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Preparation and gas sensing performances of palladium surface-modified flower-like SnO_2 nanopowders

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ABSTRACT

Flower-like SnO_2 nanopowders prepared by a hydrothermal method were surface modified with palladium via impregnation. The crystal structure, morphology, and surface chemistry states of the samples were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS), respectively. The gas sensing performances were also investigated. For a hydrothermal temperature of 220 °C, flower-like SnO_2 nanoparticles consist of nanorods with diameters of 40 nm and lengths of 100 nm. The XPS and XRD results reveal that palladium exists in the Pd^0 chemical state but the crystal is too small to be detected. The 0.3 wt% Pd modified SnO_2 sensor shows better sensitivity, up to 21, for 70 μL/L ethanol gas at an optimal working temperature of 250 °C. The quick response time (3 s) and fast recovery time (~20 s) are the main characteristics of this sensor.

1. Introduction

As an n-type wide-gap semiconductor, tin oxide (SnO_2) is regarded as an important functional material and is extensively applied in optoelectronic devices and gas sensors for detection of various toxic or explosive gases in air (Tournier & Pijolat, 1999; Yamazaki, Jin, Shen, Kikuta, & Nakatani, 2007; Zhao, 2009). It is well known that the availability of oxide and hydroxyl species on the surface is of great importance in gas sensing, which is the so-called surface phenomenon. Currently, much attention is given to the relationship between the nanostructures and the surface activity (Jiang et al., 2005; Wang, Lee, & Deivaraj, 2004; Wang, Zhu, & Yang, 2007; Xu, Liu, & Xu, 2008). Uniform spherical flower-like SnO_2 architectures assembled from micron rods with diameters of 1.7–2.0 μm were synthesized by a hydrothermal method in the presence of polyvinylpyrrolidone (PVP), and the sensor response sensitivity was only 3.65 when the concentration of ethanol was 105 μL/L (Liu, Zhang, Zhao, Chen, & Yang, 2012). Flower-like SnO_2 nanorod bundles were prepared by the PEG-400 assisted hydrothermal process, and the sensitivity to 50 μL/L ethanol gas reached 12 at working temperature (300 °C) (Zhou et al., 2010). In addition, flower-like Pt–SnO_2 nanostructures were prepared by the one-pot wet chemical method, and the sensitivity of the sensor for 200 ppm NH_3 reached 80 at the optimum working temperature of 300 °C (Liu et al., 2011). Thus, the sensing properties of sensitivity, selectivity, working temperature and thermal stability can be greatly improved by controlled preparation with a small amount of doping with transition metals (e.g., Pt, Pd, Ag) using surface modification and systematic coverage (Janmanee, Pirakitikulr, Wetchakun, Liewhiran, & Phanichphant, 2008; Jiao & Zhang, 2012; Tan et al., 2011). However, the detailed mechanism of additives in semiconductor oxides is still not well understood.

In this article, flower-like SnO_2 nanopowders were prepared by a hydrothermal method in the absence of surfactant, and tin tetrachloride ($SnCl_4{\cdot}5H_2O$) and sodium hydroxide (NaOH) were used as reactants. SnO_2 nanopowders were dipped into a $PdCl_2$ solution and subsequently heat treated. The crystal structure and gas sensing performances of the palladium surface modified SnO_2 samples were characterized.

2. Experimental

2.1. Hydrothermal synthesis of palladium modified SnO_2 nanopowders

SnO_2 nanopowders were prepared by a hydrothermal method using analytical grade $SnCl_4{\cdot}5H_2O$ and NaOH as reactants. A solution of NaOH (1.0 mol/L) was added drop wise into 20 mL of aqueous solution of $SnCl_4$ (1.0 mol/L) until the pH value was 4, and then the resulting precursor suspension was stirred for 2 h. The resulting

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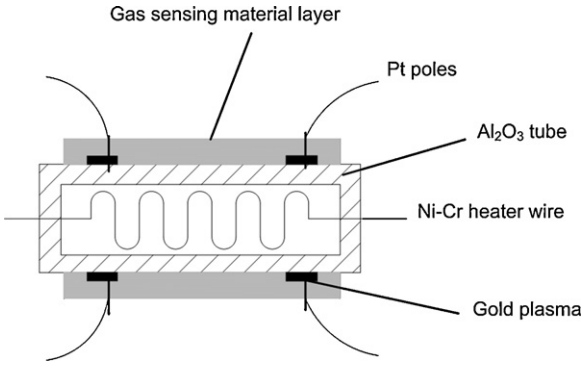

Fig. 1. Diagram of gas sensor.

mixture was transferred into a 50 mL Teflon-lined stainless autoclave, independently sealed and maintained at 180, 220, and 260 °C for 12 h, then cooled down to room temperature. The obtained precipitates were collected and washed several times with deionized water and ethanol and finally dried at 100 °C for 1 h to obtain the final polycrystalline SnO_2 nanopowders. To investigate the influence of the annealing process on the gas sensing performance of the SnO_2 sensor, the as-synthesized products were annealed at temperatures of 450, 550, and 650 °C for 1 h. In addition, partly as-synthesized SnO_2 nanopowders were dipped into a $PdCl_2$ solution, and the weight percentages of $PdCl_2$ to SnO_2 were 0.5%, 1% and 1.5%; for Pd, these were 0.3, 0.6 and 0.9 wt% when using $PdCl_2$. The mixed solution was churned for 2 h, then dried at 40 °C, followed by annealing at 550 °C for 1 h to form palladium modified SnO_2 nanopowders.

2.2. Characterization of palladium modified SnO_2 nanopowders

The crystal structure of samples was characterized by an X-ray diffractometer (XRD) (model: D8 ADVANCE, Brucker AXS, Germany, with an accelerating voltage of 40 kV) with Cu Kα radiation (λ = 1.54059 Å) and a scan rate of 8°/min at room temperature. The morphology of the synthesized powders was scanned using a scanning electron microscope (SEM) (model: Sirion 200, FEI, Holland). X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemistry state by a multi-technical surface analysis system (model: ESCALAB250, Thermo VG, America). The XPS spectra were recorded using an Al Kα (1486.6 eV) X-ray source. The binding energy of the C1s core level electron was taken to be 284.6 eV for energy calibration.

2.3. Sensor fabrication and characterization of gas sensing characteristics

The paste that formed from the mixture of palladium modified SnO_2 nanopowders and a mixed solution of deionized water and ethanol was coated onto an Al_2O_3 tube on which two gold leads had been installed at each end. The Al_2O_3 tube was approximately 4 mm in length, 1.5 mm in external diameter and 1.2 mm in internal diameter. The gas sensors were sintered at 500 °C for 1 h to evaporate the adhesive and eliminate the effect of the surface absorbed water. A spiral Ni–Cr wire, used as a heater, passed through the Al_2O_3 tube to provide a working temperature which could be adjusted in the range of 100–500 °C. The diagram of the gas sensor is shown in Fig. 1.

The surface state of the new gas sensor was unstable, which made the resistance of the sensor in air change continually, while the material surface's active sites changed slightly. To improve the stability and repeatability of the device's application, the sensors were aged at 300 °C for 4 days in air prior to use. The gas sensing characteristics were measured by a WS-30A gas sensor test apparatus. The electrical resistance of the sensor was measured in air and in ethanol gas. Test ethanol liquids were injected into the glass enclosure with a syringe through an inlet and evaporated to form ethanol gases. The sensitivity (S) was defined as $S = R_0/R_g$, where R_0 is the electrical resistance of the sensor in air, and R_g is the electrical resistance of the sensor in a test gas; the sensitivity value is an average value of three or five samples.

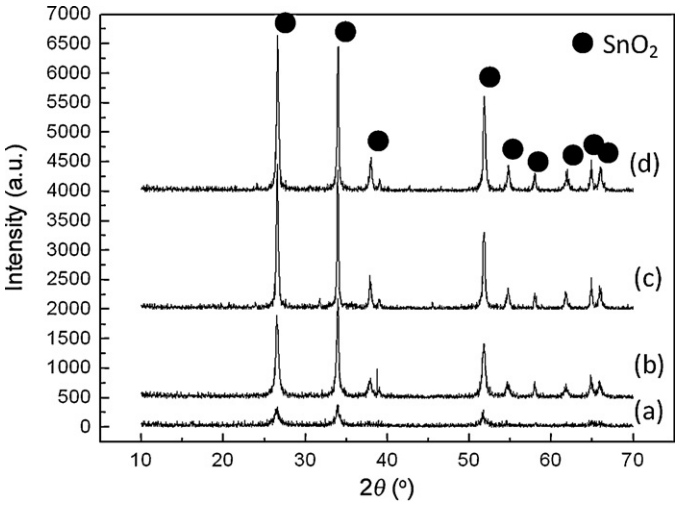

Fig. 2. XRD patterns of SnO_2 sample hydrothermal synthesized at (a) 180 °C, (b) 220 °C, (c) 260 °C, and (d) 0.9 wt% Pd modified SnO_2 sample annealed at 550 °C.

3. Results and discussion

3.1. Structure analysis

The desired SnO_2 phase was confirmed by a powder X-ray diffraction analysis. Fig. 2 shows the XRD patterns of SnO_2 samples synthesized at different hydrothermal temperatures and the 0.9 wt% Pd modified SnO_2 sample synthesized at room temperature. The diffraction peaks of these four samples all match well with the JCPDS card (No. 41-1445) reported data of rutile SnO_2 structure with peaks at $2\theta = 26.5°$, 33.9°, 37.8°, 51.7°, corresponding to the crystal planes (1 1 0), (1 0 1), (2 0 0), (2 1 1), respectively. The average grain size of all the samples was calculated according to the Scherrer formula and the results are shown in Table 1. The grain size increases with increasing hydrothermal temperature. The increase in grain size of 0.9 wt% Pd modified SnO_2 is due to the heat treatment at 550 °C. For a hydrothermal temperature of 180 °C, the strength of the diffraction peaks is lower and the degree of crystallization of SnO_2 is poor. In Fig. 2d, none of the peaks correspond to palladium, palladium chloride or other oxides of palladium, and significant changes in the lattice parameters are not obtained.

Table 1
Grain size of SnO_2 prepared at different hydrothermal temperature and 0.9 wt% Pd modified SnO_2 followed by heat treatment at 550 °C for 1 h.

SnO_2 sample	2θ (°)	FWHM (°)	Grain size (nm)
180 °C	26.500	1.012	8
220 °C	26.535	0.627	13
260 °C	26.538	0.285	28
0.9 wt% Pd modified SnO_2 sample	26.580	0.234	34

N.B. FWHM is the full width at half maximum.

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