KnE Materials Science
ASRTU Conference Proceedings
IV Sino-Russian ASRTU Symposium on Advanced Materials and Processing Technology (2016), Volume 2016

Conference Paper

1D NiO-SnO_2 Heterojunction Nanofibers as Acetone Sensor

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Abstract

1D NiO-SnO_2 nanofibers with p-n heterostructure were synthesized by electrospinning with post-synthetic heat treatment. The morphology and composition were characterized by scanning electron microscope, X-ray diffraction, and energy dispersive X-ray spectrometry. A possible growth model was proposed to describe the formation of hierarchical NiO-SnO_2. The gas sensors based on NiO-SnO_2 exhibited p-type response to acetone. The excellent acetone sensing properties may be attributed to numerous p-n junctions between NiO and SnO_2 nanograins as well as the unique architecture. The changes of energy level and space charge layer of NiO-SnO_2 heterojunction nanofibers when exposed to acetone are described in detail.

Keywords: NiO-SnO_2; Electrospinning; Heterojunctions; Acetone

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Received: 9 September 2016
Accepted: 19 September 2016
Published: 12 October 2016

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the ASRTU Conference Committee.

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1. Introduction

In recent years, nanomaterials with heterojunction structures which is conductive to the enhancement of sensing performance of a single component, have attracted wide attention in the field of gas sensors due to the synergistic effects induced by the coupling and the heterointerface between two different classes of nanomaterials [1]. As heterostructured nanomaterials have strong heterointeraction between the closely packed interface nanounits, their properties cannot be considered as a simple contact of the individual components, but more complex and more superior [2]. As a p-type semiconductor with an energy gap of 4.2 eV, there have been a large number of researches focusing on the gas sensing characteristics of different NiO-SnO_2 nanostructures, and results have exhibited enhanced sensitivities compared to the single component [3-5]. However, the discussion about the interface bonds at the p-n heterointerface that can facilitate electron transfer is not detailed.

In this report, an acetone gas sensor based on hierarchical NiO-SnO_2 nanofibers was fabricated by electrospinning. XRD results showed that NiO-SnO_2 was formed without any other impurity peaks. Hierarchical nanofibers composed of tiny nanocrystals were clearly observed from the SEM images. Meanwhile, the sensing response of the NiO-SnO_2 heterostructure manifested as NiO do, namely p-type response. In addition, electrochemical impedance spectroscopy was also examined to demonstrate the differentiation in the interface resistance of the NiO-SnO_2 nanofibers.

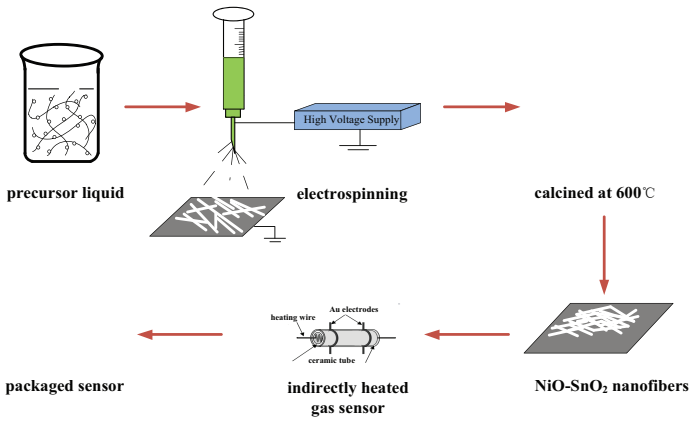

Figure 1: Schematic of the fabrication process of NiO-SnO_2 composite nanofibers based gas sensors.

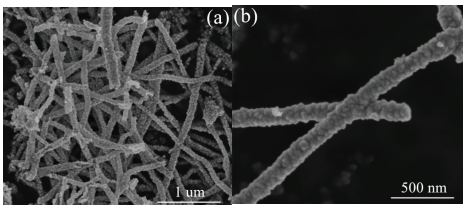

Figure 2: SEM images of NiO-SnO_2 nanofibers (a) with low magnification and (b) with high magnification.

2. Experimental Details

In a typical procedure for preparing NiO-SnO_2 composite nanofibers, precursor solution with a molar rate of 1:1, 0.36 g $SnCl_2{\cdot}2H_2O$ and 0.464 g $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in 4.7 mL of EtOH solvent at room temperature with magnetic stirring for 30 minutes. Subsequently, 0.824 g PVP and 3.9 mL of DMF were added into above solution, agitating for 24 h until a viscous emerald green precursor solution completely formed. The electrospinning parameters were as follows: the voltage and the distance between the needle (positive pole) and the collector (negative pole) were 20 kV and 15 cm, respectively. The ambient temperature and relative humidity were 14.5°C and 33 %RH. The diameter of the needle was 0.7 mm. In order to decompose PVP completely, the as-synthesized nanofibers were sintered at 600°C for 3 h in air with a slow heating rate of 1°C/min. Fig. 1 illustrates the complete schematic of NiO-SnO_2 composite nanofibers based gas sensors by simple electrospinning.

3. Characterization Results

Fig. 2 (a) and (b) display the SEM images of NiO-SnO_2 nanofibers with low magnification and high magnification, respectively. It can be seen that after calcination, the surface of the nanofibers becomes rough and is self-assembled by numerous graded nanoparticles.

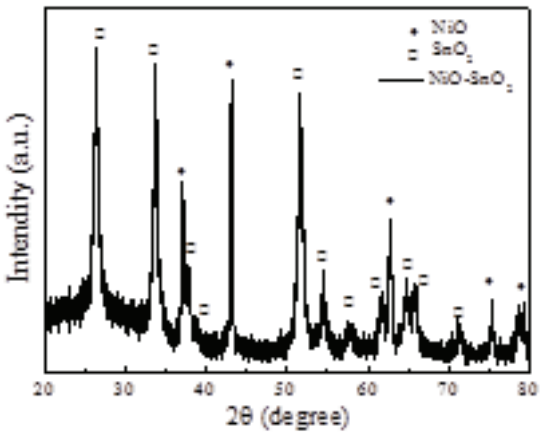

Figure 3: XRD patterns of NiO-SnO_2 nanofibers.

XRD patterns of NiO-SnO_2 nanofibers are shown in Fig. 3. It can be seen that the NiO-SnO_2 composite nanofibers have two crystalline phases of tetragonal SnO_2(JCPDF#99-0024) and cubic NiO (JCPDF#73-1523) simultaneously, indicating that the calcination temperature of 600°C is sufficient to remove PVP completely and form the two oxides.

4. Gas Sensing Properties and Mechanism

Fig. 4 (a) shows that the gas sensor based on NiO-SnO_2 nanofibers has a maximum gas response at the operating temperature of 275°C, while the sensor based on NiO shows highest responses at 325°C. As a result, 275°C and 325°C were respectively selected as the operating temperature for NiO-SnO_2 and NiO sensors in the following gas testing process. From Fig. 4 (b) it can be clearly seen that NiO-SnO_2 exhibits a better selectivity than NiO, having a preferential response to acetone. It implies that NiO-SnO_2 could be used as a very promising candidate for selective acetone detection. The transient acetone sensing characteristics of NiO and NiO-SnO_2 in a range of 20-75 ppm at their own optimal operating temperatures are shown in Fig. 4 (c) and (d), respectively. Furthermore, the long-time stability of NiO and NiO-SnO_2 are also measured. Both sensors exhibit good stability towards 20 ppm acetone in 60 days, as shown in Fig. 4 (e).

The enhanced acetone sensing properties of NiO-SnO_2 nanofibers may be ascribed to the formation of p-n junction between p-type NiO and n-type SnO_2 nanograins. The energy band structure of the NiO-SnO_2 heterojunction is shown schematically in Fig. 5 (b), without taking into account the interface states. In order to obtain equalization of Fermi levels, a relative motion of carriers, namely electronics flowing from SnO_2 to NiO, while holes in the opposite direction occur in the physical interface between p-type NiO and n-type SnO_2, resulting in band bending. At the same time, an electronic depletion layer has been formed on the surface of SnO_2 while an electronic accumulation layer on the side of NiO, as shown in Fig. 5 (b). Before introducing acetone, the oxygen molecules in air will capture electrons from the conduction bands of both

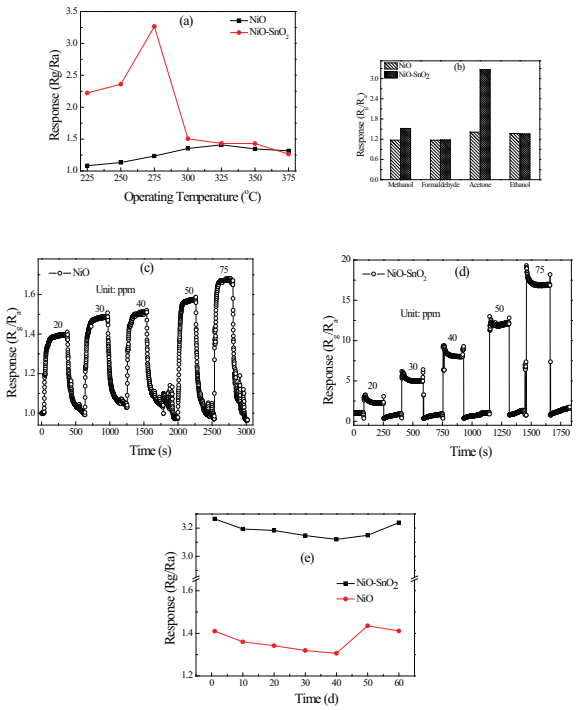

Figure 4: (a) Responses of the sensors based on NiO and NiO-SnO_2 nanofibers to 10 ppm acetone as a function of operating temperature. (b) Responses of NiO and NiO-SnO_2 to various gases including methanol, formaldehyde, acetone and ethanol. (c)(d) Dynamic sensing response of NiO and NiO-SnO_2 to acetone in a range of 20-75 ppm. (e) Stability of NiO and NiO-SnO_2 to 20 ppm acetone.

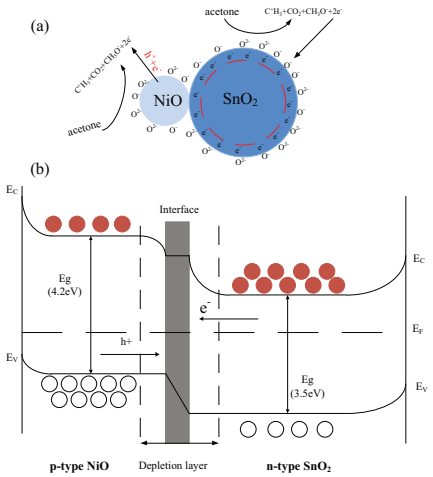

Figure 5: (a) Schematic model for the p-type NiO/n-type SnO_2 heterostructure based sensor when exposed to acetone. (b) Proposed band structure for p-type NiO/n-type SnO_2 heterostructure. E_c: lower level of conduction band; E_f: Fermi level; E_v: upper level of valance band.

SnO_2 and NiO. The adsorption of oxygen results in the further widening of electron depletion layer and hole depletion layer on the surface of SnO_2 and NiO, respectively. Therefore, compared with bare NiO, the NiO-SnO_2 nanofibers perform with a much higher initial resistance due to the p-n heterojunction effect. Upon exposure to acetone gas, the acetone molecules react with chemically adsorbed oxygen ions and release

the captured electrons back to Ni vacancies; thereby the resistance of the NiO-SnO_2 nanofibers increases. Herein, according to the significantly increased initial resistance and the degenerated in the equivalent hole concentration of the NiO-SnO_2 nanofibers due to the p-n heterojunction effect, the sensitivity of the NiO-SnO_2 nanofibers toward acetone will obviously improve.

5. Conclusion

In order to obtain as more p-n heterojunction as possible, heterojunction nanofibers with 1:1 molar ratio of NiO to SnO_2 were fabricated via simple electrospinning technique. It was found that the NiO-SnO_2 nanofibers exhibited an enhanced p-type response to acetone compared to bare NiO. The p-type sensitivity of NiO-SnO_2 nanofibers may be ascribed to the more NiO content than SnO_2. Basing on the heterojunction theory, the initial resistance of NiO-SnO_2 nanofibers is higher than that of bare NiO due to the equalization of different Feimi levels. Meanwhile, the built-in electrical field at the heterujunction can effectively block the acetone adsorption-induced local electrons in the SnO_2 to NiO, which contributes to the increasing of equivalent hole concentration in the NiO-SnO_2 nanofibers and then leads to the improvement of sensitivities.

Acknowledgement

The project was supported by the National Natural Science Foundation of China (61574025, 61131004) and the Fundamental Research Funds for the Central Universities.

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