress or even eliminate the sensing response to form a reference device in sensing array.

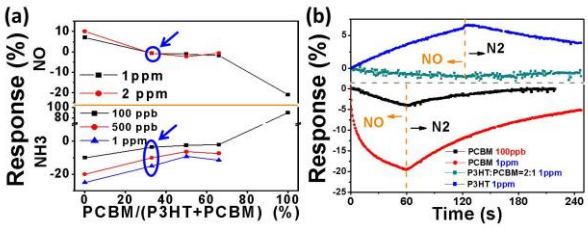

Fig. 3 (a) The response to ammonia and to nitric oxide of VNJ diodes with different PCBM ratio. (b) The real-time response to nitric oxide of VNJ diodes with pure PCBM, pure P3HT and blended P3HT/PCBM (2:1, PCBM ratio as 33%)

4. Conclusions

This work successfully demonstrated ammonia and nitric oxide gas sensor with ppb-regime sensitivity. Furthermore, by mixing n-type and p-type organic semiconductors, the sensing response can be modulated. The results may extend in future work to realize the sensitive sensing array with good selectivity.

Acknowledgements

This work is supported by Ministry of Science and Technology of Taiwan under Contract No. 103-2622-E-009 -011 -CC2.

References

[1] J.W. Jeong, Y.D. Lee, Y.M. Kim, Y.W. Park, J.H. Choi, T.H. Park, C.D. Soo, S.M. Won, I.K Han, and B.K. Ju, Sensors and Actuators B **146** (2010) 40.

[2] B. Li, G. Sauve´, M.C. Iovu, M. Jeffries-EL, R. Zhang, J. Cooper, S. Santhanam, L. Schultz, J.C. Revelli, A.G. Kusne, T. Kowalewski, J.L. Snyder, L.E. Weiss, G.K. Fedder, R.D. McCullough, and D.N. Lambeth, Nano Lett. **6** (2006) 1598.

[3] S. Ji, X. Wang, C. Liu, H. Wang, T. Wang, and D. Yan, Organic Electronics **14** (2013) 821.

[4] M.Z. Dai, Y.L. Lin, H.C. Lin, H.W. Zan, K.T. Chang, H.F. Meng, J.W. Liao, M.J. Tsai, and H. Cheng, Anal. Chem. **85** (2013) 3110.

[5] J. Yu, X. Yu, L. Zhang, and H. Zeng, Sensors and Actuators B **173** (2012) 133.

[6] Y. Zeng, W. Huang, W. Shi, and J. Yu, Appl. Phys. A **118** (2014) 1279.

[7] F. Zhang, C. Di, N. Berdunov, Y. Hu, Y. Hu, X. Gao, Q. Meng, H. Sirringhaus, and D. Zhu, Adv. Mater. **25** (2013) 1401.