Physica B 405 (2010) 1345–1348

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Gas-sensing properties of SnO_2–TiO_2-based sensor for volatile organic compound gas and its sensing mechanism

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ARTICLE INFO

Article history:
Received 28 September 2009
Received in revised form
29 November 2009
Accepted 30 November 2009

Keywords:
Selectivity
VOCs
SnO_2–TiO_2
Molecule orbit

ABSTRACT

We report the microstructure and gas-sensing properties of the SnO_2–TiO_2 composite oxide dope with Ag ion prepared by the sol–gel method. Of all various volatile organic compounds (VOCs) such as ethanol, methanol, acetone and formaldehyde were examined, the sensor exhibits remarkable selectivity to each VOCs at different operating temperature. Further investigations based on quantum chemistry calculation show that difference orbital energy of VOCs molecule may be a qualitative factor to affect the selectivity of the sensor.

1. Introduction

The evaluation of indoor air quality has become an extremely urgent environmental issue. Indoor pollutants, which mainly consist of volatile organic compounds (VOCs) such as formaldehyde, benzene, toluene and xylene, may cause the environmental illnesses known as building-related sickness [1–4].

Semiconductor metal oxide gas sensor can be promising candidates for monitoring VOCs due to its many advantages such as simple manufacture technique, low cost, rapid response and recovery time. [5–10] However, one of the critical issues currently limiting the wide use of these oxides is lack of selectivity towards different VOCs. It is difficult to distinguish each VOCs species owing to their similar composition elements and molecular structure. Although great deal of effects have been out into improving the selectivity of the sensing material to VOCs, the selectivity is remain the most difficult issue for VOCs sensor research [11].

Therefore, in this work, we propose a mixed oxide of SnO_2–TiO_2 doped with Ag ion, in order to improve the selectivity to VOCs. As expected, we find that this mixed oxide exhibits special selective to each VOCs at different operating temperature, thereby holding technological promise for monitoring VOCs. Furthermore, based on quantum chemistry calculation, we examined the orbital energy of different VOCs molecule and qualitative explained the present mechanism of selectivity.

2. Experiment process

2.1. Preparation of sensing materials

Colloidal solution of TiO_2 was prepared by first mixing 10 ml of tetra butyl titanium (Wako Pure Chemical, 95%) with 4 ml isopropyl alcohol. The mixture was then gradually added to 150 ml deionized water. The solution was well stirred several hours until the sol was formed. The sol was subsequently transferred into a well-sealed autoclave vessel containing 0.5 M teramethy-ammonium hydroxide solution. Peptization occurred after heating at 120 °C for 6 h. The second step, as for the preparation of SnO_2 colloidal solution, $SnCl_4 \cdot 5H_2O$ (Wako Pure Chemical, 95%) was dissolved in ethanol (0.4 M), and then the solution was well stirred and refluxed for 3 h. A 5.5 M aqueous ammonia solution (Wako Pure Chemical, 25–27.9%) was added dropwise to a refluxed solution, which consequently forms precipitates. The resultant precipitate was washed thoroughly with deionized water. In the end, the SnO_2–TiO_2 colloidal solutions were prepared by mixing TiO_2 colloidal solution with SnO_2 colloidal solution for Sn/Ti=7/1. Simultaneity suitable amount of $AgNO_3$ solution was added into the mixed colloidal solution. Then the colloidal solution was dried to gel and crush into powder, finally the powder was annealed in air at 450 °C for 2 h, at a heating rate of 6 °C/min.

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doi:10.1016/j.physb.2009.11.086

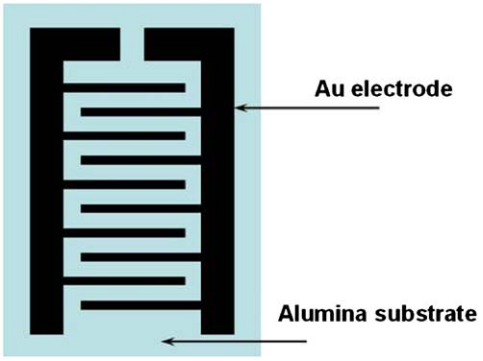

Fig. 1. Schematic of thick film device.

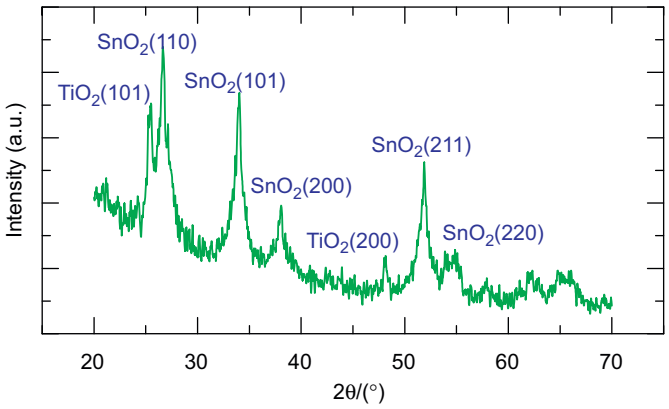

Fig. 2. XRD pattern of SnO_2–TiO_2 sample.

2.2. Preparation of gas sensor

The sensor device fabricated in this study was of thick film type, as shown in Fig. 1 The powder samples obtained mixed with diethanolamine and the resulting paste were screen printed on an alumina substrate attached with a pair of comb-type Au electrodes (distance between electrodes is 200 μM) and sintered at 500 °C for 3 h.

2.3. Measurements and analyses

The XRD (XD-5A) analysis of mixed solid powder was conducted using Cu radiation to determine the phases and the grain size. The microstructure of the thick film was analyzed using AFM (CSPM4000).

Gas sensing properties of the sensor was characterized by a static system. The gas inlet and the air admittance valves are made at the base plate in order to inject the test gas and air. The temperature of the sensor is controlled by varying the current flow through the heater. The test gas is injected inside the bell jar through a needle valve. The electrical characteristics of the sensor are observed by changing its temperature from 200 to 400 °C.

Gas-sensing studies were carried out under laboratory condition (30 °C, 40% relative humidity) after the gas sensor was powered at 100 °C 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).

3. Results and discussion

3.1. Characteristic of sensing material

Fig. 2 shows the XRD pattern of TiO_2–SnO_2 sample, we can observe that the sample included anatase TiO_2 phase and rutile SnO_2 phase. The TiO_2 peaks emerge in the XRD spectrum after doping, meaning that we have successfully incorporated TiO_2 into SnO_2. The particle sizes D are measured from XRD peaks based on the Scherrer equation [12]:

$$D = 0.89\lambda/(\beta \cos\theta)$$

where D is the mean size of particle, λ is the X-ray wavelength (Cu-0.154056 nm), β is the full-width at half-maximum of XRD peaks and $D = 0.89\lambda/(\beta \cos\theta)$is the Braggs angle.

Average particle size of sample is calculated from the broadening of the (1 1 0) XRD peak, which is about 30 nm.

Fig. 3. shows the morphological images of TiO_2–SnO_2 thick film. Islands can be observed on top of the surface. In addition, the sample exhibits the good crystal shape and uniform size of grain.

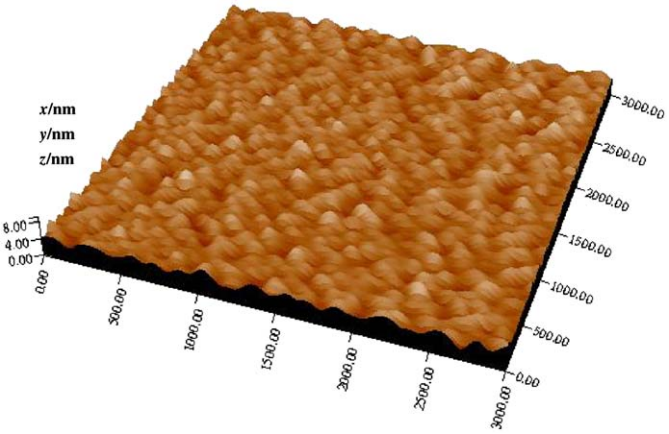

Fig. 3. AFM image of SnO_2–TiO_2 sample.

3.2. Gas-sensing properties

Gas response to four kinds of VOCs was tested in this study, such as ethanol, methanol, acetone and formaldehyde, etc.

The sensitivity to 200 ppm VOCs of the sensor considerably changed with different operating temperatures. As shown in Fig. 4. 280, 320, 340 and 360 °C were suggested to the optimum operating temperature for ethanol, methanol, acetone and formaldehyde detection, respectively, due to the sensor showed the maximum sensitivity at corresponding operating temperature. This can be understood by considering that a dynamic equilibrium state will occur between the initial adsorption and the subsequent desorption, as the operating temperature keeps increasing [13]. The amount of adsorbed VOCs increase when the operating temperature becomes high and the adsorption attains a balance at a suitable temperature (namely optimum operating temperature) because the adsorption is an exothermic reaction. If the operating temperature keeps on increasing, the amount of gas adsorbed will reduce, and the balance will change to desorption, resulting in a decreased gas sensitivity when the operating temperature surpass the optimum values [11].

According to the discussion above, we test the response-recovery property of the sensor at 280 °C, which is one of the optimum temperatures.

Owing to this optimum operating temperature fits for detecting ethanol, not surprise, the sensor shows the strongest sensing signal for ethanol as shown in Fig. 5, while for other VOCs such as methanol, acetone and formaldehyde somewhat weak. So in this way, we can easy to define the VOCs species according to the corresponding sensing signal.

3.3. Gas-sensing selectivity mechanism

Although many works have been conducted on TiO_2 or SnO_2-based sensor, its gas-sensing mechanism remains controversial. The current understanding of the sensing behaviors of metal oxide, which is based mainly on experimental studies via a trial-and-error design fashion, can be summarized by follow.

Gas-sensing properties are dominantly controlled by the surface adsorption which made the surface energy and the conductance changed. Namely, the selectivity of the sensor is influenced by several factors such as the LUMO (lowest unoccupied molecule orbit) energy of gas molecule and the amount of gas adsorption on the sensing material at different operating temperature. If the value of LUMO energy is lower, the energy needing for the gas sensing reaction will reduce and the sensing signal can be enhanced. So the sensors can detect the target gas at low operating temperature.

In different states of adsorption, the gas molecules have different electron affinity which led to different conductance of the gas sensor after VOCs adsorption. The electron affinity is affected by the orbital energy of the gas molecule. The Lowing LUMO energy will make the gas molecule possess the stronger ability in capturing electrons [14]. This effect will stimulate the electron transfer between the gas molecule and the surface of sensing material, and hence the sensitivity of the sensor will be increased.

In order to understand the mechanism for the sensor showing selectivity at different operating temperature, we investigated the distinction of the orbital energy of the VOCs molecule through quantum chemistry calculation. Gas molecule models for calculation were built up through the Gaussian view program as shown in Fig. 6.

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

As the result shown in Fig. 7, the value of LUMO energy for ethanol, methanol, acetone and formaldehyde is 0.12572, 0.19728, 0.20525 and 0.21965 eV, respectively. Based on the analysis above, it can be concluded that the ability of capturing electron weaken in order of ethanol, methanol, acetone, formaldehyde. Therefore, the possibility of electron transfer between the gas molecule and surface of the sensing material diminishes in sequence of ethanol, methanol, acetone, formaldehyde. At the low operating temperature about 280 °C, the sensor exhibits evidently response to ethanol as its lower LUMO energy, while the optimum operating temperature increases gradually for detecting the other gases such as methanol, acetone and formaldehyde. The theoretical result is in agreement with our experiment. Theses findings can interpret qualitatively the mechanism of the sensor exhibiting selectivity at different operating temperature.

As we all known, the operating temperature of the gas sensor is decided by several factors, it contains the orbital energy of gas molecule, adsorption mode and amount of VOCs and so on. So in order to clarify the mechanism of selectivity, it will need to research further more.

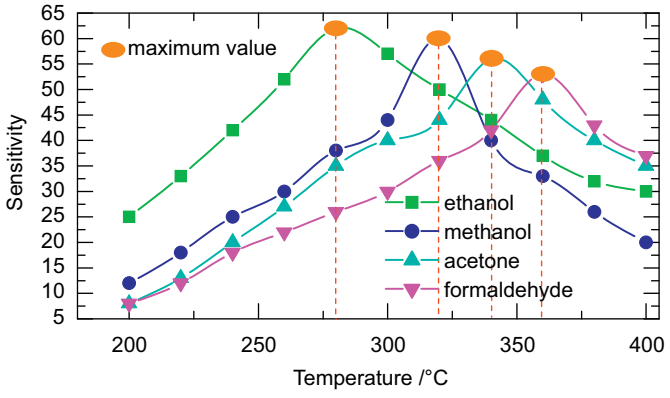

Fig. 4. The sensitivity of SnO_2–TiO_2 sensor to different operating temperature.

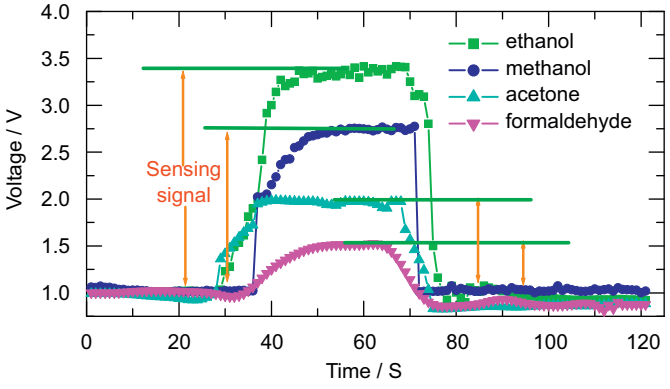

Fig. 5. Response-recovery characteristics of sensors.

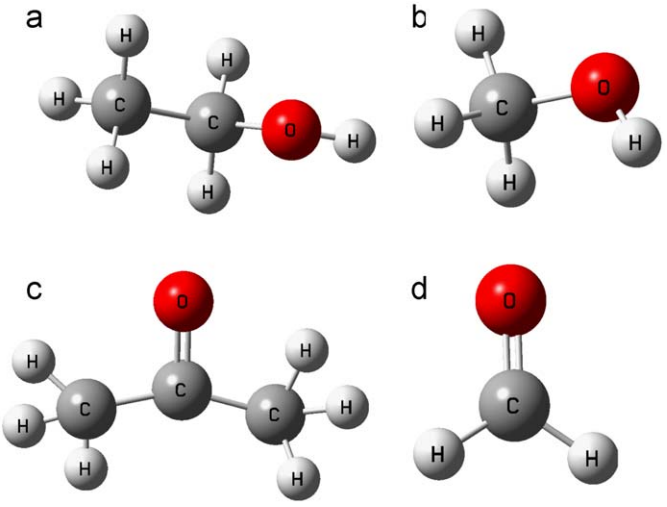

Fig. 6. Model of VOCs molecule, (a) ethanol, (b) methanol, (c) acetone and (d) formaldehyde.

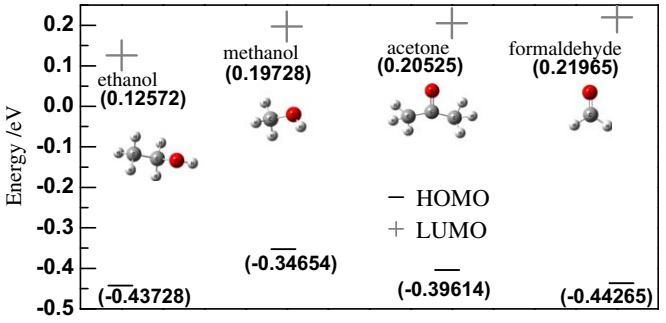

Fig. 7. Orbital energy of VOCs molecule.

4. Conclusion

We have applied a sol–gel method to fabricate the sensing material SnO_2–TiO_2 doped with Ag ion powder and investigated their microstructures and gas-sensing properties. We have found that the sensor exhibited remarkable selectivity to each VOCs such as ethanol, methanol, acetone and formaldehyde at different operating temperature. From the discussion based on quantum chemistry calculation, we can deduce that LUMO energy may be a qualitative factor to affect the selectivity of the sensor. These findings demonstrate the potential use of this sensor distinguish VOCs species at different operating temperature for which gas has different LUMO energy. This paper presents a possibility to realize the selectivity to VOCs through controlling the operating temperature, although further studies on such effect are needed.

Acknowledgments

The authors thank to Dr. ZC. Wang, Prof. S.Tsukimoto and M.Saito for editorial help with the English manuscript and useful discussion. This work was funded in part by the Chinese Scholarship Council (CSC) project (LJC20093012).

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