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Processing–microstructure–property correlations of gas sensors based on ZnO nanotetrapods

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ABSTRACT

After gas sensors based on ZnO nanotetrapods (T-ZnO) were processed by sintering at different temperatures from 350 to 850 °C, a strong correlation was interestingly found among the sintering processing, material microstructure and gas-sensing properties. With increasing sintering temperature from 350 to 750 °C, the feet and cross of T-ZnO became gradually shorter and bigger, respectively. And subsequently tetrahedron-shaped ZnO nanoparticles were produced instead of T-ZnO at 850 °C. The morphological evolution was explained by a new physical model involving Thomson effect, leading to a decrease in the specific surface area. In addition, the contact between feet got better and then became poorer. Meanwhile, surface defects of T-ZnO were also altered: zinc interstitial ($Zn_i^{\bullet\bullet}$) was decreased in its amount while oxygen vacancy ($V_O^{\times}$) showed an inverse trend as sintering temperature increased. Moreover, the best gas-sensing performance toward formaldehyde and methanol was obtained after sintering at 450 °C. This was mainly attributed to the synergetic effect between the best grain contact (meaning that more T-ZnO can make contributions to the sensor response) and more zinc interstitial as well as larger specific surface area (supplying more chemisorbed oxygen). Our work could offer important guidance for the process selection and material design to develop nanostructure-based sensors.

1. Introduction

Metal oxide semiconductor gas sensors have attracted much attention due to their low cost, high sensitivity, fast response, relative simplicity and portability [1,2]. Usually, the fabrication process of these sensors includes three following steps: preparation of a paste containing a raw sensing material, film deposition of the paste on the substrates with Au or Pt electrodes and subsequent sintering treatment [3]. To obtain sensors with excellent stability and response, sintering treatment is a very crucial process for producing sintering necks among many grains and forming a good contact between an electrode and sensing materials. Sintering necks and good contact can guarantee sensors' reliability and validity in the resistance measurement [4]. On the other hand, sintering treatment can alter microstructures (including morphology and surface defect) of sensing materials and put important impacts on the sensor performance [1,2]. Thus, there is an important relationship among the sintering treatment, material microstructure and gas-sensing properties for gas sensors. However, to the best of our knowledge, there are few reports about the processing–microstructure–property correlations of nanostructure-based sensors.

Among various gas-sensing materials, ZnO nanocrystals have been recognized as one of the most promising materials due to their high performance and low cost [5]. Certainly, a lot of work has been reported on the morphological evolution of ZnO nanoparticles during sintering process and their sintering mechanism includes surface diffusion and sublimation of ZnO [6–15]. When ZnO nanoparticles are subjected to a high temperature ($T > 300$ °C) [12,13], simultaneous surface and boundary diffusion occurs and grains grow up. On the other hand, the evaporation of lattice constituents on the ZnO surface is also considered as a dominant sintering mechanism by Kim [14]. This conclusion is supported by experimental results that rough surface of ZnO film is eventually evolved into two-dimensional flat (0 0 0 1) surface at 800 °C and quasi saw-like structures are produced instead of comb-shaped structures during annealing process at 800 °C in air for 10 h [15]. Meanwhile, surface defects on these ZnO nanocrystals are deeply dependent on the sintering temperature. In this sense, sintering process can effectively control the microstructures of ZnO nanocrystals [16]. Recently, T-ZnO based sensor has exhibited excellent gas-sensing properties [17,18] although it is usually subjected to sintering treatment at a high temperature of 650 °C [19]. However, such a sintering treatment for T-ZnO based

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sensors has no theoretical support and thus is quite doubtable. In addition, there are no reports about microstructure change of T-ZnO with increasing sintering temperature, even for its sintering process at 650 °C. Therefore, it is of great significance to investigate processing–microstruture–property correlations of gas sensors based on T-ZnO.

In this work, the microstructure (including morphology and surface defect) change of T-ZnO was investigated via controlling the sintering temperature. As sintering temperature was increased from 350 to 850 °C, most feet of T-ZnO became gradually shorter, and finally disappeared in accompany with the formation of tetrahedron. In order to explain the morphological evolution, a new physical model involving Thomson effect was proposed. Simultaneously, zinc interstitial was decreased in its amount while oxygen vacancy exhibited an inverse trend. The effect of material microstructure on the gas-sensing properties of T-ZnO based sensors was discussed in detail. A synergetic effect between the best grain contact and more zinc interstitial as well as larger specific surface area was proposed to account for the highest response of T-ZnO based sensor at the sintering temperature of 450 °C. These reports could shed a light on the process selection and material design for the development of nanostructure-based gas sensors.

2. Experimental procedures

2.1. Fabrication of sensors

T-ZnO was prepared by a method of vapor-phase oxidation from the metallic zinc. This synthesis process was described in detail in our previous work [19]. The as-prepared powder was mixed with a suitable amount of alcohol to form a paste. Then, the resulting paste was coated directly on the outer surface of an alumina tube on which a pair of Au electrodes and four Pt wires had been printed previously, followed by drying at 80 °C for about 2 h and subsequent annealing at 350 °C for 2 h. Finally, a small Ni–Cr alloy coil was inserted into the tube as a heater, which provided working temperature for the gas sensor [20]. For comparison, other gas sensors were processed by sintering at different temperatures from 450 to 850 °C to study the effect of sintering temperature on the material microstructure and sensor performance. In order to improve the long-term stability, these sensors were kept at a working temperature of 320 °C in air for 3 days.

2.2. Measurement of gas-sensing properties

Gas-sensing properties were investigated using a dynamic measurement system which was developed by our laboratory. The measurement system was mainly composed of flow control system, test chamber, power supply and signal control system as shown in Fig. 1(a). Total flow was kept constant at 400 mL/min controlled by flow control system. And the target gas at different concentrations could be obtained by changing the mixing flow ratio of dry air and target gas using mass flow controllers. Sensors were settled in the test chamber which was linked with data collection card and computer by electronic circuits. In addition, working temperature was kept constant during each measurement by supplying a constant voltage on the sensor heater. Detailed measurement process was described by other authors [21]. A schematic drawing of the electrical circuit for the gas sensor is shown in Fig. 1(b). It is composed of a heating loop and a measuring circuit. By varying the heating voltage (V_H), operating temperature of the sensor could be adjusted. The sensing element of the sensor is connected with a standard resistor (R_L) of 0.47–1 MΩ in series. By monitoring output voltage (V_{output}) across the load resistance (R_L) under an applied voltage of dc (10 V), the electrical resistance of the sensor in air (R_a) or test gas (R_g) can be obtained as following:

$$R_a = \frac{10-(V_{output})_{air}}{(V_{output})_{air}} R_L \quad (1)$$

$$R_g = \frac{10-(V_{output})_{gas}}{(V_{output})_{gas}} R_L \quad (2)$$

where R_L is a constant load resistance, $(V_{output})_{air}$ and $(V_{output})_{gas}$ stand for the output voltage across the load resistance in air and in test gas, respectively. The sensor response (S) is defined as the ratio of the electrical resistance in air (R_a) to that in target gas (R_g):

$$S = \frac{R_a}{R_g} = \frac{[10-(V_{output})_{air}]*(V_{output})_{gas}}{[10-(V_{output})_{gas}]*(V_{output})_{air}} \quad (3)$$

2.3. Characterization

The crystal structure of as-prepared product was identified by an X-ray diffractometer (D/Max-3B) using Cu Kα1 radiation (λ = 1.5406 Å) in the 2θ range from 20 to 70°. The morphology of the product was observed by transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) with a FEI Tecnai G220 microscope working at 200 kV. Morphologies of resulting thick films on the sensor surface were observed by field-emission scanning electron microscopy (FSEM, FEI Sirion 200) with an acceleration voltage of 20 kV. To calculate the surface area of thick films, samples were first scraped from these sintered films and then collected. Then, N_2 adsorption/desorption measurements were carried out at 77 K using a Micromeritics ASAP 2020 system after the samples were degassed at 80 °C in a vacuum for 10 h. BET surface area of samples was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. The electron spin state and structure on the surface of T-ZnO samples were measured by a Bruker-EPRA300 electron paramagnetic resonance (EPR) spectrometry. Room-temperature photoluminescence (PL) spectra of samples were detected with a fluorescence spectrophotometer

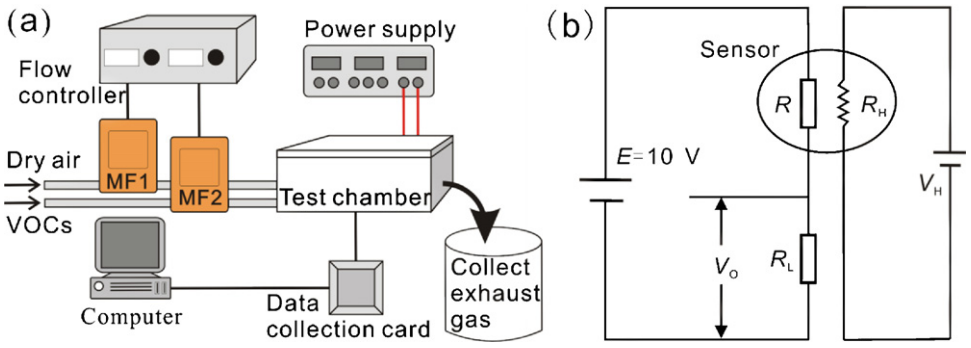

Fig. 1. (a) Dynamic measurement system and (b) schematic diagram of the measuring electrical circuit for the sensor.