Sensitive properties of In-based compound semiconductor oxide to Cl_2 gas*

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Abstract: Aiming at detecting Cl_2 gas, this study was made on how to make In-based compound semiconductor oxide gas sensor. The micro-property and sensitivity of In-based gas sensing material were analyzed and its gas sensitive mechanism was also discussed. Adopting constant temperature chemical coprecipitation, the compound oxides such as In–Nb, In–Cd and In–Mg were synthesized, respectively. The products were sintered at 600 °C and characterized by the Scanning Electron Microscope (SEM), showing the grain size almost about 50–60 nm. The test results show that the sensitivities of In–Nb, In–Cd and In–Mg materials under the concentration of 50×10^{-6} in Cl_2 gas are above 100 times, 4 times and 10 times, respectively. The response time of In–Nb, In–Cd and In–Mg materials is about 30, 60 and 30 s, and the recovery time less than 2, 10 and 2 min, respectively. Among them, the In–Nb material was found to have a relatively high conductivity and ideal sensitivity to Cl_2 gas, which showed rather good selectivity and stability, and could detect the minimum concentration of 0.5×10^{-6} with the sensitivity of 2.2, and the upper limit concentration of 500×10^{-6}. The power loss of the device is around 220 mW under the heating voltage of 3 V.

Key words: In_2O_3; Nb_2O_5; sensitive property; chlorine gas sensor
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1. Introduction

In recent years, much attention has been devoted to the increasing role of semiconductor oxide gas sensors played in the alarm and detection of leaking gas, which also has been emphasized in modern security detection. Materials of semiconductor oxides used in traditional gas sensors include tin dioxide (SnO_2), zinc oxide (ZnO), and ferric oxide (Fe_2O_3), etc. They are mainly applicable to the detection of combustible gases.

With the arrival of new sensing material of indium trioxide (In_2O_3) in the 1990s[1], argument about its sensitivity for different hybridizations gradually increases, which makes the topic prevalent in this area[2]. Although researches on sensitivities of nitrogen dioxide (NO_2), carbon monoxide (CO), and hydrogen (H_2), etc. are available[3–5], reports on detecting Cl_2 gas as the objective are much fewer[6,7]. Moreover, most of them are solid electrolytic electrochemical sensors[8], which cannot realize the gas detection of high concentration especially in complicated environment. With the higher requirements of sensors qualified for detecting, further studies on new semiconductor sensing materials and their practical application will be made in toxic gases detection[9].

The diversities of sensitive properties in the compound oxides of In–Nb, In–Cd, and In–Mg are studied in this paper. By comparison, the optimal solution for hybridization is determined, and the sensing mechanism of In-based compound oxides is also analyzed.

2. Experiment

2.1. Syntheses of sensing materials

$In(NO_3)_3$ (0.018 mol) and Nb_2O_5 (0.003 mol) were dissolved in deionized water, then citric acid (10 wt%) was added to spread the compounds, and finally aqueous ammonia (25%) was dropped into the mixture until the PH reached 8. It was stirred for 2 h under a constant temperature of 50 °C with the same PH of 8, and then white precipitates showed up, after washing, filtering, drying at 120 °C under a low vacuum for 2 h and calcining at 600 °C for 3 h, the yellowy In–Nb oxide powder was obtained. According to the synthetic conditions mentioned above, the compound oxides of In–Cd with the molar ratio (3 : 1) and In–Mg with the molar ratio (6 : 1) were synthesized by introducing the method of chemical coprecipitation.

2.2. Device preparation and its test

After the compound oxide of In–Nb was ground completely in a carnelian mortar, H_2PtCl_6 (0.3 wt%) was added to adjust the resistance. Next, the mixture was made slurry by adding terpineol, smeared on the electrodes of Al_2O_3 ceramic

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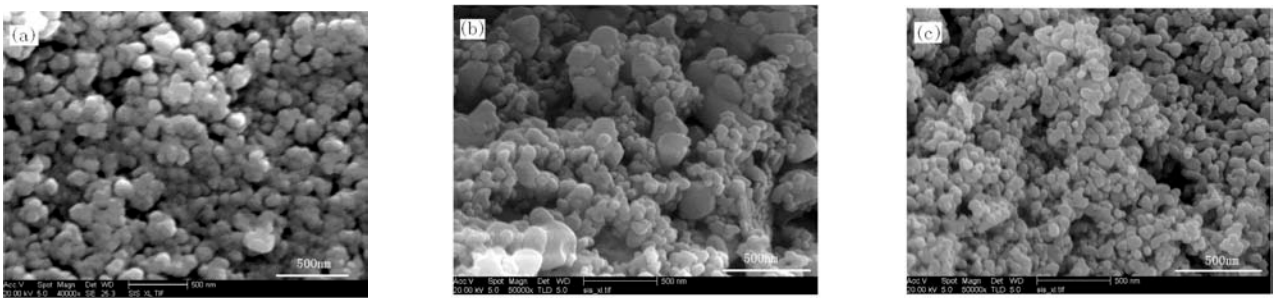

Fig. 1. Characterization of materials sintered at 600 °C by SEM: (a) In–Nb; (b) In–Cd; (c) In–Mg.

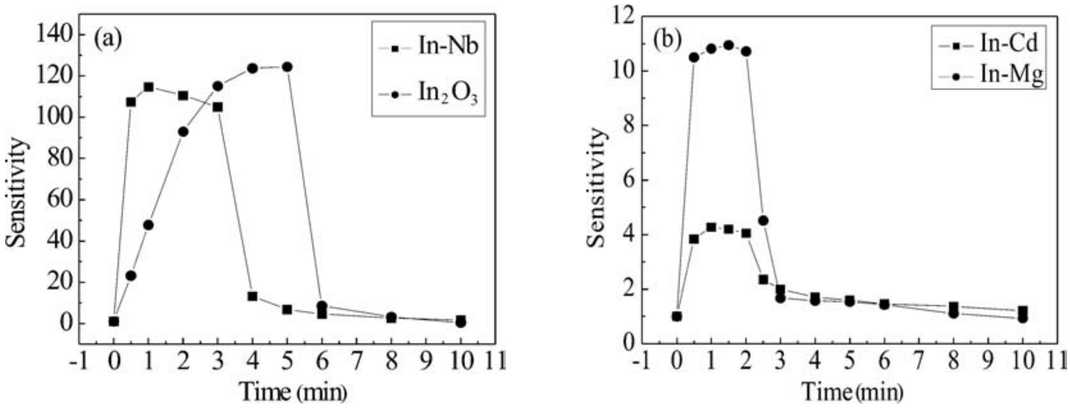

Fig. 2. Response and recovery characteristic curves: (a) In–Nb and In_2O_3; (b) In–Cd and In–Mg.

tube uniformly, dried for 12 h at room temperature, and sintered for 3 h at a high temperature of 600 °C. The electrodes were welded on the support, packed, aged for 120 h, and the device was tested by the static volumetric method. The compound oxides of In–Cd and In–Mg powders used in the device were processed in the same way. Here, the gas sensitivity is defined as the ratio R_g/R_a, where R_g and R_a are the resistance of sensors after and before Cl_2 gas introduction, respectively.

3. Results and discussion

3.1. Microstructure and characterization of materials

Microstructures of the materials were characterized and analyzed by SEM technology. Figure 1 shows the morphologies of In–Nb, In–Cd and In–Mg materials, which were sintered at 600 °C. As can be seen from Figs. 1(a) and 1(c), both the In–Nb and In–Mg materials were uniformly distributed, whose granular sizes were approximately 60 and 50 nm, respectively. Obviously, regrowth, aggregation and the structure of island appeared in the compound oxide of In–Cd, whose granular size was approximately 50–60 nm, as shown in Fig. 1(b).

The In-based nano-oxides were synthesized by introducing chemical coprecipitation method, whose granular sizes apparently increased with the rise of annealing temperature. The film made by thick-film technology was loosen and lacunose, which was good for physicochemical adsorption of the gas.

3.2. Analysis of gas sensitivity

3.2.1. Influence of different dopants on the gas sensitivity

Both In_2O_3 and its hybrid In-based compound oxides are n-type semiconductors, which are considered as good gas sensing materials. In the presence of oxidizing Cl_2 gas, the conductivity decreases sharply, and the resistance increases. The sensitive properties of materials can be changed by different dopants at different working temperatures. The response and recovery characteristic curves of In–Nb, In_2O_3, In–Cd and In–Mg materials, which were operated at the heating voltage of 3V and the concentration of Cl_2 gas of 50×10^{-6}, were shown in Fig. 2, respectively. In the process of chemical syntheses of In_2O_3 doped with Nb, Cd and Mg, the conductivity varied in different degree. The conductivity of In–Nb and In–Cd increased by 1000 times, and that of In–Mg decreased by 10 times, which indicates that the response time of In-based compound oxide shortened after doping. Figure 2 illustrates the response time of In–Nb, In_2O_3, In–Cd and In–Mg materials, 300 s for In_2O_3, 30 s for In–Nb and In–Mg, 60 s for In–Cd, and their recovery time was less than few minutes with the exception of In–Cd material, which took about 10 min to recover. At the same time, the sensitivities of In_2O_3, In–Nb, In–Cd and In–Mg materials could be calculated, and they were 125, 115, 4.5 and 11, respectively as shown in Fig. 2.

Comparing the experimental data, both In–Nb and In–Cd materials exhibit a good conductivity to Cl_2 gas, but they are quite different. The response and recovery time of the former was much shorter than that of the latter; furthermore, In–Nb material showed a better sensitivity than that of In–Cd.

3.2.2. Stability and selectivity

Under the heating voltage of 3 V, the thermal stability of these materials was recorded in every 12 h during the period of 120 h. Figure 3 shows that In–Nb and In–Cd materials have a

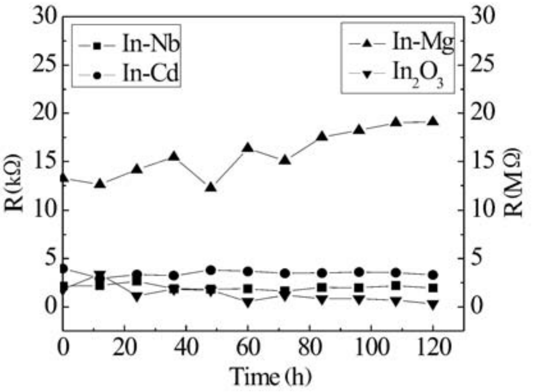

Fig. 3. Thermal stability of different doping materials during 120 h.

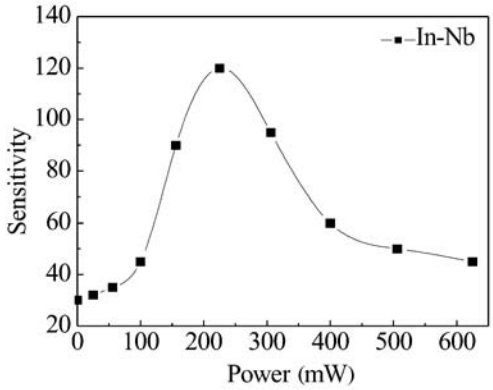

Fig. 4. Relationship between heating power and sensitivity.

good thermal stability, with the resistance of about 2×10^3 Ω. However, In–Mg and In_2O_3 materials have a bad thermal stability, with the resistance of more than 10^6 Ω. Therefore, In–Nb compound oxide should be an ideal sensing material used in Cl_2 gas detection.

Considering Cl_2 gas in practical use and transportation, the experiment was carried out to detect the sensitivity of different affecting gases in the detection. These gases included liquefied natural gas (LNG), NH_3, CO, NO_2 and CH_4. The experimental data were listed in Table 1, of which Cl_2 gas showed the highest sensitivity and the sensitivity of the others were less than 5. That means Cl_2 gas sensors of In–Nb compound oxide have a good selectivity to different gases.

3.2.3. Influence of heating power on sensitivity

The sensitivity of inorganic semiconductor sensing materials changes with the temperature, in other words, the sensitivity would be different if the heating power changes. Figure 4 shows the relationship between heating power and sensitivity of In–Nb material in the Cl_2 gas with the concentration of 50×10^{-6}. The sensitivity increased during the heating power no more than 220 mW, but fell when the heating power went up again. Here, the optimal heating power for the sensor was about 220 mW. Dramatically, both the response and recovery time would lengthen if the power below 220 mW, and if the power above this, the response and recovery time would shorten. In most cases, we choose 220 mW for the heating power in the experiments.

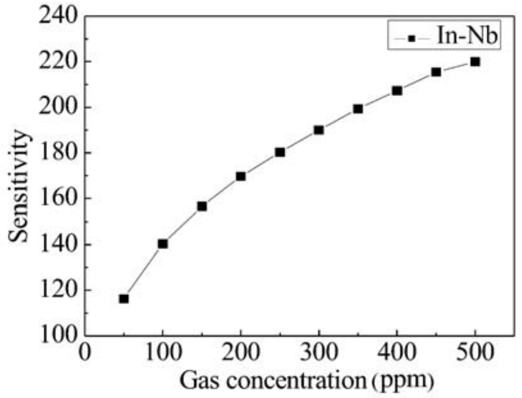

Fig. 5. Relationship of gas concentration and sensitivity.

Table 1. Sensitivity of In–Nb compound oxide in different gases.

Gas	Concentration ($\times 10^{-6}$)	Sensitivity
Cl_2	50	115
LNG	50	4
NH_3	50	0.01
CO	2000	0.5
NO_2	50	3.5
CH_4	2000	0.99

3.2.4. Gas concentration and sensitivity

The relationship between gas concentration and sensitivity of In–Nb material was shown in Fig. 5. In the presence of Cl_2 gas, the resistance of In-based semiconductor oxide increased due to its donating the electrons and the higher the concentration, the more electrons being donated, which would increase the resistance. Meanwhile, the sensors were placed in the Cl_2 gas of low concentration; the result showed that they could detect the minimum concentration of 0.5×10^{-6} and with the sensitivity of 2.2.

3.3. Sensing mechanism of the materials

As an n-type semiconductor typically, In_2O_3 enables its conductivity to increase by increasing the number of oxygen vacancies and indium ions of interspaces after treated in the condition of low oxygen or vacuum. The main reaction is as follows:

$$O_O^\times \rightleftharpoons V_O^\times + \frac{1}{2}O_2 \tag{1}$$

$$V_O^\times \rightleftharpoons V_O^+ + e^-. \tag{2}$$

The conductivity of the materials can be remarkably changed by doping, which can be explained by the principle that cations of high or low valence substituted for indium ions in the lattice will cause the gain and loss of electron, which is equal to appearance of holes and free electrons.

As a strong oxidizing gas, Cl_2 gas receives the electrons from the In-based compound oxide when they contact each other, causing the conductivity to fall. The reaction is as follows:

$$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-_{ads}. \tag{3}$$

In the process of sintering, oxygen holes and ionization are formed in In-based compound oxide materials. The free electrons ionized in this way share the conduction of materials. When exposed to the air, electrons on the materials surface will be consumed by oxygen molecules in the air, which brings the conductivity to fall and forms the adsorbent oxygen ions (O^{2-}_{ads}). As to oxidative ability, Cl_2 gas is much stronger than O_2 gas, and they can be described by the following reaction:

$$O^{2-}_{ads} + \frac{1}{2}Cl_2 \rightleftharpoons Cl^{-}_{ads} + \frac{1}{2}O_2 + e^{-}. \tag{4}$$

From reaction (4), we can see that the free electrons are produced; simultaneously, reaction (3) follows. As the free electrons between surface and interspaces of crystal grains decrease, and potential barrier between crystal grains builds up, the conductivity of the materials decreases. In fact, the mechanism is much more complicated because it is affected by many factors such as material ratio, sintering temperature, gas pressure and the defect state.

4. Conclusion

The synthesis of In_2O_3 doped with Nb, Cd and Mg was reasonably realized by introducing the method of constant chemical co-precipitation, and they were sintered at the same temperature of 600 °C. The result showed that the conductivity of In–Nb and In–Cd materials increased by 1000 times, and both had a good thermal stability. Particularly, In–Nb material showed a high sensitivity, a short response and recovery time, and a good selectivity, which can be an ideal candidate for the sensing material of Cl_2 gas sensor. Therefore, the further exploitation of In–Nb material will be of practical utility.

References

[1] Takeuchi M, Watanabe Y, Ozawa S. Gas-sensitive properties of ultra fine In_2O_3 particle layers prepared by gas evaporation technique. Appl Surf Sci, 1991, 48/49: 526

[2] Zhong Tiegang, Liang Xishuang, Liu Fengmin, et al. Research on Nb–In compound oxide chlorine gas sensor. Chinese Journal of Sensors and Actuators, 2007, 20(10): 2155 (in Chinese)

[3] Ivanovskaya M, Gurlo A, Bogdanov P. Mechanism of O_3 and NO_2 detection and sensitivity of In_2O_3 sensors. Sensors and Actuators B, 2001, 77: 264

[4] Matsubara I, Murayama N, Shin W, et al. Organically hybridized In_2O_3 thin film gas sensors. Semiconductor Materials for Sensing Symposium, 2005: 13

[5] Shukla S, Agrawal R, Ludwig L, et al. Room temperature hydrogen gas sensitivity of nanocrystalline-doped tin oxide sensor incorporated into MEMS device. Semiconductor Materials for Sensing Symposium, 2005: 51

[6] Miyata T, Hikosaka T, Minami T. High sensitivity chlorine gas sensors using multi-component transparent conducting oxide thin films. Sensors and Actuators B (Chemical), 2000, B69(1/2): 16

[7] Tamaki J, Naruo C, Yamamoto Y, et al. Sensing properties to dilute chlorine gas of indium oxide based thin film sensors prepared by EB evaporation. 11th International Conference on Solid-State Sensors and Actuators, Digest of Technical Papers, 2001, 2: 1718

[8] Yan Y, Miura N, Yamazoe N. Potentiometric sensor using stabilized zirconia for chlorine gas. Sensors and Actuators, B: Chemical, 1995, B24(1–3): 287

[9] Shi Yunfen, Shi Yunbo, Sun Mojie, et al. A PdPc-PANI modified SAW sensor and phosphorous-containing toxic gas detection. Journal of Semiconductors, 2008, 29(5): 998 (in Chinese)