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Full Length Article

CO sensing properties and mechanism of Pd doped SnO_2 thick-films

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ABSTRACT

Pd doped SnO_2 nano-particles were synthesized using co-precipitation method. The resistances of the samples first decrease and then increase, which maybe influenced by the Pd doping and temperature effect. The CO response of SnO_2 was improved by doping with Pd. At low temperature range, the response decreases with increasing of operating temperature, which was caused by the physical adsorption. At higher operating temperature (160–400 °C), the response of Pd doped SnO_2 for CO increases at first, undergoes a maximum at 260 °C, and finally drops. The 1.5 wt.% PdO doping SnO_2 was verified to be significantly sensitive. The largest gas sensitive response of 6.59 was found at 260 °C in 400 ppm CO atmosphere. For 200 ppm CO, the response and recovery time were about 43 s and 10 s, respectively. The possible CO sensing mechanisms for Pd doped SnO_2 sensors were investigated with first principles calculations. The calculation results showed that CO molecule can grab O from the pre-adsorbed oxygen on Pd_4 cluster or the PdO cluster on the SnO_2 (110) surface forming CO_2. These processes may play important role in CO sensing for Pd doped SnO_2. The calculated result is a good explanation of the experimental observation.

1. Introduction

Carbon monoxide (CO) is a colorless, odorless, hazardous, and poisonous gas, which results from the incomplete combustion of fossil fuels in automobiles, power plants and industrial plants. CO can cause great harm to the body by bonding tightly with the hemoglobin, preventing the combination to oxygen [1]. The permissible exposure limit for CO recommended by the US Occupational Safety and Health Administration (OSHA) is 35 ppm (ten h ceiling limit), whereas the US National Institute for Occupational Safety and Health (NIOSH) suggests a limit of 50 ppm (eight h ceiling limit) [2]. Accordingly, there is a need to develop highly sensitive, selective, and reliable sensors for detection of low CO concentrations in factories, indoor atmosphere, vehicle emissions and natural gas emission real-time. Several types of CO sensor have been proposed and some have already become commercially available [3–25]. Among them, the sensing materials of metal oxide demonstrating some advantages such as structure stability, high sensitivity and inexpensive cost have attracted more and more attention in recent years. As an *n*-type semiconductor with wide band gap (Eg = 3.6 eV), SnO_2 has excellent chemical adsorption and electrical properties toward oxidizing and reducing gases detection [3–7]. The resistance of the *n*-type semiconductor sensor decreased abruptly on the injection of CO, and then increased rapidly and recovered to its initial value after the test gas was released. The most accepted mechanism for gas sensing in semiconductor materials, involves the adsorption of oxygen species on its surface. When the sensors were exposed to air, O_2 adsorb on the surface and create chemisorbed oxygen species by capturing electrons from the *n*-type semiconductor surface which decreases their conductivity. When the reducing gases such as H_2, CO and NO are introduced at moderate temperature, the reducing gases may react with oxygen species adsorbed on the outer surface of *n*-type semiconductor and releases the trapped electrons back to the conduction of *n*-type semiconductor, which increases the carrier concentration and decreases the resistance of *n*-type semiconductor [7,16]. Therefore, the gas sensing properties of metal oxides are closely related to their chemical composition.

Many efforts have been made to improve the performance of SnO_2 through modulating the microstructure, surface modification with heavy metal elements and doping with metal elements. Among these, modification surface properties by coating SnO_2 with heavy metals like Au, Ag, Pd, Pt has been known to be effective for improvement the sensing performance [9–18] due to their exceptional catalytic activities, brought about by the adsorption of an analyte such as CO and H_2 on the surface of the sensor. Several Pd doped SnO_2-based carbon monoxide sensors have been reported in the literature. For instance, Marikutsa et al. have reported that

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the Pd-modified SnO_2 nanocrystalline prepared by sol–gel method shows better gas sensing performances to SnO_2 compared with the pure homogeneity [9]. Yin et al. reported that Pd doping SnO_2 thin films exhibit improved CO sensing performances [19]. Schweizer-Berberich et al. have reported that the Pd-doped SnO_2 nanoparticle show distinctly enhanced CO sensing properties [20]. Trung et al. found that Pd nanoparticles decorating on the surface of SnO_2 nanowires with hydrothermal method show distinctly enhanced CO sensing properties [21]. Lee et al. reporated that the PdO decoration on the SnO_2 prepared by RF reactive sputter deposition promote response towards carbon monoxide compared with pristine SnO_2 [22]. Harbeck et al. also found that Pd-doped SnO_2 thin films show distinctly enhanced CO sensing properties [12]. The remarkable improvements in sensing behaviors based on the reported works about the Pd doped SnO_2 nanostructures so far have put forward an exciting opportunity for further enhancing the CO sensing performance of SnO_2. As reported, the dramatic improvement in sensing performance observed upon sensitization with Pd was ascribed to the combined effect of spillover of atomic oxygen formed catalytically on the Pd particles then migrating onto the tin oxide, and the back spillover effect in which weakly bound molecular oxygen migrate to the Pd and are catalytically dissociated [9,11,15,19–22,24,25]. As a result, both the delivery of activate species to, and the capture of precursors from the SnO_2 nanostructure surface are promoted by catalytically active Pd nanoparticles. Many papers have reported the sensing response of pure SnO_2 and Pd doping SnO_2, and most of them are performed at high temperatures. In this work, sensing performances to CO at room temperature for Pd doped SnO_2 and pure SnO_2 thick film sensors were investigated. Density functional theory (DFT) calculations have become a powerful research tool for providing information at the atomic and electronic levels in recent years and provide accurate energetic and electronic properties of materials. DFT has also been used to study the atomic and electronic structures, as well as the sensing mechanism of gases with doped and undoped SnO_2 surfaces. It is indicated from several literatures that on the CO sensing both of doped and undoped SnO_2 surfaces with the first principle calculations [1,26–32]. In this work, Pd was selected as the second metal oxide to couple with SnO_2, and the sensing performances of composites with different Pd contents were measured. The first principles calculations were performed in order to reveal the sensing mechanism of Pd doped SnO_2 in the consideration of oxygen in detail. The interaction modes of CO molecules with Pd_4 cluster or PdO cluster covered on SnO_2 surface are examined in the framework of ab initio calculations and the relationship of these results with experimental observations is also discussed.

2. Experimental

2.1. Synthesis and characterization of nanocrystalline SnO_2

The nanocrystalline SnO_2 powders were prepared by co-precipitation method. $SnCl_4{\cdot}5H_2O$ was dissolved in deionized water. An appropriate amount of $NH_3{\cdot}H_2O$ was added dropwise to the vigorously stirred solution. The final *pH* value was adjusted to about 8 to promote a complete precipitation. The resulting slurry was filtered, washed with distilled water repeatedly, and finally dried in air at 120 °C for 20 h. The dried powders were milled and preheated at 350 °C for 4 h.

Then, the powders obtained above were mixed with an appropriate amount of palladium chloride ($PdCl_2$) and milled for 2 h, followed by annealing in an oven at 600 °C for 5 h to obtain the SnO_2 powders doped with Pd at the ratio of 0 wt%, 1 wt%, 1.5 wt%, 2 wt% and 2.5 wt%. The structure of resultant powders was characterized by means of X-ray powder diffractions, transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS).

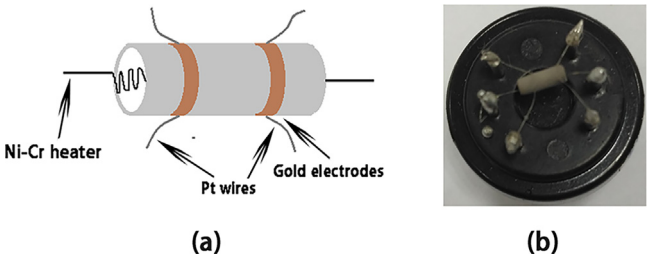

Fig. 1. (a) schematic diagram of the thick film sensor; (b) Fabricated sensor.

2.2. Fabrication and measurements of sensors

The as-prepared powders were mixed with a suitable amount of deionized water to form a homogeneous paste. The paste was coated manually onto a prefabricated alumina tube attached with a pair of gold electrodes and platinum wires to form a thick film, then a Ni–Cr heating wire was inserted in the tube to form a inside-heated gas sensor. The sensors are annealed at 240 °C for 48 h on the aging equipment in air. The schematic image and photograph of the as-fabricated sensor are shown in Fig. 1. The gas sensing response in the experiment is defined as $S = R_a/R_g$, where R_a is the initial sensor resistance and R_g is the resistance during the exposure.

3. Results and discussion

The X-ray diffraction patterns of pure SnO_2 and Pd/SnO_2 composites with different Pd mass ratios annealed at 600 °C for 5 h are shown in Fig. 2. All the major peaks can be indexed to the tetragonal rutile structure of SnO_2, which is consistent with the standard data file (JCPDS 21–1250). But there is no indication of the presence of any dopants-related diffraction peaks for the corresponding to the loaded Pd or PdO_x, which may be ascribed to the fact that the Pd content is much lower in the Pd-doped SnO_2, compared to Sn or O. The difficulty detecting the Pd-doped sample may be also due to the overlap of diffraction peaks [11]. The average grain sizes D were estimated by means of Scherrer method. The obtained D values were about 11 nm, 10 nm, 6 nm, 9.1 nm and 6 nm for SnO_2 with doped $PdCl_2$ concentration of 0, 1, 1.5, 2 and 2.5 wt%, respectively. A high-resolution TEM (HRTEM) image and the corresponding selected area electron diffraction (SAED) pattern of the powders SnO_2 with 1.5 wt% Pd addition are shown in Fig. 3 indicating that the sample has the tetragonal SnO_2 rutile structure indeed. However, no palladium containing phases have been detected apparently owing to its low content.

The temperature dependence of the resistances in air for Pd doped SnO_2 thick film sensors are shown in Fig. 4. The resistance of the sensor is largely modified by Pd doping. As reported, the Pd mainly exited on the surface of SnO_2 in the form of PdO [9,10,14,22–24,33,34]. The electrical conductance of the SnO_2 thin film at room temperature is decreased after the doping of Pd, indicating the formation of the P-N junction between the SnO_2 support and PdO [22]. Similar conductance reduction for Pd-decorated *n*-type oxides have been reported previously [34,36–38]. In the temperature range 80–400 °C, the resistance of pure SnO_2 decreases with the increase of working temperature. It shows the semiconductor characteristic. From 20–250 °C, the resistances of Pd doped SnO_2 first decrease and then increase. It may be caused for the doping of Pd and the Pd exhibits strong metallic properties. At the temperature range from 250 °C to 400 °C, the number of carriers increases with the increasing of temperature and the resistances of Pd doped SnO_2 decrease. The observed decrease in