Preparation of Porphyrin/ZnO Organic-Inorganic Hybrid and Its Hydrogen Sensing Property at Low Temperature

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Received: January 09, 2017; Accepted: July 06, 2017

Abstract

Gas sensor based on a microbelt of ZnO coated the fluorinated tetraphenylporphyrin (H2TPPF) layer structured islands were developed for detection of H_2 at low temperature. ZnO single microbelt was synthesized by thermal evaporation at 500-600 °C, which was used to coat H2TPPF directly via supersonic molecular beam deposition (SuMBD) on the surface of ZnO microbelt for the gas sensor application. The morphology of the ZnO microbelt sensor was examined by field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). The diameter and length of the microbelt were 5 μm and 220 μm, respectively. The porphyrin islands height was few tens of nanometers. The fabricated sensor showed a good response to hydrogen at quite low working temperature. The mechanism of the hybrid sensor needs to be studied further in future.

Keywords: Gas sensors, ZnO microbelt, porphyrin, hydrogen, hybrid.

1. Introduction

The field of organic−inorganic hybrid nanocomposites is a rapidly growing area of research in advanced functional materials science [1]. These materials are made of nanoscaled organic and inorganic counterparts, where in the interaction at molecular level generates unique properties at the interface. The properties of hybrid nanocomposite materials depend not only on the properties of the irindividual constituents, but also on their morphology and interfacial characteristics.

The drawbacks for single inorganic or single organic sensing materials, namely, high operating temperature and low selectivity for inorganic sensing materials, and poor chemical stability and mechanical strength for organic sensing materials, could restrict their practical application. The organic/inorganic hybrid materials with different combinations of the two components, expected to obtain new kind composite materials with synergetic or complementary behaviors, have received more and more attentions worldwide and become attractive for many new electronic, optical, magnetic or catalytic applications since their properties or performances can be improved, considering the possibility to combine the advantages of organic and inorganic counterparts [2].

Zinc oxide is one of the most studied metal oxides and among the most promising materials for gas sensing also for its stability, safety and biocompatibility that make it suitable for a wide range of applications [3,4]. The increased surface-to-volume ratio of quasi-1D ZnO nanowires provides them a much greater response compared to bulk ZnO and ZnO thin films.

Porphyrins are among the most versatile ligand platform, forming a wide range of metal complexes. The ligand flexibility of porphyrins makes them suitable to form hybrid materials, where the richness of porphyrin binding interactions strongly contributes and enriches the overall gas sensing [5].

The cooperation of porphyrins and ZnO gives rise to hybrid structures whose properties may exceed those of the individual constituents. Herein we studied the gas sensing properties of hybrid material between ZnO and porphyrin to hydrogen at low temperature.

2. Experimental

2.1. ZnO microbelts growth

The zinc oxide microbelts were synthesized by a solid-vapor process. Three grams of ZnO powder were loaded in an alumina boat, then positioned in the middle of an alumina tube. An Al_2O_3 pad was used as substrate, which was placed downstream from the ZnO source powder at 20 cm to the end of the tube.

The tube was then inserted in a horizontal tube

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furnace, in which the source material was situated at the highest temperature. The deposition chamber was pumped down to around 2.5 Pascal overnight to evacuate residual oxygen and water vapor. Then the source powder was heated to 1475°C. Argon carrier gas was introduced at a flow rate of 50 sccm (standard cubic centimeters per minute) once the temperature reached 300°C.

The source was heated at 1475°C for 60 min. The ZnO microbelts were deposited onto the alumina substrate, which was placed at a temperature of 500-600°C under a pressure of 1000 Pascal. Then the furnace was turned off, and the tube was naturally cooled down to room temperature under argon flow.

2.2. Microsensor fabrication

The alumina substrate covered with ZnO microbelts was gently scratched on top of a thin (125 microns) kapton substrate. Subsequently, a single zinc oxide microbelt was selected and positioned manually under an optical microscope. Once it was in the appropriate position, two silver-paste drops were used to contact the two extremities. Thus, the microbelt becomes a single-crystalline bridge that can be used as a conductometric gas sensor.

2.3. Organic decoration via SuMBD

The microbelt functionalization was carried out via supersonic molecular beam deposition. A detailed description of the technique and the apparatus is given elsewhere [6,7]. Basically, H2TPPF was seeded in a supersonic beam of He, reaching a kinetic energy of ~7 eV and impinging the substrate in a chamber at a base pressure of $1 \cdot 10^{-7}$ mbar.

The typical organic arrival rate on the substrate was about 0.1 nm/min, as evaluated from a quartz microbalance, and has been kept constant during all experiments. The microbelt was deposited a layer of fluorinated tetraphenylporphyrin molecules (99.9%, Sigma Aldrich) with a nominal thickness of about 26 nm.

2.4. Sensor measurement

Gas sensing properties of the microsensor were studied in a home-built apparatus including a test chamber, a sensor holder which can be heated up to 500°C, some mass flow controllers connected to high purity gas bottles, a multimeter (Keithley 2700), an electrometer (Keithely 6487A), and a home-built data acquisition system (Agilent, WEE Pro). The sensing measurements were run with an operating voltage of 1 V between the electrodes. We used the definition of response as the ratio between the resistance of the device during the gas injection and its resistance in air. Response and recovery times are defined as the time to reach 90% of the complete response and to recovery 90% of it.

3. Results and discussion

3.1. Material characterization

Fig. 1 shows SEM images of ZnO microbelt and its surface after coating with H2TPPF. The SEM image illustrates a single-crystalline microbelt whose uncovered part is 220 microns long (Fig. 1a). The belt width is around 5 microns, while its height seems to be about a couple of microns. And as can be seen in Fig. 1b, the fluorinated tetraphenylporphyrin molecules do not form a smooth layer, but aggregate in fractal islands whose height is few tens of nanometers. Fig.1c is an optical image which shows the whole sensor on silicon substrate.

X-ray diffraction spectroscopy has been carried out in order to study the structure of the nanomaterials. The XRD analysis was performed by Bragg-Brentano geometry with a Panalitycal X'Pert Pro diffractometer with $CuK_{\alpha 1}$ radiation λ=0.15406 nm. The XRD spectra in Fig. 2 show no presence of peaks coming from impurities, confirming the good crystalline nature of microbelt as pure wurtzite (hexagonal) ZnO with lattice constants of a = 3.249 Å and c = 5.206 Å, consistent with the standard values in the reference data (JCPDS 36-1451 card).

3.2. Gas sensing Properties

To evaluate the response intensity, in this paper we use the sensor percentage response S% which is defined as $S\% = (R_{gas} - R_{air}) / R_{air} \cdot 100$, where R_{gas} and R_{air} are the resistance of the device with tested reducing gas or without it, respectively.

All the experiments have been carried out responding to 100 ppm of hydrogen gas at different working temperatures, from 50°C to 100°C. As we can see in Fig. 4c, the hybrid sensor almost had no response to hydrogen at 50°C, the resistance of the sensor had no significant change at this point of temperature.

At higher working temperatures, 75°C and 100°C, resistance of the sensor changed abruptly when the sensor was exposed to 100 ppm of hydrogen (Fig.4a,b).

The response of the hybrid sensor is did not change much when working temperature increased from 75°C to 100°C, from to. The response values were shown in Table 1.

As we know, ZnO is an n-type semiconductor, usually this material responds to gas at high temperature, around 300-500°C [3]. Hydrogen is popular to known as a reducing gas, releasing electrons when gas molecules adsorb on the metal oxide surface. Theoretically, resistance of the hybrid sensor should decrease with presence of hydrogen. In our study the hybrid sensor shows clear change in resistance when the sensor was exposed to hydrogen at quite low temperatures (≤100ºC), the resistance increased.

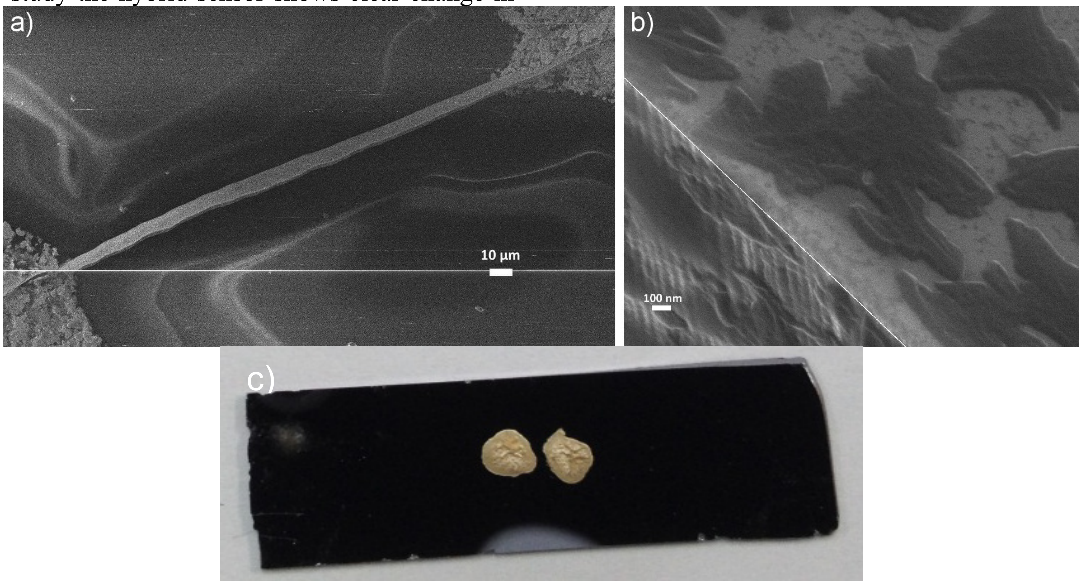

Fig. 1. SEM images: a) single ZnO microbelt bridging two silver paste drops and b) functionalized microbelt surface (the dark spots are H2TPPF islands on the top surface of the ZnO belt). c): optical image of the whole sensor.

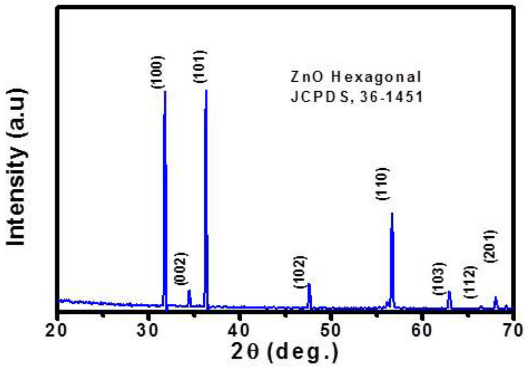

Fig. 2. XRD pattern of the single ZnO microbelt.

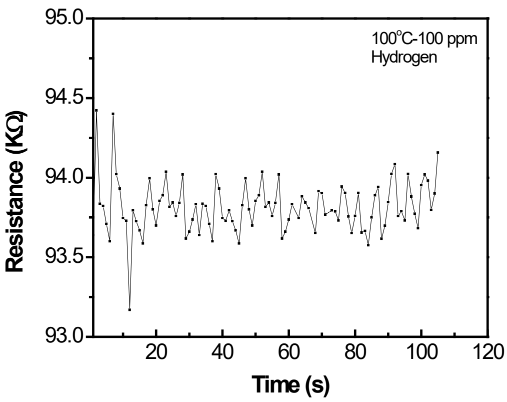

Fig 3. Response transients of the ZnO microbelt to 100 ppm of hydrogen at 100ºC.

At the same time, the ZnO single microbelt sensor was also investigated sensing to hydrogen at 100ºC (Fig. 3). The single microbelt of ZnO did not show any change in resistance in the presence of hydrogen. In other words, the single microbelt of ZnO did not respond to hydrogen at 100ºC.

The organic layer effect on the microdevice is not only a decrease of the operating temperature, but also a change in the sensing mechanism of the system as a whole: the resistance of the decorated microbelt increases when the H_2 gas in injected, and decreases when it is evacuated from the chamber.

This means that the sensing mechanism happens at the organic level, and is then transferred at the metal oxide structures that acts as a transducer.

Our study is the first research on hydrogen sensing of the hybrid ZnO-porphyrin mircodevice at low working temperature. The sensing mechanism of the hybrid structrure should be investigated further in future studies.

Table 1. Response of the hybrid sensor ZnO microbelt-porphyrin to 100 ppm hydrogen.

Working temperature	50ºC	75ºC	100ºC
Response	no		

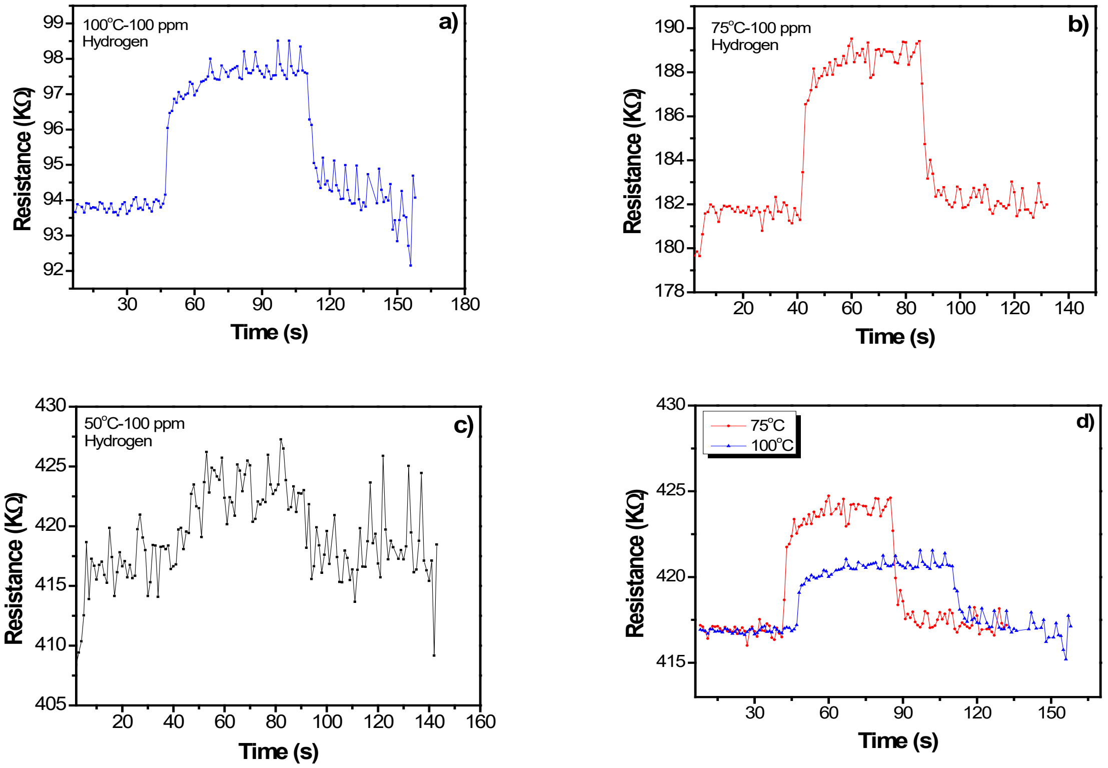

Fig. 4. Response transients of the hybrid sensor ZnO microbelt-porphyrin to 100 ppm hydrogen at different working temperatures: a) 100°C, b) 75°C and c) 50°C. d) Response transients of the hybrid sensor to 100ppm of H_2 gas, at different working temperatures (red line: 75°C, blue line: 100°C).

4. Conclusion

The hybrid sensor was fabricated successfully by thermal evaporation and SuMBD. The ZnO microbelt had 220 microns long and 5 microns wide while its height seems to be about a couple of microns. Porphyrin islands was formed with height is few tens of nanometers. The hybrid sensor showed a relative response to hydrogen at low temperature. The result indicated the strong influence of porphyrin on ZnO gas sensing properties. The sensing mechanism of the hybrid structure should be investigated further in future studies.

Acknowledgments

This work was financially supported by Hanoi University of Science and Technology (HUST) under the grant number **T2016-PC-126**.

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