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A novel hetero-structure sensor based on Au/Mg-doped TiO_2/SnO_2 nanosheets directly grown on Al_2O_3 ceramic tubes

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ABSTRACT

Chemiresistive gas sensors with novel nanostructures, high response and reliable fabrication process have been fabricated successfully by designing Au/Mg-doped TiO_2/SnO_2 nanosheets hetero-structures. Mg doping was used to decrease the work function of TiO_2, which can lead to the electrons in TiO_2 greatly depleted due to the formation of Schottky contact and *n-n* heterojunction. SnO_2 nanosheets were directly grown on Al_2O_3 tube with a cost-effective hydrothermal process. By employing pulsed laser deposition (PLD) and direct current sputtering methods, the construction of gold (Au) nanoparticles-loaded Mg-doped TiO_2/SnO_2 heterostructure is highly controllable and reproducible. In comparison with pristine SnO_2 and TiO_2/SnO_2, Mg-doped TiO_2/SnO_2 sensors exhibit high response (30.4) and short response time (9 s) to 50 ppm TEA gas, which is about 6 times higher than pure SnO_2 sensor and 2 times higher than TiO_2/SnO_2 sensor at a working temperature of 260 °C. The mechanism for sensing property enhancing of the Au/Mg-doped TiO_2/SnO_2 sensor was also discussed in detail with the semiconductor depletion layer model introduced by Au-TiO_2 Schottky contact and TiO_2/SnO_2 *n-n* heterojunction.

1. Introduction

Tin dioxide (SnO_2), as one of the most important n-type oxide semiconductor with wide band gap energy of 3.6 eV, has been widely used for gas sensors [1–4]. It has been well reported that the sensing performances of SnO_2 nanomaterials are greatly affected by the geometrical factors and surface area [5–7]. Therefore, it is highly important to construct a special morphological moiety which possess higher surface to volume ratio and hence show better sensing performance [7]. In this direction, many efforts have been paid to develop novel structures of SnO_2, such as SnO_2 nanowires [8–10], SnO_2 nanotubes [11,12], SnO_2 nanosheets [7,13,14], and so on, to improve the gas sensing properties. Particularly, SnO_2 nanosheets have been paid great attention due to their high surface area to volume ratio and stability [14–16]. For example, Lee et al. [14] synthesized sheet-like SnO_2 powder at room temperature. Then, Wang et al. [17] fabricated three-dimensional (3D) hierarchical tin dioxide (SnO_2) nanoflowers constructed by two-dimensional (2D) nanosheets by a simple one-pot low-temperature (90 °C) hydrothermal strategy. However, these cannot be used for wide practical applications because of the power-consuming and low-yield process of sensor fabrication [18]. In 2010, Bie et al. [19] synthesized SnO_2 nanosheets directly on Al_2O_3 tube, which simplified the sensor fabrication process, but the high working temperature and low response hinder their applications. Thus, a gas sensor with low working temperature and high response is in urgent need.

Recently, hetero-nanostructures consisting of two or more metal oxides and noble metal particles sensitized oxide semiconductor have attracted increasing attention due to their possibilities of integrating the physical and chemical properties of these oxides, which may improve the sensing performances [20]. The sensing mechanism can be explained by the Schottky contact or spillover effect of noble metal and the change of resistance caused by formation of heterojunction. For example, Li et al. [21] prepared Au@ZnO yolk-shell nanospheres gas sensor and its response to 100 ppm acetone was about 2 ~ 3 times higher than that of ZnO hollow (solid) nanorods. Lee et al. [22] synthesized ZnO-In_2O_3 composite nanofibers, which exhibited higher response and selectivity to TMA than pure ZnO or In_2O_3 nanofibers. Kim et al. [23] prepared CuO-ZnO composite hollow spheres, showed much

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higher response to H_2S than pristine ZnO hollow spheres. Based on the above theoretical mechanisms, a new designing nanostructure, like M-MOS-MOS nanostructure, may further improve the sensing performances.

Here, a new nanostructure of Au/Mg-doped TiO_2/SnO_2 nanosheets was designed, based on the Schottky contact of Au and TiO_2, and heterojunction of TiO_2 and SnO_2 nanosheets. The pristine SnO_2, TiO_2/SnO_2, and Mg-doped TiO_2/SnO_2 and Au/Mg-doped TiO_2/SnO_2 nanosheets were directly grown on the Al_2O_3 tube by combination of hydrothermal method and pulsed laser deposition and DC- sputtering process, which can be used directly for gas sensor without slurry-coating fabrication process. As an n-type semiconductor with a wide bandgap of 3.2 eV [24], TiO_2 has been well known and used as gas sensing material because of its reversible and large changes in the electrical resistance and the exceptional chemical stability [25]. Mg doping was used to lower the work function of TiO_2, which can lead to the electrons in TiO_2 greatly depleted due to the formation of Schottky contact and *n-n* heterojunction in addition with the adsorption of oxygen molecules. The sensor measurement results indicate that Au/Mg-doped TiO_2/SnO_2 nanosheets sensor exhibit a dramatic response enhancement to TEA gas which is about 6 times higher than pure SnO_2 sensor and 2 times higher than TiO_2/SnO_2 sensor at relative low temperature (~260 °C). The sensing properties and their gas sensing mechanism are discussed in detail in the following sections.

2. Experimental

2.1. Direct growth of SnO_2 nanosheets on Al_2O_3 ceramic tubes

All the chemicals were purchased from Sinopharm Chemical Reagent (Shanghai, China). SnO_2 nanosheets were prepared by a typical procedure, 0.9026 g $SnCl_2{\cdot}2H_2O$ was dissolved in 100 ml distilled water to prepare a 0.04 M $SnCl_2{\cdot}2H_2O$ solution. After that, this solution was mixed with 0.04 M $CO(NH_2)_2$ solution under stirring. Finally, the mixed solution and the cleaned Al_2O_3 tubes with predesigned gold electrodes were transferred into Teflon-lined stainless steel autoclaves, sealed and heated at 95 ∘C for 24 h. Then the obtained nanosheets sample was thoroughly washed with deionized water and ethanol several times and finally annealed at 500 °C for 4 h.

2.2. Growth of TiO_2/SnO_2 heterojunction nanosheets and loading of Au nanoparticles

TiO_2 targets doped with MgO of different atomic concentration (0 and 2 mol%) made from 5 N powders were first pressed at 10 MPa and then sintered at 1200 °C for 10 h. And a layer of Mg-doped TiO_2 nanoparticles with different atomic concentration (0 and 2 mol%) was deposited onto the surface of SnO_2 nanosheets by pulsed laser deposition (PLD) with 1000 laser pulses at room temperature. A KrF laser of 1 mJ/cm^2 and an oxygen partial pressure of 3×10^{-4} Pa were typically applied. The TiO_2/SnO_2 nanosheets heterojunction with pristine and Mg doped TiO_2 nanoparticle layer were grown. After that, Au nanoparticles were loaded onto the core-shell nanosheets by DC- sputtering with working time of 30 s. Thus, different gas sensors directly fabricated with SnO_2 nanosheets, named as S sensor, and TiO_2/SnO_2 nanosheets heterojunction, named as ST sensor, Mg-doped TiO_2/SnO_2 heterojunction, named as STM sensor, and the last named STMA sensor (Au/Mg-doped TiO_2/SnO_2) were ready for further measurement. The specific process was shown in Fig.1.

2.3. Material characterizations and sensor properties

The morphology microstructure, and composition of TiO_2/SnO_2 nanosheets were measured by a field emission scanning electron microscope (FESEM, FEI QUANTA FEG250) equipped with an energy dispersive X-ray spectroscopy (EDS, INCA MAX-50) and a high-resolution transmission electron microscope (HRTEM, JEM-2100 F, JEOL) with an energy dispersive X-ray spectroscopy (EDX, OXFORD LINK-ISIS). The phase composition and purity of the SnO_2 nanosheets was examined by X-ray diffraction (XRD, D8-Advance, Bruker). X-ray photoelectron spectrum (XPS) analysis was conducted using an Al KaX-ray source (1486.6 eV) on a Thermo-VG ESCALAB MKII spectrometer. The gas sensing properties were tested using a computer-controlled WS-30 A gas-sensing measurement system. The test gas was injected into the testing chamber using a micro-syringe and the concentrations of the target gases were obtained by the static gas distribution method, which was calculated by the following formula [26]:

$$Q = \frac{V \times \phi \times M}{22.4 \times d \times \rho} \times 10^{-9} \times \frac{273 + T_R}{273 + T_B} \quad (1)$$

Where Q (mL) is the liquid volume of the volatile compound, V (mL) is the volume of the testing chamber, ϕ is the required gas volume fraction, M (g mol^{-1}) is the molecular weight, d (g cm^{-3}) is the specific gravity, and ρ is the purity of the volatile testing liquid, T_R and T_B (°C) are the temperatures at ambient and test chamber, respectively. At a certain TEA concentration, the corresponding response of the sensor increases rapidly and reaches its equilibrium. Once the target gas is removed, the response decreases quickly to the baseline. The sensor response is defined as the ratio of the resistances measured in air (R_a) and in the tested gas atmosphere (R_g): $S = R_a/R_g$. The response time (T_{res}) is defined as the time required by the sensor to achieve 90% of its maximum response after the gas injection, whereas the recovery time (T_{recov}) is the time taken by the sensor to reach 10% of its initial resistance after removal of the gas.

3. Results and discussion

3.1. Characterizations of SnO_2–based nanosheets

The general morphologies of the SnO_2 materials grown directly on Al_2O_3 tubes were investigated by FESEM and the results are demonstrated in Fig. 2(a). As confirmed by the FESEM observations, the prepared material stands vertically on the substrate and grown in very high density. The thickness of a typical single SnO_2 nanosheet is ~15 nm. Moreover, the thickness of sensing layer on the surface of the Al_2O_3 tube is about 170 nm as shown in Fig. S3 in the supplementary material. Interestingly, it was observed that the nanosheets interconnect with each other and form an open network with large surface area that could increase the adsorption sites and contribute to the adsorption of target gas molecules. To examine the phase composition and purity, the prepared SnO_2 nanosheets were analyzed by X-ray diffraction pattern. Fig. 2(b) shows the typical XRD pattern of the prepared SnO_2 nanosheets. It was observed that the XRD pattern exhibit sharper and clearer diffraction peaks and all the observed diffraction peaks are indexed to tetragonal rutile structure of pure SnO_2 and matched with JCPDS Card No. 41-1445. Except for SnO_2, no other diffraction reflections were detected in the pattern, which further confirms that the SnO_2 nanosheets are well crystalline and pure SnO_2. Fig. 2(c) shows the morphology of SnO_2 nanosheets after a thin layer of TiO_2 nanoparticles was deposited onto their surface by PLD process with laser pulses of 1000. The corresponding EDS spectrum of TiO_2/SnO_2 samples shows the peaks of Ti, Sn and O clearly, as shown in Fig. 2(d). The peaks of Al can be also observed in the spectra, which are attributed to the Al_2O_3 tube. In order to further regulate the sensing performance of SnO_2 nanosheets sensor, we synthesized Mg-doped TiO_2/SnO_2 nanosheets, as shown in Fig. 2(e–f), which clearly shows the peak of Mg. After that, the nanosheets were also decorated by Au nanoparticles, and the corresponding FESEM and corresponding EDS pattern were shown in Fig. 2(g–h).

Furthermore, TEM was used to characterize the nanostructure and crystallinity of the synthesized Au/Mg-doped TiO_2/SnO_2 nanosheets. Fig. 3(a) is the typical TEM image of sheet-like SnO_2. For the SAED