Research on the Sensing Behaviors of Tin Oxide Based Chemical Sensor to Methane

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Abstract

In this study, pure and metal doped SnO2 nanostructures were successfully prepared via a facile and simple hydrothermal method, and characterized by X-ray powder diffraction and scanning electron microscopy, respectively. Based on the Scherrer formula, the average particle size of the synthesized samples was calculated to be about 30 nm. Thick film sensors were fabricated and their sensing behaviors to methane were investigated. The optimum operating voltage for the fabricated pure and doped sensor to CH4 gas were measured at 5.0 V and 4.0 V, and the corresponding maximum response value were 1.90 and 5.53. And the response and recovery time of the doped sensor to CH4 is 23 s and 37 s, respectively.

Keywords

Sensing behaviors, tin oxide, chemical sensor, methane.

1. Introduction

Power transformer is the core of the power system. As one of the most important apparatus in power transmission, its operation conditions directly affect the safety and reliability of the power system [1]. Once the power transformer malfunction, it will give the national economy caused great damage. At present, most of the large power transformers are still oil-immersed transformers, when the transformer internal paper oil insulation fault occurs due to overheating or partial discharge, it may generate gaseous compounds such as hydrogen, carbon oxides, low molecular hydrocarbons and most of them may dissolve in transformer oil [2-4]. Many effective off-line and on-line diagnostic methods, like dissolved gas-in-oil analysis or the Duval Triangle method, have been established over the years for preventive and predicative maintenance of power transformer [5].

Semiconductor metal oxide nanostructures have appealed a large amount of interests in the past few years resulting from their electronic and physical properties [6]. It provides a substantial promising candidate for a wide range of applications, such as catalyst materials, solar cell, magnetic materials, optoelectronic devices, and gas sensors. Among all semiconductor metal oxides investigated, SnO_2 with a wide direct band gap Eg = 3.6 eV has attracted an eye-catching attention due to its physical and chemical properties. It has been frequently utilized to detect a great deal species of gases, both for oxidizing and reducing gases, like NH_3, H_2S and C_2H_5OH, resulting from their high selectivity and sensitivity.

It is generally known that the morphologies of the sensing materials or doping modification have a direct and significant influence on the sensing performances of the sensor to a tested gas, such as sensitivity, selectivity and response time. In this paper, we employed the hydrothermal reaction method to prepare pure and doped SnO_2 sensing materials and investigate their sensing properties to methane.

2. Hydrothermal Synthesis

All of chemicals utilized are of analytical purity reagents from Chongqing Chuandong Chemical Reagent Company and are used without any further purification. In a typical procedure of hydrothermal reaction for pure SnO_2 nanostructures, 3.5 g of $SnCl_4 \cdot 5H_2O$, was dissolved into 30 ml basic mixture of ethanol and water (1/1, V/V) to form a transparent solution in a breaker possessing

50 ml capacity. Then, 4.2 ml of hydrochloric acid and 0.3 g PEG was added into the mixture solution under magnetically vigorous stirring for 30 min. Hereafter, the solution was transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 160 °C for 24 h in an electric furnace. After reaction, the autoclave was cooled to room temperature naturally, harvested by centrifugation, washed with distilled water and absolute ethanol several times to remove the ions possibly remaining in the final product, and finally dried at 80 °C in air for further use. Doped SnO_2 samples were obtained in the same process mentioned above, and some metallic salts like Pd, Pt, Ag, Rh, Ir were added to the precursor solution.

3. Structural Characterization

X-ray powder diffraction XRD was taken to identify the crystalline phase composition of the prepared SnO_2 samples over the range of 20–80° with Cu radiation as the X-ray source.

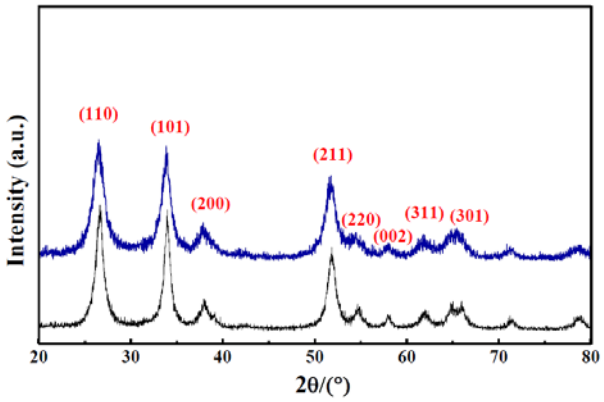

Fig. 1 The XRD patterns of the synthesized pure and doped SnO2 nanostructures

On can clearly see in Fig. 1 that for both samples the main characteristic peaks (110), (101), (211) appeared in 27.9 °, 34.3 °, 52.4 ° respectively, perfectly indexed corresponding to the tetragonal rutile phase of SnO_2 with lattice constants of a=4.738 Å and c=3.188 Å. The average particle size of the sample is measured from the XRD peaks based on the Scherrer formula,

$$D=0.89\gamma/(\beta\cos\theta) \quad (1)$$

Where D is the mean particle size of the powder, γ is the X-ray wavelength, β is the full-width at half maximun of XRD peaks and θ is the bragg angle. According to the broadending of the (110) diffraction line, the average particle size calculated is about 30 nm.

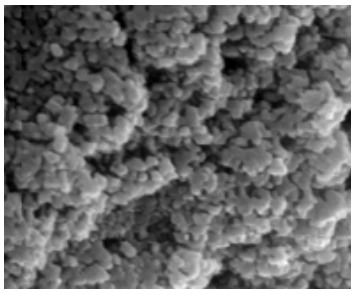

Fig. 2 The SEM image of the synthesized doped SnO2 nanostructures

The surface morphology of the synthesized pure and doped SnO_2 nanostructures was characterized using scanning electron microscopy SEM. Fig. 2 shows the SEM image of the prepared doped SnO_2 samples. The sample exhibits good dispersion, and the particles are uniform in shape and particle size.

4. Sensing Behaviors

The gas sensors based on the synthesized sensing materials were fabricated using thick films. Firstly, the obtained sample was dispersed in the ethanol into slurry, and then it was coated on to an Al_2O_3 ceramic tube by a small brush to form a thick film between two parallel Au electrodes, which had been previously printed on the tube. The thickness of sensing films was about 10-20 um. There are

two Au electrodes, which are placed at the both end sides of the tube. Then, a Ni-Cr heating wire was inserted into the tube. The distance between two electrodes is estimated to be 6 mm, and the diameter of the tube is 1.2 mm. Finally, the fabricated sensor was dried in air at 80 °C to volatilize the organic solvent and further aged in an aging test chamber for 36 h.

Table 1 Sensitivity of the sensors to 100 μL/L of CH4 at different working voltage

	3.5 V	4.0 V	4.5 V	5.0 V	5.5 V
Pure SnO_2	1.23	1.56	1.71	1.90	1.45
Doped SnO_2	2.47	5.53	3.89	3.13	2.42

Gas sensing studies are carried out under laboratory condition with room temperature and humidity. The relative variation of the gas sensor resistance, gas response, in this paper is defined as S = Vg/Va, where Vg and Va represent the testing voltage of the sensor in N_2 and in targeted gas, respectively. The response and recovery time were defined as the time required by the sensor to achieve 90% of the total resistance change in the case of gas adsorption or gas desorption. All gas-sensing property measurements were repeated several times in order to ensure the reproducibility of the gas sensing response. Table 1 and Fig. 3 show the sensitivity of the pure and doped sensors to 100 μL/L of CH_4 at different working voltage.

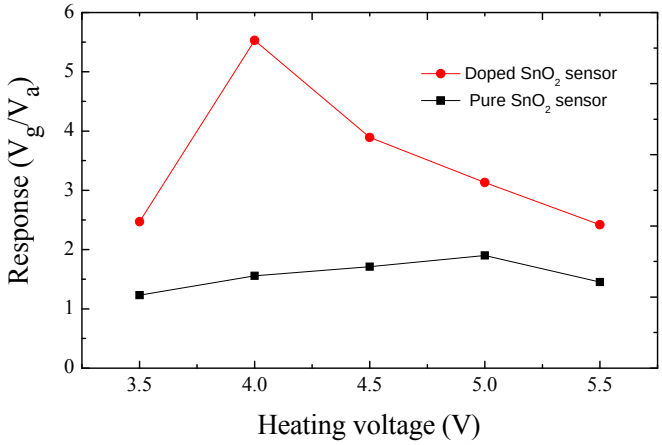

Fig. 3 Sensitivity of the sensors to o 100 μL/L of CH4 at different working voltage

As shown in Table 1 and Fig 3, for each sensor, its response value increases rapidly and obtains the maximum value, and then decreases with further increasing working voltage. The optimum operating voltage of the fabricated pure and doped sensor to CH_4 were measured at 5.0 V and 4.0 V, where the sensor exhibits the maximum gas response. And the corresponding maximum response value is 1.90 and 5.53, respectively. According to the definition above, the response and recovery time of the doped sensor is measured to be about 23 s and 37 s, respectively.

5. Conclusion

SnO_2 based nanostructures were successfully prepared via a facile and simple hydrothermal method, and characterized by X-ray powder diffraction and scanning electron microscopy, respectively. The average particle size of the synthesized samples was measured to be about 30 nm. The optimum operating voltage of the fabricated pure and doped sensor to CH_4 gas were 5.0 V and 4.0 V. The corresponding maximum response value were 1.90 and 5.53. The response and recovery time of the doped sensor to CH_4 were 23 s and 37 s, respectively.

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