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In-Situ Fabrication of SnO_2 Nanowires/Carbon Nanotubes Heterojunctions Based NO_2 Gas Sensors

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Abstract

Heterojunctions of metal oxides and single-walled carbon nanotubes (SWCNTs) have attracted great attention because of their unique physical properties and giant potential applications. In this study, we report the fabrication of NO_2 gas sensors using heterojunctions made of SnO_2 nanowires and SWCNTs. The single crystal SnO_2 nanowires were grown on Pt electrodes via thermal evaporation. A thin film of SWCNTs was synthesized directly on top of the SnO_2 nanowires to form the SnO_2/SWCNTs heterojunctions by arc-discharge method. The morphology and characteristics of the SnO_2/SWCNTs heterojunctions were characterized by a scanning electron microscopy (SEM) and a Raman spectroscopy. Current-voltage (I-V) characteristics and gas sensing properties of the SnO_2/SWCNTs device were investigated. Results point out that the response of the SnO_2/SWCNTs device was very high compared to that of individual materials, reaching up to $S(R_{gas}/R_{air}) = 50$ when exposed to 1 ppm NO_2 at 100 °C.

Keywords: Heterojunction, gas sensor, nanowires, carbon nanotubes.

1. Introduction

Metal oxide one-dimensional (1D) nanostructures have been regarded as promising candidates for high performance gas sensors because of their large surface-to-volume ratio. However, their high operating temperature is major drawback. Many efforts have been made to improve the sensing properties, and reducing the working temperature of metal oxide 1D nanostructures such as doping, adding catalysts and constructing heterojunctions. Among these methods, constructing heterojunctions have been proposed to be an effective way to modulate their properties. Most of the previous studies on heterojunctions focused on those formed by metal oxide and noble metal. Gigantic enhancement of gas sensing has been obtained by using Schottky contacts at the interface between ZnO nanowires and Pt electrodes [1,2]. Schottky contact between ZnO nanorods and Pt thin film was fabricated and tested for H_2 sensing [3]. However, in order to maximize the potential advantages of heterojunctions for such applications, complicated and expensive fabrication processes are required. Fabrication typically starts from the placement of nanomaterials onto desired substrates, followed by lithography, e-beam evaporation and focused ion beam steps to produce the metallic contacts to the ends of nanostructures [1,2]. Recently, due to distinctive properties of carbon nanomaterials, the heterojunctions between 1D nanostructures and carbon nanomaterials were also studied. The *p-n* heterojunctions of SWCNTs and SnO_2 nanowires were demonstrated for high sensitivity UV irradiation [4]. Schottky contacts between ZnO nanorods and graphene were reported for high sensitivity ethanol sensors [5]. Schottky junctions between graphene and SnO_2 nanowires were fabricated for high response to NO_2 gas [6]. In these studies, carbon nanomaterial layers were normal made by transferring technique thus the research results still remain quite limited.

This work reports the fabrication and characterization of heterojunctions between SnO_2 nanowires and SWCNTs. Single crystal SnO_2 nanowires were grown in situ on Pt electrodes via thermal evaporation. Then the SWCNTs were synthesized directly on top of nanowires to bridge the two finges of comb-like electrodes by arc-discharge method. The direct growth of SWCNTs on the nanowires can be easy controlled the thickness of SWCNTs to fabricate well-defined heterojunction gas sensors. The strong adhesion between the SWCNTs and the nanowires can improves not only the electrical contacts between them but also the operational stability. The direct fabrication processing of SnO_2/SWCNTs heterojunctions can also be suitable for mass production.

2. Experimental

2.1. Growth of SnO_2 nanowires

Design of the SnO_2/SWCNTs sensor is shown in Fig. 1(A). The sensor includes SnO_2 nanowires grown on Pt electrodes, and a thin film of SWNTs. SWNTs were grown by arc-discharge system (Fig.

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1(B) whereas SnO_2 nanowires were grown by CVD method (Fig. 1(C)). In details, single crystalline SnO_2 nanowires were growth directly on interdigitated electrodes (IDEs) via thermal evaporation. High purity tin powders (99.9%, Sigma Aldrich) were used as the reaction source. For growing nanowires, 0.1 g tin powder was load in the alumina boat which is placed inside the little quartz tube that is pulled into a large quartz tube in a horizontal tube electric furnace. The distance between the electrodes and boat was fixed at 2 cm. The whole system was evacuated to a pressure of 1.5×10^{-1} Torr using a rotary pump and purged using high purity argon. Then the furnace was heated up to 750 ºC in 15 mins from room temperature and maintained for 20 mins under a flow of oxygen at 0.5 sccm. Finally, the system was cooled down naturally to room temperature. The morphology and characateristics of the synthesized materials were studied by a scanning electron microscope (SEM, JEOL 7600F) and Raman spectroscopy.

2.2 Arc-discharge synthesis of CNTs

Carbon nanotubes were synthesized directly on top of the nanowires to form the SnO_2/SWCNTs heterojunctions by arc-discharge method. A scheme of the arc-discharge system is shown in Fig. 1(C). After the growth of the SnO_2 nanowires, the comb-like electrodes were mounted on the wall of an arc-discharge chamber for in situ SWCNTs deposition. The detailed synthesized procedure of SWCNTs can be found in the reference [7]. Ethanol treatment was done to increase the contact between SWCNTs and substrate.

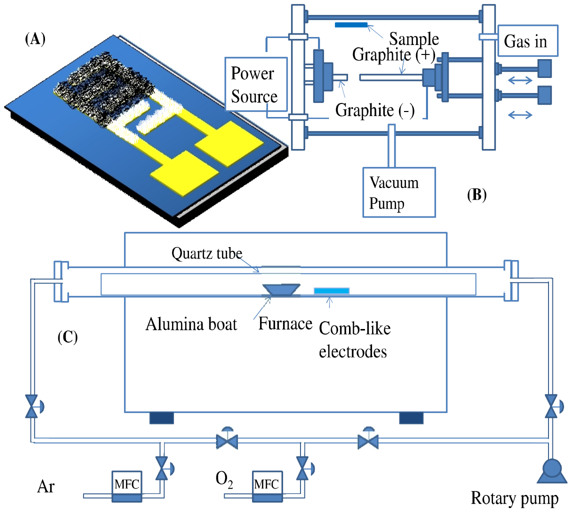

Fig. 1. (A) design of gas sensor, (B) arc-discharge system, (C) CVD system.

2.3 Sensor characterization

The SnO_2/SWCNTs heterojunctions were characterized by using scanning electron microscope (SEM) and Raman spectroscopy. Current-voltage charecteristics (I-V) and gas sensing properties of the samples were studied using a flow-through technique. The gases were flown through the chamber using mass flow controllers. A total flow rate of 400 sccm dry air and NO_2 100 ppm were used as carrier and target gases. The flow rate of gas could be varied to get the concentration of NO_2 from 0.1 to 1 ppm. The working temperature of the sensor could be controlled in the range of 50 ºC-200 ºC. The electrical signal was measured by a programmable Keithley 2400, which was controlled by a LabView program.

3. Results and discussion

The morphology of the SnO_2/SWCNTs heterojunctions was observed by SEM and the images are shown in Fig. 1(A-D). The comb-like electrode has five fingers with interspaces of 100 µm [Fig. 1(A)]. As shown in Fig. 1(B), a layer of high density SnO_2 nanowires completely covers the fingers. The nanowires are not long enough to connect the fingers. Fig. 1(C) represents the SEM images SWCNTs arc-discharge grown on top of SnO_2 nanowires. The enlarged image of SWCNTs layer is seen in Fig. 1(D). It can be seen that SWCNTs films is high porous. The nanowires are coated with SWCNTs network films to form electrical contact between the fingers in sensing measurements.

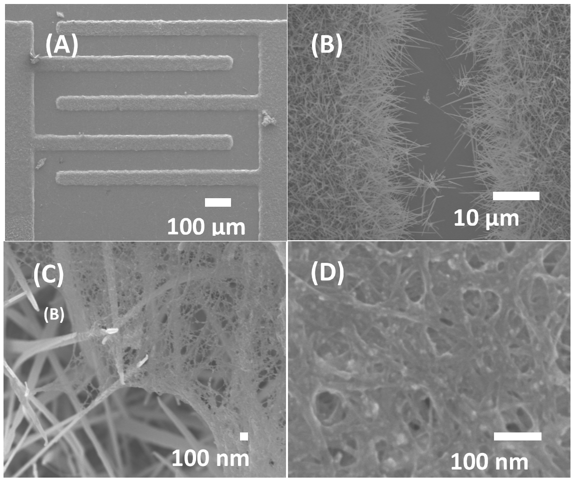

Fig. 2. SEM images of SnO_2/SWCNTs heterojunctions: (A) Comb-like electrode; (B) pristine SnO_2 nanowires; (C) SnO_2/SWCNTs junctions; (D) enlarged image of CNTs.

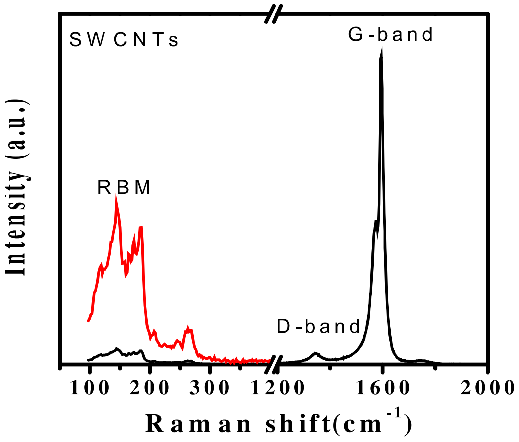

Fig. 3. Raman spectra of the synthesized SWCNTs.

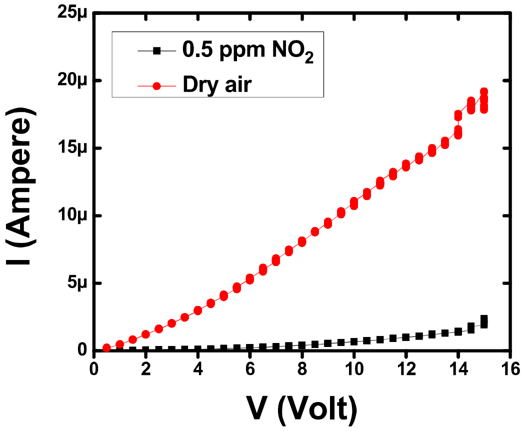

Fig. 4. I-V curves of the SnO_2/SWCNTs heterojunction sensors measured in air and in 0.5 ppm NO_2 at 150 °C.

Raman spectroscopy was used to confirm the successful synthesis of SWCNTs over the SnO_2 nanowires. The typical peaks at ~1340 cm^{-1} and ~ 1590 cm^{-1} to the D-band and G-band of SWCNTs, are clearly seen in Fig. 2. The very high G-band with respect to the D-band is a typical feature of the SWNTs having high crystalline quality. The typical Raman spectrum of SWCNTs can be seen in the reference [7].

Fig. 4 represents the current–voltage (I-V) characteristics of the gas sensor based on SnO_2/SWCNTs heterojunction. The I-V curves show non-linear characteristics as a result of the heterojunction. This demonstrates the potential barrier formed at interface between SWCNTs and SnO_2 nanowires. The potential barrier of the heterojunction plays an important role in the gas sensing mechanisms. There is a significant difference between I-V curve of heterojunction in air and NO_2. The response of the sensor (I_a/I_g) as a function of bias voltage has maximum value at 5 V.

The NO_2 sensing properties of SnO_2/SWCNTs heterojunctions were examined by varying temperatures from 50 °C to 200 °C (Fig. 5). The change in electrical resistance of the sensor to 0.1, 0.2, 0.5 and 1 ppm NO_2 is shown in Fig. 5.

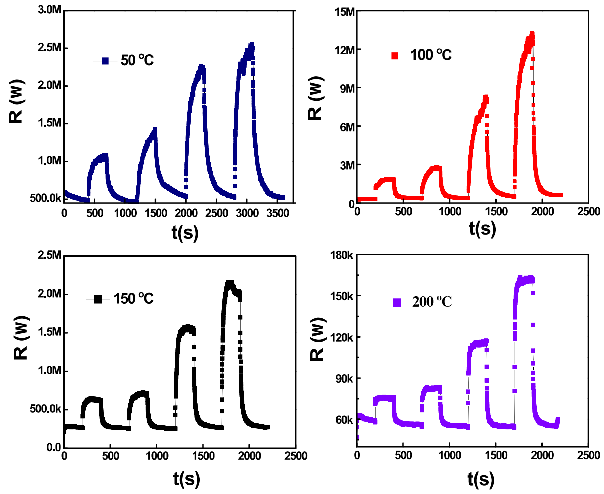

Fig. 5. Transient resistance versus time of the device measured at 50 °C, 100 °C, 150 °C and 200 °C.

The sensor resistance increased sharply upon exposure to NO_2 and then decreased to its initial resistance when the chamber was purged with dry air. Such those results confirm the potential application in monitoring highly toxic NO_2 gas.

4. Conclusion

In conclusion, heterojunctions between SnO_2 nanowires and SWCNTs were successfully fabricated for gas sensor application. The single crystal SnO_2 nanowires were grown on Pt electrodes via thermal evaporation. SWCNTs were synthesized directly on top of the nanowires to form the SnO_2/SWCNTs heterojunctions by arc-discharge method. The sensor showed very high response compared to that of individual materials, reaching up to S (R_{gas}/R_{air}) = 50 when exposed to 1 ppm NO_2 at moderate temperature of 100 °C. Those results indicated that SnO_2/SWCNTs heterojunctions are promising structure for high sensitivity NO_2 gas sensor at low temperature.

Acknowledgment

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References

[1] T. Wei, P. Yeh, S. Lu, Z.L. Wang, Gigantic enhancement in sensitivity using Schottky contacted nanowire nanosensor, J. Am. Chem. Soc. 131 (2009) 17690.

[2] Y. Hu, J. Zhou, P.H. Yeh, Z. Li, T.Y. Wei, Z.L. Wang, Supersensitive, fast-response nanowire sensors by using Schottky contacts, Adv. Mater. 22 (2010) 3327.

[3] J. Yu, S.J. Ippolito, W. Wlodarski, M. Strano, K. Kalantar-zadeh, Nanorod based Schottky contact gas sensors in reversed bias condition, Nanotechnology. 21 (2010) 265502.

[4] J. Yoon, K.W. Min, J. Kim, G.T. Kim and J.S. Ha, p–n hetero-junction diode arrays of p-type single walled carbon nanotubes and aligned n-type SnO_2 nanowires, Nanotechnology, 23 (2012) 265301.

[5] J. Yi, J.M. Lee, W. Il Park, Vertically aligned ZnO nanorods and graphene hybrid architectures for high-sensitive flexible gas sensors, Sensors Actuators B. 155 (2011) 264.

[6] V.V. Quang, N.V. Dung, N.S. Trong, N.D. Hoa, N.V. Duy, and N.V. Hieu, Outstanding gas sensing performance of graphene/SnO_2 nanowire Schottky junctions, Applied Physics Letters 105, (2014) 013107.

[7] N.D. Hoa, N.V. Quy, Y.S. Cho, D.J. Kim, Porous single-wall carbon nanotube films formed by in Situ arc-discharge deposition for gas sensors application, Sensors and Actuators B, 135 (2009) 656.

[8] Q.T. M. Nguyet, N. V. Duy, N.T. Phuong, N. N. Trung, C. M. Hung N. D. Hoa , N. V. Hieu, Superior enhancement of NO_2 gas response using n-p-n transition of carbon nanotubes/SnO_2 nanowires heterojunctions, Sensors and Actuators B: Chemical, *238* (2017), 1120.