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Correlation between microstructure and gas sensing properties of hierarchical porous tin oxide topologically synthesized on coplanar sensors' surface

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ABSTRACT

Gas sensing performance of hierarchical porous (HP) nanostructured metal oxide can be improved by microstructure modulation. However, these microstructure-modulated HP structures are too delicate to stand the destruction from conventional fabrication processes of gas sensors. To solve this problem, effective surface area and ratio between different phases of HP structures based on topological transformation were modulated by sintering treatment in situ on coplanar sensors' surface. A strong correlation between effective surface area, crystal structures and gas-sensing properties was revealed. During sintering temperature from 400 °C to 650 °C, gas response increased to formaldehyde with increasing effective surface area, while decreased from 650 °C to 800 °C since the influence of phase transformation from orthorhombic SnO_2 to rutile SnO_2 overcame the change of effective surface area. A conclusion that the gas sensing performance of orthorhombic SnO_2 was superior to that of rutile SnO_2 was thus carried out. This was mainly attributed to the loose building block ($[SnO_6]^{8-}$) of orthorhombic SnO_2 which could produce much oxygen vacancies, as verified by XPS, PL and EPR. In brief, this work shed a light on the process of sensor design to obtain gas sensing material with microstructure-modulated HP structure.

1. Introduction

Metal oxide (MO) sensors are widely used for the detection of toxic gases in air [1]. As we know, their gas-sensing mechanism involves the reaction of the gas with oxygen species adsorbed on the surface of the semiconducting oxide [2]. In this sense, hierarchical porous (HP) structure of semiconducting oxide which contains numerous channels for gas transport and less aggregated configurations for surface reaction is beneficial to gas sensing performance [3]. On the other hand, this reaction occurring on the surface of semiconducting oxide is also known to depend on various factors of microstructure such as effective surface area [4,5] and crystal structures [6,7] of gas sensing material. This indicates that gas sensing performance of HP structure can be further improved by means of microstructure modulation. However, the microstructure-modulated HP structure of metal oxides can be easily affected by the conventional fabrication process of gas sensors which contains two steps: synthesizing sensing material with modulated microstructure; manufacturing sensor by coating as-synthesized material (usually mixed with organic binder by ultrasonic treatment or milling) onto certain substrate (usually coated by printing and followed by calcination) [6,8]. The shear force from ultrasonic treatment and driven force for atomic diffusion from calcination can exert great influences not only on fragile HP structures [9] but also on susceptible microstructure such as effective surface area [10] and crystal structures [11], resulting in a deteriorated gas sensing performance. Moreover, incorrect correlations between microstructure and gas sensing performance are thus induced because microstructure is usually characterized before sensor manufacturing [12]. Therefore, an effective method to fabricate gas sensor with microstructure-modulated HP structures, which are free from the adverse effects of fabrication processes

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of gas sensors, is significant in establishing relationship between microstructure and gas sensing properties and further improving gas sensing performance.

Nowadays, growing methods have been applied in avoiding the adverse effects of fabrication processes by integrating materials synthesis and sensors manufacturing. Namely, gas sensing materials are synthesized in situ on the surface of gas sensors directly in these cases. For instance, a new process for the fabrication of practical sensing device was reported by II-Doo Kim using the TiO_2/PVAc precursor directly electrospunned onto interdigitated Pt electrode arrays, where ultrasonic and screen printing treatment was avoided [13]. Yi et al. [14] provided a viable method to obtain undamaged In_2O_3 network which was fabricated on sensors' surface directly by structure replication from sacrificial CNTs which had been printed previously. Jia et al. [15] fabricated porous metal oxide films with controllable morphology on the surface of gas sensors based on a monolayer colloidal crystal template (polystyrene spheres) and solution dipping. Recently, we have proposed a new facile method to prepared undamaged HP-SnO_2 topologically transformed from tin oxalate in situ on the coplanar sensors' surface [16]. These studies inspire us that we can obtain microstructure-modulated HP structures which are free from the adverse effects of fabrication processes of gas sensors by modulating the microstructure of HP structures synthesized by these methods. To the best of our knowledge such a strategy to obtain microstructure-modulated HP structure to improve gas sensing performance has not attracted much attention. On the other hand, it is no doubt that the crystal structures of gas sensing material, possessing their own atom configuration and defects, plays a key role in the gas sensing performance [17]. However, there is still no theoretical support for crystal-structures effect on gas sensing performance. Therefore, it is of great significance to obtain the correlation between microstructure such as crystal structures and gas sensing performance by a facile integration of material synthesis, sensor manufacturing and microstructure modulation.

In this work, the microstructures of HP-SnO_2, containing orthorhombic SnO_2 and rutile SnO_2, were controlled by sintering treatment on the coplanar sensors' surface [16,18]. As sintering temperature increased from 400 to 800 °C, the relative amount of orthorhombic SnO_2 decreased and the effective surface area of bulk SnO_2 exhibited an inverse trend. The optimal microstructures with best gas sensing performance were obtained after sintering at 650 °C which was mainly attributed to the synergetic effect between surface area and crystal structures of HP-SnO_2. A conclusion that the gas sensing performance of orthorhombic SnO_2 was superior to that of rutile SnO_2 was carried out. This was attributed to the loose building block of orthorhombic SnO_2 which could produce much oxygen vacancy defects as verified by XPS, PL and EPR. Moreover, a comparison of sensing properties between the sensors fabricated by our method and traditional method was also made, indicating traditional method had great effect on microstructure of HP structures and its gas sensing performance. In brief, this work shed a light on the processes of sensor design to obtain gas sensing material with microstructure-modulated HP structure.

2. Experimental

2.1. Preparation of tin oxalate paste

The tin oxalate was of analytical grade and used as received without further purification in our experiments, purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. A certain amount of tin oxalate mixed with organic solution which composed of terpineol, butyl carbitol, di-*n*-butyl phthalate, span 85 and ethylcellulose (with weight ratios at 55:30:10:4:1) and can be volatilized and removed totally before 400 °C were put into the ball milling pot, and milled for 6 h at the rate of 300 rotations/min. The collected paste was kept in the refrigerator before screen-printing process.

2.2. Fabrication of coplanar gas sensors

The coplanar structure has the advantages of compact structure, well mechanical stability, higher space utilization ratio, low power consumption and so on [19]. Fabrication of substrate of sensor device with Au electrodes and RuO_2 resister as heater material was described in our previous work [20]. Gas sensors were fabricated as follows and also depicted in Fig. S1: the Au electrodes were printed on the cleaned alumina ceramic chip by screen printing, and then sintered at 850 °C for 15 min after drying at room temperature; under the same processes, the RuO_2 resistor was printed on the electrodes by screen printing. Finally, tin oxalate paste was printed on the chip, the area of each gas sensing film was about 1 mm × 1 mm, and thickness was about 10 μm. The sintering temperature of as-handled alumina ceramics was set at 400 °C for 0.5 h and subsequently maintained at different higher temperature for 0.5 h (i.e., 400–800 °C) to obtain different microstructures of orthorhombic SnO_2. The sintering temperature above 400 °C was needed according to the result of TG–DSC shown in Fig. S2. In this work, all of the products were named as SXXX for convenience, where XXX denoted the different subsequent temperature in °C. Then the gas sensors were soldered onto TO8-003 supports (Yixing City Jitai Electronics) to form gas-sensing devices using gold wires and a welding machine. In the end, the devices were aged at 320 °C for 3 days in the air to enhance their stability. In addition, sensor fabricated by conventional processes was also realized to verify the effect of sensor manufacturing on the microstructures of sensing materials and the gas-sensing performance. This sensor was fabricated as follows: first, paste was prepared by mixing organic solution with tin oxide which had obtained by sintering tin oxalate at 650 °C and then this mixture was milled for 6 h. Finally, tin oxide paste was printed on the chip by screen printing and sintered at 550 °C for 2 h, a common temperature used in sintering treatment [21,22]. This sensor was named as C650.

2.3. Characterization

The crystal structures of precursor and as-synthesized tin oxide collected from sensing film were measured on Philips X'Pert X-ray diffractometer with Cu Kα1 radiation in the 2θ range from 10° to 90°. Field-emission scanning electron microscopy (FESEM) was employed to analyze the morphology of the films with a FEI sirion 200 microscope, operated at an acceleration voltage of 20 kV. Transmission electron microscope (TEM) measurements were performed with a JEM-2100 microscope working at 200 kV. The nitrogen adsorption–desorption isotherms at 77 K were measured by using an ASAP 2020 analyzer and the pore size distribution was calculated from the desorption branch of the nitrogen isotherms using the Barrett–Joyner–Halenda method. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos XSAM800 spectrometer employing Al-Kα radiation. Thermogravimetric (TG) analysis and differential scanning calorimetric (DSC) measurements were carried out using a PerkinElmer Pyris Diamond analyzer in air and argon in the temperature range from 50 to 600 °C with the heating rate of 10 °C/min. Room-temperature photoluminescence (PL) spectra of samples were detected with a fluorescence spectrophotometer (LabRAM HR800, Horiba JobinYvon) using a He–Cd laser (~325 nm) as the excitation source. The electron spin state and structure on the surface of these samples were measured by a Bruker-EPRA300 electron paramagnetic resonance (EPR) spectrometry.