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Electroless plated SnO_2–Pd–Au composite thin film for room temperature H_2 detection

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ABSTRACT

Extremely thin SnO_2 nanosheets with high surface area were fabricated through a one-pot hydrothermal method. In this work, gas sensing property of the SnO_2 nanosheets was studied. SnO_2–Pd–Au mixed thin films were prepared by electroless deposition of Pd, Au, and nanostructured SnO_2 onto the surface of a high resistance alumina substrate. The whole fabrication process was carried out at room temperature without any thermal treatment required. The films deposited on the alumina substrate were characterized by SEM and EDS. The co-deposited Au improved the electric conductance of the sensing film. A relatively large amount of Pd (Pd/Sn ratio around 1:1) was obtained for the film instead of the usually low doping value of Pd (~0.1% level) for SnO_2 hydrogen sensor. It has been found that the SnO_2–Pd–Au composite film sensor has fast response in the range of 134–1469 ppm toward hydrogen gas at room temperature. The sensor also shows good stability and repeatability. Effects of annealing condition of the sensing film on H_2 gas sensing performance was investigated as well. A possible machnism for SnO_2–Pd room temperature hydrogen sensing is proposed.

1. Introduction

Since the first commercially available catalytic elements were developed, gas sensors applied in various fields including domestic or industrial security, environmental emission monitoring, medical, agribusiness controls, have been extensively studied [1,2]. Particularly, increasing attention has been paid on resistive type gas sensors based on semiconducting metal oxides [3–6], such as SnO_2, TiO_2, WO_3, In_2O_3, ZnO, Fe_2O_3, in practice for detecting different types of reducing gases. Among these oxides, SnO_2 is regarded as a key functional material for hydrogen gas detection as a wide band gap semiconductor with a high surface-area-to-bulk ratio [7–9]. However, besides lack of selectivity, usually SnO_2 based hydrogen sensors are required to be operated at high temperatures of 250–600 °C to have enough response [10–13], not suitable for room temperature hydrogen leakage detection.

The sensor performance such as sensitivity, selectivity, operating temperature and long-term stability is strongly dependent on the particle (grain) size, pore size and grain boundary characteristics [14]. Recently, extremely thin SnO_2 nanosheets have been successfully synthesized through a one-pot hydrothermal method [15]. The SnO_2 nanosheets possess extremely high Brunauer–Emmett–Teller (BET) surface area and pore volume. The inherent characteristics of this new material make it a possible candidate for low temperature hydrogen gas sensors.

Till now, several approaches have been used to improve SnO_2 sensor performance, including nanoscale crystallites, additives and surface functionalization [16]. Various additives such as Pd, Pt, Ag_2O, In_2O_3, La_2O_3 have been studied [17–19]. Particularly, Pd-doping has already been widely used to reduce response time, increase sensitivity, and lower working temperature for SnO_2 based hydrogen sensors [20–26]. For instance, Pd (~0.16 wt%)-SnO_2 was sputtered on various substrates to get highly oriented polycrystalline Pd-doped SnO_2 films, some of which had a considerably high H_2 sensitivity at 400–550 °C [20]. Pd nanoparticle surface modified SnO_2 nanorod thin films were prepared for gas sensors operated at 150–450 °C, indicating that Pd enhanced the response and selectivity towards hydrogen [21]. Surface doping by Pd (0.1–0.2%) improved gas sensing characteristics of SnO_2 thin films including increasing the gas response, optimizing operating temperatures, and decreasing response time [25]. But the beneficial influence of surface Pd additives depends on the film structure and operating temperatures. Hydrogen gas sensors were fabricated based on networks of Pd nanoparticles deposited tin dioxide nanowires,

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showing high sensitivity and fast response time upon exposure to 10,000 ppm H_2 at room temperature [26]. However, most of the reported work on Pd doped SnO_2 for hydrogen sensing still requires high temperature operation [20,21]. And the fabrication process for the sensing materials was complicated [20,21,26].

On the other hand, Pd itself has also been used as a popular material for H_2 sensing based on its reversible reaction with hydrogen to form PdH_x. Nonetheless, there are still some disadvantages involved with pure palladium material such as the phase transition at low H_2 concentrations down to 7 Torr at 300 K, which is an irreversible process [27]. Moreover, the response time is not ideal for real-time monitoring of flowing hydrogen gas streams [28]. In our previous work, Pd was modified by introducing Ag to make a mixed metal nanofilm to overcome these problems, and the Pd/Ag nanofilm demonstrated fast response and good reversibility toward hydrogen gas at room temperature [29].

In this work, the feasibility of a SnO_2–Pd–Au system for hydrogen sensing was studied and evaluated. A thin film sensor was fabricated by a simple electroless plating approach to deposit Pd, Au and nanostructured SnO_2 onto the surface of an alumina substrate, and the electric resistance change of the SnO_2–Pd–Au system upon exposure to various concentrations of hydrogen at room temperature was recorded as the sensing signal. The fabrication process and characterization of the SnO_2–Pd–Au system as well as the sensing performance are presented and discussed. Based on the sensing performance, a possible mechanism for room temperature hydrogen sensing for the Pd–SnO_2 system is also proposed.

2. Experimental

2.1. Preparation of the SnO_2 nanosheets

SnO_2 nanosheets were synthesized using one-pot hydrothermal method as previously reported [15]. Briefly, tin dichloride dihydrate ($SnCl_2{\cdot}2H_2O$, Alfa Aesar, 98%) was added to an ethanol solution at pH around 11 to reach a Sn (II) concentration of 15.8 mM. Upon formation of white turbid suspension, the solution was magnetically stirred for 1 h. After transferred to a Teflon-lined stainless steel autoclave and then heated in a muffle at 120 °C for 6 h, a yellow product was prepared after centrifugation and dried at 50 °C overnight. The product was characterized by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, Philips FEI 200CX). The synthesized SnO_2 nanosheets were used in the following experiment without any further treatment.

2.2. Fabrication of the SnO_2–Pd–Au film sensor

SnO_2–Pd–Au film sensors were fabricated using composite electroless coating technique as previously reported [30]. A pre-cleaned piece of 1 cm × 1 cm alumina substrate was calcined at 500 °C for 2 h, thereafter immersed in a freshly prepared $SnCl_2$ solution (30 g/L) following with a $Ag(NH_3)_2OH$ solution (10 g/L) for 10 min each. After each step, the substrates were rinsed with de-ionized water to remove unreacted species. Then the surface activated alumina substrate was transferred to a small beaker, which contains 0.0143 g Na_2SO_3 (97.0%, Yongjia Chemical Reagent Co., Zhejiang), certain amount of $PdCl_2$ (AR, Xinliang Chemical Reagent Co., Shanghai) and the as prepared SnO_2 nanosheets dispersed in 1 mL de-ionized water, and sonicated for 10 min. Subsequently, the beaker was transferred to an ice water mixture, added in 50 μL $Na_3Au(SO_3)_2$ (Au 50 g/L, Changzhou Chemical Institute, Jiangsu) and 50 μL formaldehyde (AR, Sinopharm Chemical Reagent Co., Shanghai). Twenty minutes later, the substrate was coated with a gray metallic thin film, and let dry under ambient condition. Field emission scanning electron microscope (FSEM; FEI, SIRION-100) and X-ray energy dispersion spectroscopy (EDS; EDAX, GENESIS 4000) were applied to characterize surface morphology of the SnO_2–Pd–Au thin film deposited on the alumina substrate. EDS was conducted by scanning a relatively large region (about 10 μm × 10 μm) to produce an average Pd/Sn ratio for each sample. X-ray photoelectron spectroscopy (XPS; VG ESCALAB MARK II) was performed to figure out the oxidation state of Pd in the film.

2.3. Sensing performance

The film sensor was linked to an Agilent 34901A data acquisition/switch unit, and then placed in the middle of a quartz chamber connected to a gas flowing system. Flow rates of hydrogen gas and synthetic air were controlled and monitored with float-type flowmeters (Huanqiu LZB-4). Various concentrations of hydrogen were realized by dilution of hydrogen gas with synthetic air during the tests. Change in electric resistance of the thin film upon exposure to different hydrogen concentrations was recorded as the sensing signal. In the experiment, at first, synthetic air was flown into the test chamber until constant sensor resistance was obtained as R_0. Then different concentrations of hydrogen gas were introduced into the system and changed electric resistance of the sensor upon exposure to hydrogen was recorded as R. The response of the sensor is defined as the relative resistance change:

$$S = \left| \frac{R - R_0}{R_0} \right| \times 100\% \quad (1)$$

The influence of annealing treatment for the sensing element was also studied. Some film sensor was annealed at 100 °C and 200 °C in air for 2 h in sequence and the sensing performance toward hydrogen after the annealing treatment was evaluated. All gas sensing tests were conducted at room temperature (20 ± 1 °C with a relative humidity of 36–50%).

3. Results and discussion

3.1. Characterization of the SnO_2 nanosheets and the SnO_2–Pd–Au thin film

The as prepared SnO_2 was characterized by SEM and TEM. Fig. 1(A) and (B) display SEM images of the as prepared SnO_2. The assembled nanosheets show a three-dimensional, flower-like morphology. The inherent structure is shown in a TEM image (Fig. 1C). In this diagram, light regions suggest planar or bended thin sheets lying on the substrate, with the edge length most likely no more than 100 nm in both dimensions. While dark regions indicate that the sheets may either lie aslant, perpendicular to the substrate or spontaneously convolute during the reaction process. XRD result (see Supporting information of Ref. [15]) indicates that the SnO_2 nano sheets have a pure tetragonal rutile phase which is essential for SnO_2 based gas sensors.

During the electroless SnO_2–Pd–Au film fabrication, excessive formaldehyde would reduce both Au^{3+} and Pd^{2+} to elemental Au and Pd, which endowed the film a metallic color and improved its electric conductance. XPS results indicated a single oxidation state of Pd at the bonding energy of elemental Pd (3d 5/2, 335.0 eV) (Supporting information available).

The fabricated SnO_2–Pd–Au composite film deposited on the alumina substrate was characterized by SEM and EDS. Fig. 2(A) displays an SEM image of the bare alumina substrate, which has a pebble-like surface with micron level roughness. Fig. 2(B) and (C) shows SEM images of the SnO_2–Pd–Au thin film deposited on the alumina substrate. From the diagrams, the alumina substrate is coated with a layer of metal consisted of nano grains of Au and Pd. The SnO_2 nanoparticles can be identified by the relatively large size