Nano SnO_2 Based Gas Sensor for Formaldehyde Gas Detection

ZENG Wen, LIU Tian-mo
(College of Materials Science and Engineering, Chongqing University, Chongqing 400030, China)

Abstract: Nano SnO_2 powder was prepared with sol-gel method. The crystallite size and structure of this material were characterized with X-ray diffraction (XRD) and atomic force microscope (AFM). The gas sensors were made from mixed solid powder which contained nano SnO_2 base doped with nano TiO_2 powder (molar ratio of SnO_2 to TiO_2 of 9 ∶ 1) and Ag^+ (content of Ag^+ of about 0.2%—0.4% according to the molar ratio). The formaldehyde gas sensing properties of this mixed solid powder were characterized with gas sensing measurement. Test results show that SnO_2 based gas sensors exhibit good sensitivity to 200×10^{-6} formaldehyde gas at operating temperature of 300 ℃ and good gas sensing selectivity to formaldehyde at different operating temperatures. The result of theoretical calculation shows that difference in orbital energy of gas molecular is a qualitative factor for gas sensing selectivity at different operating temperatures.

Keywords: SnO_2; formaldehyde; gas sensor

纳米 SnO_2 基气敏元件对甲醛气体的检测

曾 文, 刘天模
(重庆大学材料科学与工程学院, 重庆 400030)

摘 要: 采用溶胶-凝胶法制备了纳米 SnO_2粉末,利用 X射线衍射仪 (XRD)以及原子力显微镜 (AFM)对材料的晶体结构及晶粒尺寸进行了表征. 采用制备的纳米 SnO_2作为基底材料,掺杂纳米 TiO_2粉末 (SnO_2与 TiO_2的物质的量之比为 9∶1)以及少量的 Ag^+ (物质的量百分比为 0.2%～0.4%),以此材料制成气敏元件,检测了元件的甲醛气敏性能. 结果表明:该元件在工作温度为 300 ℃时,对 200×10^{-6}的甲醛具有较好的敏感性,在不同的工作温度下,元件表现出良好的气敏选择性. 理论计算表明,气体分子轨道能量的差异是元件气敏选择性的定性因素.

关键词: SnO_2; 甲醛; 气敏元件
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It is well known that reducing the gases to be detected removes some of the adsorbed oxygen and modulates the height of the potential barriers, thus changing the overall conductivity and creating the sensor signal[1-3]. Traditionally, metal oxides such as SnO_2 and TiO_2 have been used for sensors to reduce gas species such as CO and H_2. SnO_2 sensors utilize low temperature chemisorption (below 400 ℃) of environmental gases on the surface, which results in electron exchange and a change in its resistance. However, over 400 ℃, SnO_2 exhibits poor sensing performance. On the other hand, TiO_2 is stable at higher temperature but the sensitivity of TiO_2 sensors is usually not so good as that of SnO_2 sensors[4-7].

Recently, several attempts to combine the advanta-

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作者简介: 曾 文 (1982—),男,博士研究生.
通讯作者: 刘天模,教授, tmliu@cqu.edu.cn.

ges of TiO_2 and SnO_2 by mixing them together have been reported[8-10]. In this paper, a new sensing material SnO_2-TiO_2-Ag^+ solid powder system was obtained by mixing nano SnO_2 with TiO_2 (P25, 99.9% average grain size 25 nm) and Ag^+, and the gas sensing properties for formaldehyde of this material was tested.

1 Experiment

1.1 Preparation of nano SnO_2

Nano SnO_2 powder was prepared with sol-gel technology. $SnCl_4 \cdot 5H_2O$ (Wako Pure Chemical) was dissolved in 70 mL ethanol. The solution was well stirred and then refluxed for 3 h at 70 ℃. 35 mL aqueous ammonia solution (Wako Pure Chemical, 25%—27.9%) was added dropwise to the refluxed solution and the resulting precipitate was washed thoroughly with deionized water. Then SnO_2 colloidal solution was prepared by addition of deionized water. Finally the powder was annealed in air at 450 ℃ for 2 h, at a heating rate of 10 ℃/min.

1.2 Preparation of gas sensing material and gas sensor

Samples of gas sensing material were prepared by mixing SnO_2 powder prepared in the above way and TiO_2 (P25, 99.5% average grain size 25 nm). The mixing process was carried out by rubbing in the agate mortar for 10 times (1 h each time). The mixed powder was composed of 90% SnO_2 and 10% TiO_2.

The paste of mixed powder was formed by addition of suitable amount ethanol and $AgNO_3$ solution (content of Ag^+ about 0.2%—0.4%), which was then coated on Al_2O_3 tubes (4 mm in length, 1.2 mm in external diameter and 0.8 mm in internal diameter) where Au electrode wires had been fixed at each end. Finally, the ceramic tubes were sintered at 300 ℃ for 2 h after dried in air to remove ethanol. A small Ni-Cr alloy coil was placed through Al_2O_3 tubes to adjust the heating power.

1.3 Measurement and analyses

X-ray diffraction (XRD, XD-5A) analysis of the mixed solid powder was conducted using Cu radiation to determine its phases and grain size. The microstructure of nano SnO_2 was analyzed with atomic force microscope (AFM, CSPM4000).

Gas sensing properties of sensors were characterized with a static system. The static system consisted of a practically airtight chamber in which the sample was placed. The gas inlet and the air admittance valves were at the base plate in order to inject the test gas and air. In the static system, gas sensing properties of the sensor were tested in the following sequence. The temperature of the sensor was controlled by varying the current flow through the heater. The test gas was injected into the bell jar through a needle valve. The electrical characteristics of the sensor were observed by changing its temperature from 100 ℃ to 400 ℃ in air.

Gas-sensing studies were carried out in the static system under laboratory condition (30 ℃, 40% relative humidity) after the gas sensor was powered at 100 ℃ for 120 h in the air. In this paper, gas sensitivity was defined as the ratio of resistance (R_0) in air to that in the tested gas (R).

2 Results and discussion

2.1 Characteristics of nano SnO_2

2.1.1 XRD pattern of SnO_2

X-ray diffraction pattern of the SnO_2 powder annealed at 450 ℃ for 2 h is shown in Fig. 1. Compared with JCPDS (41-1445) standard pattern, the pattern reveals a rutile SnO_2 phase. The sizes of crystallites have been calculated with Scherrer formula[11]. The average size of crystallites for SnO_2 is 30 nm.

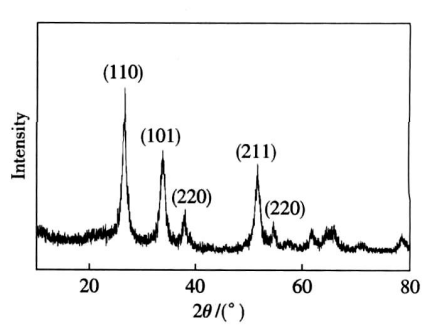

Fig. 1 X-ray diffraction patterns of SnO_2

2.1.2 AFM characterization of SnO_2

The microstructure of SnO_2 is analyzed with AFM. Fig. 2 shows the AFM image (Fig. 2(a) is ichnography and Fig. 2(b) is stereography) of the sample annealed at 450 ℃ for 2 h.

SnO_2 grains are island like and uniform in size distribution. The mean particle size of SnO_2 determined with

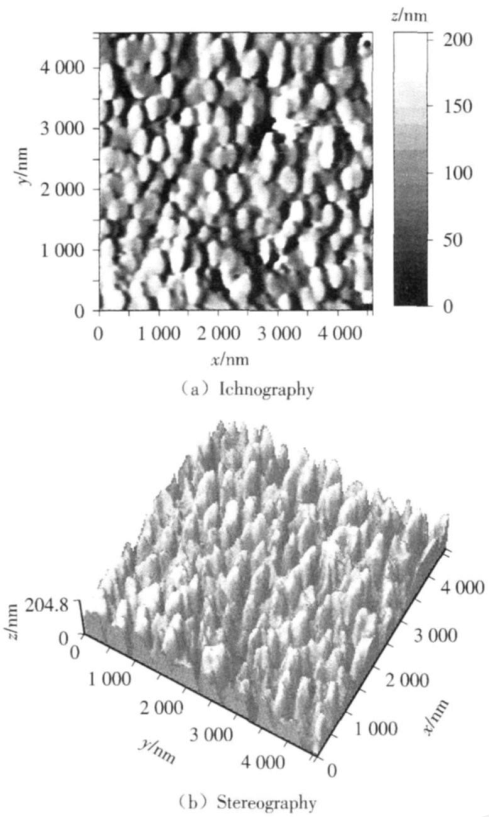

Fig. 2　AFM pattern of SnO_2

AFM is 38 nm, which is a bit bigger than the value obtained from XRD pattern. Because of the magnifying effect of AFM, the diameter of grains will be bigger than their real diameter [12].

2.2　Gas-sensing properties

The sensitivities to formaldehyde, methanol, acetone, toluene and xylene are shown as function of the operating temperature in Fig. 3.

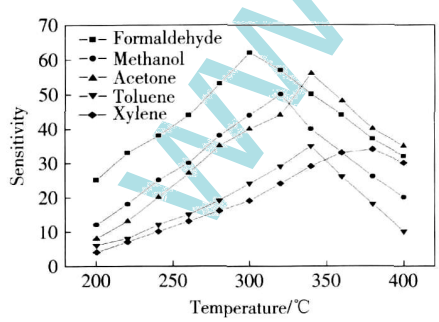

Fig. 3　Sensitivity vs. the operating temperature

The sensitivity is greatly affected by the operating temperature. The highest sensitivities to methanol, acetone, toluene and xylene are obtained at about 320—380 ℃, whereas the highest sensitivity temperature to formaldehyde is lower, at about 300 ℃. The maximum sensitivity to 200 $\times10^{-6}$ formaldehyde vapor is estimated to be 62 at 300 ℃. By changing the operating temperature, it is possible to predict VOCs (volatile organic compounds).

Fig. 4 shows the relationship between sensitivity and tested gas concentration for the sensor operated at 300 ℃ which is the optimal operating temperature to test formaldehyde. The sensor exhibits a good dependence on formaldehyde gas concentration from 50 $\times10^{-6}$ to 400 $\times10^{-6}$. The curve for formaldehyde gas is quasi-linear. It shows that the sensor exhibits good selectivity for formaldehyde gas, the sensitivity of which surpasses that of other interfering gases such as methanol, acetone, toluene and xylene at 300 ℃. Moreover, the sensitivity to 50 $\times10^{-6}$ formaldehyde gas exceeds 20, which can meet practical demand.

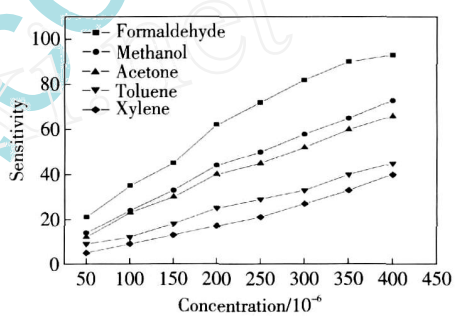

Fig. 4　Sensitivity vs. concentration at 300 ℃

Fig. 5 shows the typical response-recovery characteristic of the sensor to 200 $\times10^{-6}$ formaldehyde at 300 ℃. Response time and recovery time are the two important parameters to characterize sensors. Response time is defined as the time taken to reach 90% of the response after gas is introduced. Recovery time is defined as the time taken to reach 90% of the recovery after the gas is turned off. It is clearly shown in Fig. 5 that recovery is fast yet response takes more time. Response time and recovery time are 28 s and 17 s respectively.

In this paper, the stability of gas sensor is defined as the changing range of the sensitivity in a certain period of time. Sensitivity is measured every 5 days and the period is 50 days. The result is shown in Fig. 6.

The sensitivity of sensor to 200 $\times10^{-6}$ formaldehyde at 300 ℃ is between 19.7 and 20. Although the sensitivity decreases with time, the changing range of the sensitivity is 0.1—0.3. The sensor shows excellent stability in detection of the formaldehyde gas.

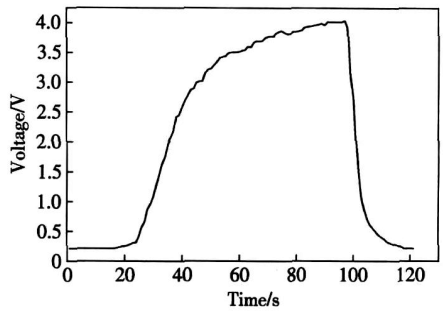

Fig. 5 Response and recovery behavior of the sensor to 200 × 10⁻⁶ formaldehyde at 300 ℃

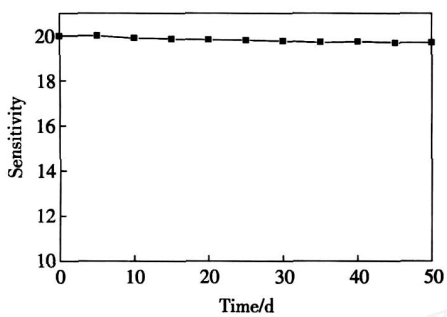

Fig. 6 Stability of the sensor to formaldehyde

2.3 Gas sensing mechanism

As has been generally reported, SnO_2 is a typical n-type semiconductor, and its gas sensing mechanism is surface controlled. With the increase of the operating temperature in the air, the atmospheric oxygen is adsorbed on the surface and grain boundaries, and exists in various forms, namely, O_2^-, O^-, O^{2-}, etc, as the following reactions occur[13]:

$$O_{2gas} \longrightarrow O_{2ads}$$

$$O_{2ads} + e^- \longrightarrow O_{2ads}^-$$

$$O_{2ads}^- + e^- \longrightarrow 2O_{ads}^-$$

$$O_{ads}^- + e^- \longrightarrow O_{ads}^{2-}$$

The valence electrons are trapped by the chemisorbed oxygen, which results in the increase in the resistance. When the sensors are exposed to the reduced gas such as formaldehyde gas, the chemisorbed oxygen can give rise to the following reaction:

$$HCHO\ (g) = (HCHO)_{ads}$$

$$(HCHO)_{ads} + 2(O_{ads})^{2-} = CO_2 + H_2O\ (g) + 4e^-$$

Electrons are released from the above reactions. Hence, the resistance of gas-sensing materials decreases and the detection of formaldehyde gas is realized.

Gas-sensing properties are affected by the surface adsorption which changes the surface energy and the conductance. The selectivity at different operating temperatures is decided by two factors: one is the energy of gas molecule of the LUMO (lowest unoccupies molecule orbit), and the other is the adsorption amount of the sensing material at different operating temperatures. If the energy of gas molecules of LUMO is lower, the reaction energy for gas sensing will decrease and the sensitivity will be enhanced. So the gas sensors can work at low operating temperature.

In different states of adsorption, the gas molecules present different electron affinities, which leads to different conductances of the gas sensor after adsorption of the gas. The electron affinity is affected by the energy of the molecule orbit. The lower the energy of LUMO, the stronger the capability of electron capture.

In order to analyze the selectivity of gas sensor at different operating temperatures, the distinction of the orbit energy of the VOCs gas has been analyzed with theoretical calculation. Gas molecule model for calculation has been built up with the ChemDraw program. The structure of gas molecule is shown in Fig. 7.

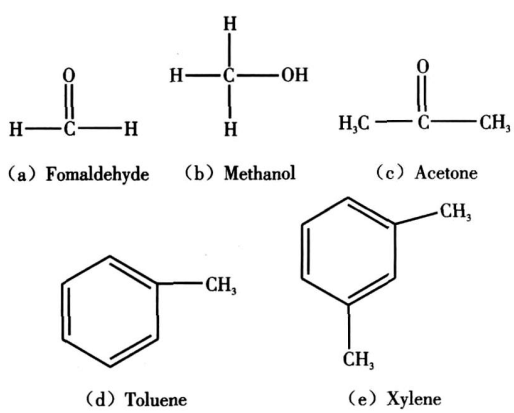

Fig. 7 Structure of gas molecule

The calculations are performed with Gaussian03 program. The ab initio Hartree Fock (HF) level of the theory has been employed with the contracted basis set for B3LYP/6-31G to calculate the energy of the HOMO (highest occupies molecule orbit) and LUMO.

As Tab. 1 shows, the capability of electron capture decreases in the order of formaldehyde, methanol, acetone, toluene and xylene. The ability of electric charge transfer between the gas molecule and surface of the sens-

ing material diminishes in the sequence of formaldehyde, methanol, acetone, toluene and xylene. At the low operating temperature of about 300 ℃, it has good sensitivity to formaldehyde, while the optimal operating temperature increases in the detection of other gases. It is a qualitative interpretation for the selectivity of gas sensor at different operating temperatures.

Tab. 1　Orbital energy of gas molecule

Gas molecule	HOMO	LUMO
Formaldehyde	- 0.437 28	0.165 72
Methanol	- 0.346 54	0.197 28
Acetone	- 0.396 14	0.229 25
Toluene	- 0.442 65	0.232 65
Xylene	- 0.425 67	0.265 82

The operating temperature of the gas sensor is decided by several factors, such as the orbital energy of gas molecule, adsorption amount of the sensing material at different operating temperatures. In order to clarify the mechanism of selectivity, it is necessary to conduct further research.

3　Conclusions

Nano SnO_2 powder has been produced with sol-gel method and the average size of grain is about 30 nm. The sensors made from nano SnO_2 doped with TiO_2 and Ag^+ exhibit excellent formaldehyde sensing performance at 300 ℃ and the sensitivity reaches 62 to 200 $\times 10^{-6}$ formaldehyde gas. The selectivity to formaldehyde can be obtained by sensors operating at a special temperature (300 ℃). The response time is 28 s and the recovery time is 17 s for tested formaldehyde. The selectivity of gas sensor at different operating temperatures is affected by the orbital energy of gas molecule. The lower the energy of LUMO, the lower the operating temperature in the detection of the gas.

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