

Gas sensitivity of indium oxide

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Received 2 March 2009; accepted 30 May 2009

Abstract: The yellow indium oxide nanoparticles were prepared by sintering the white deposition at 500 °C. The crystalline indium chloride and ammonia were used as the starting material. The results show that, by analyzing the particles through X-ray diffraction and TEM, the particles are very small, spherical, and the particle size is about 40 nm. The direct-heat components made from indium oxide in Cl₂ and NO₂ was tested respectively, the component is far more sensitive to NO₂ than to Cl₂ at low heating temperature, and the status is reversed at high heating temperature.

Key words: indium oxide; gas sensor; gas sensitivity

1 Introduction

Gas sensor is a device which rapidly responds to the tested gases in the environment and translates them into the appropriate physical signals, so as to test type and concentration of gases. Since the 1960s, the traditional semiconductor gas-sensing materials have been greatly studied and applied by scholars, represented by SnO₂, Fe₂O₃ and ZnO. With features of high sensitivity, low cost and mature technology, semiconductor gas sensors are widely used. In₂O₃, as a functional material with a tremendous application in the photoelectric field, has been a long concern, whereas, it is rarely studied in the gas-sensing aspect. As a new type of gas-sensing material, it is hopeful to improve the selectivity and stability of traditional gas-sensing material and lower the component working temperature[1–6]. In this work, the nanometer indium oxide was prepared through liquid precipitation method, and its morphology characterization and gas-sensing properties was studied.

2 Experimental

2.1 Reagents and apparatuses

Reagents were ammonia, analytical pure. Apparatuses were: InCl₃·4H₂O, analytical pure, muffle

furnace, oven, magnetic stirrer, agate mortar, Philips X-pert mpd pro XRD diffractometer, and Tecnai G20 S-TWIN 200 kV TEM.

2.2 Preparation of materials

A certain amount of InCl₃·4H₂O deionized water was stirred to make it dissolved. Slowly dripping ammonia, a milk-white precipitate appeared. Keep dripping ammonia, and control the pH value until the solution was alkaline, it was completely precipitated. At this point, stop dripping ammonia, and repeatedly washed ionic impurities, mainly chloride, with distilled water. The washed solution was put into oven, and then dried to obtain a white powder. The powder was placed into muffle furnace of 500 °C, and calcined for 2 h, and yellow In₂O₃ powder is obtained.

2.3 Characterization

The powder was characterized with Philips X-pert mpd pro XRD diffractometer and Tecnai G20 S-TWIN 200 kV TEM.

2.4 Preparation of components and test of gas-sensing device performance

Components adopted the traditional sintered heater-type structure under sintering conditions of 500 °C and 2 h. Component P1: pure In₂O₃ and component P2: In₂O₃

(10% SiO₂) were prepared, after aging for 2 weeks, respectively.

Test of device adopted static distribution. The basic test schematic diagram (see Fig.1). In Fig.1, V_h is the heating voltage for the components, V_c is the total voltage for the test, V , and V_{out} is the voltage on the sample resistor R_L , V . The gas sensing characteristics of the gas-sensing components is reflected by measuring the voltage changes of sample resistance. The sensitivity of the components is defined as

$$S_1 = R_g / R_a \quad (1)$$

where R_g and R_a are resistance values (Ω) of components in the tested gas (oxidizing gas) and in the air, respectively. On the contrary, in reducing atmosphere, the sensitivity is defined as

$$S_2 = R_a / R_g \quad (2)$$

The sample resistance is 1 mol/L, V_c adopts 5 V voltage.

3 Results and discussions

3.1 Analysis of XRD and TEM of material

Fig.2 shows the XRD pattern of prepared nanometer indium oxide powder. Compared with the standard card 01-071-2195, there are indium oxide crystals in good crystal condition. α , β and γ are all 90°, with same lattice constant, that is, they are simple cubic lattice. The average grain diameter calculated by Sherrer formula is 41.54 nm.

Fig.3 shows TEM images of indium oxide with staff of 10 nm and 200 nm, respectively. From Fig.3, we can see that they are spherical shape, even in size and distribution, about 40 nm, which is corresponding to the results of XRD analysis.

3.2 Analysis of gas-sensing properties of materials

The components P1 and P2 in different atmosphere were tested. The relationship between sensitivity of Cl₂

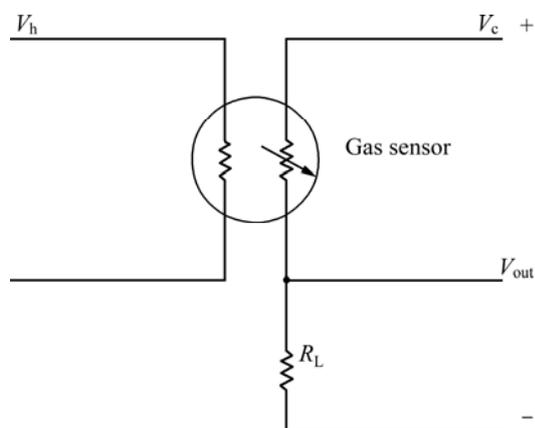


Fig.1 Structure of sensor

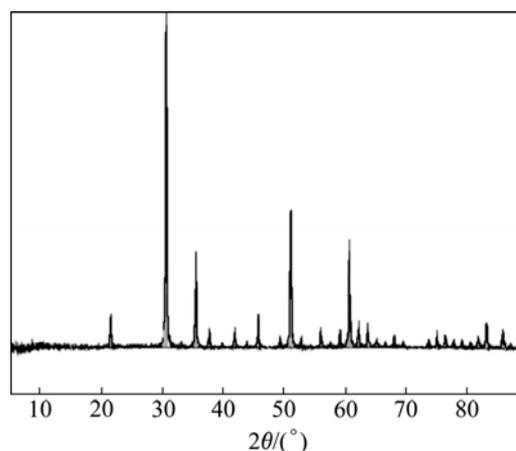


Fig.2 XRD pattern of In₂O₃

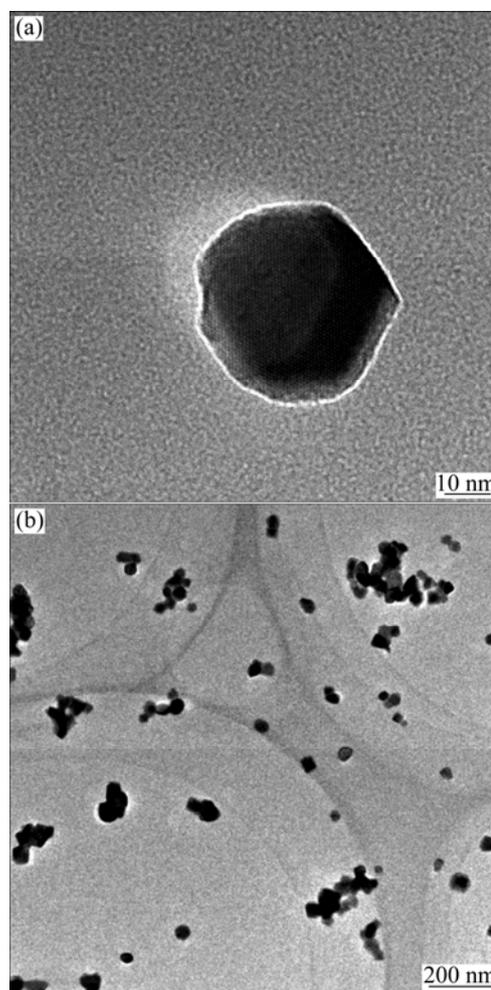


Fig.3 TEM images of indium oxide: (a) In₂O₃ single sphere; (b) In₂O₃

and NO₂ and heating voltage is shown in Fig.4 The tested gases in Fig.4 are 1×10^{-5} Cl₂ and 5×10^{-5} NO₂, respectively. In general, the components respond to both two gases rapidly within 2 to 3 s, the stability can be achieved.

In low temperature atmosphere, both components 1

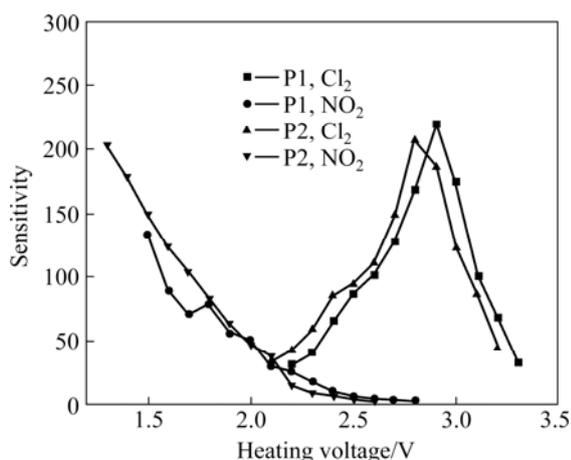


Fig.4 Relationship between sensitivity of Cl₂ and NO₂ and heating voltage

and 2 show a high sensitivity to NO₂, but recovery time of P1 reaches 2 min under 1.7 V, and within 1 min under 1.9 V. The recovery time of P2 can reach 1 min under 1.7 V, so, the incorporation of silicon oxide improves its recovery performance. In lower temperature, the sensitivity is not given because of its poor recovery property.

In high temperature atmosphere, components show high sensitivity to chlorine. Comparing the component 2, the addition of silica lowers the optimum working temperature. Meanwhile, from prospect of recovery properties, the optimum recovery time of P2 is about 130 s, whereas the optimum recovery time of P1 is 170 s.

Tests were also carried on other gases, but none of the rest shows high gas sensitivity.

3.3 Mechanism

Indium oxide is an N-type semiconductor material with structure of bixbyite[7–8]. In the course of calcination, a large amount of oxygen vacancies are produced, resulting in over In, and the lack of oxygen. The superfluous indium-ions appear in the gaps of crystals. From electro-neutrality condition, we can know that indium-ions can grasp the nearby electron, which is easy to fall off, that is, it is quasi-free-electron, therefore, indium oxide is N-type semiconductor. When meeting highly oxidizing gases, the quasi-free electron will be taken away, so that the carrier on the surface will reduce and the resistance increases. On the contrary, when gases reduce, resistance reduces. As indium oxide is a material with low resistance, when gases meet with strong oxidizability, free-electrons on its surface will be consumed, and then become a high resistance. From this point, the indium oxide material has a high capability in testing oxidizing gas.

The experiments results show that the materials can respond to the oxidizing gas rapidly, but the recovery

time is long, for a few minutes. Because analysis of oxidizing gas is accompanied with the process of chemical adsorption of oxygen[9–10], which also consumes free electron, so as to make the recovery slow.

As a highly stable compound, the incorporation of silicon dioxide doesn't bring a great improvement to the sensitivity. However, it lowers working temperature and reduces the recovery time. The author preliminarily analyzes the incorporation distribution, which makes the material loose and more conducive to the adsorption-desorption.

4 Conclusions

There is high sensitivity to Cl₂ and NO₂ at different temperatures.

References

- [1] ZHAN Zi-li, XU Jia-qiang, JIANG Deng-gao. State of In₂O₃-based gas sensors [J]. Journal of Transducer Technology, 2003, 22(3): 1–3. (in Chinese)
- [2] XU Peng-cheng, CHENG Zhi-xuan, PAN Qing-yi, XU Jia-qiang, XIANG Qun, YU Wei-jun, CHU Yu-ling. High aspect ratio In₂O₃ nanowires: Synthesis, mechanism and NO₂ gas-sensing properties [J]. Sensors and Actuators B: Chemical, 2008, 130: 802–808.
- [3] ALI M, WANG C Y, RÖHLIG C C, CIMALLA V, STAUDEN T, AMBACHER O. NO_x sensing properties of In₂O₃ thin films grown by MOCVD [J]. Sensors and Actuators B: Chemical, 2008, 129(1): 467–472.
- [4] VOMIERO A, BIANCHI S, COMINI E, FAGLIA G, FERRONI M, POLI N, SBERVEGLIERI G. In₂O₃ nanowires for gas sensors: Morphology and sensing characterization [J]. Thin Solid Films, 2007, 515: 8356–8359.
- [5] KOROTCENKOV G, BORIS I, CORNET A, RODRIGUEZ J, CIRERA A, GOLOVANOV V, LYCHKOVSKY Y, KARKOTSKY G. The influence of additives on gas sensing and structural properties of In₂O₃-based ceramics [J]. Sensors and Actuators B: Chemical, 2007, 120(2): 657–664.
- [6] FORLEO A, FRANCIOSO L, EPIFANI M, CAPONE S, TAURINO A M, SICILIANO P. NO₂-gas-sensing properties of mixed In₂O₃-SnO₂ thin films [J]. Thin Solid Film, 2005, 490(1): 68–73.
- [7] LING Bing-tao, JIANG An-xi, XU Jia-qiang. Preparation and character of In₂O₃ gas sensing materials [J]. Rare Metal Materials and Engineering, 2004, 10: 1093–1095.
- [8] FRANCIOSO L, RUSSO M, TAURINO A M, SICILIANO P. Micrometric patterning process of sol-gel SnO₂, In₂O₃ and WO₃ thin film for gas sensing applications: Towards silicon technology integration [J]. Sensors and Actuators B: Chemical, 2006, 119(1): 159–166.
- [9] ZHAO Zhen-guo, DING Ding, CHENG Hu-min. Preparation of ZnO powder by chelate decomposition method [J]. Acta Scientiarum Naturalium Universitatis Pekinensis 1996, 32: 693–697.
- [10] KIM J M, PARK J K, KIM K N, KIM C H, JANG H G. Synthesis of In₂O₃ nano-materials with various shapes [J]. Current Applied Physics, 2006, 6: 198–201.

(Edited by LI Yan-hong)