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Porous WO_3-NiO Thin Films Prepared by Sol-Gel Method for Selective Acetone Gas Detection

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Abstract

Porous WO_3-NiO thin films were prepared by sol-gel method. The microstructure and surface morphology were characterized by using X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The acetone vapor sensing properties were investigated as functions of NiO content, acetone concentration, sintering temperature, and porous structure. Electrical properties were studied by conductivity measurement. As prepared WO_3-NiO thin films show well response towards acetone gas. The sensitivity of 1.0 mol % Ni-doped WO_3 thin films to 20 ppm acetone gas sintered at 500 °C for 1h attained 5.83. Therefore, Ni-doped WO_3 thin films show the principal possibility of application of semiconducting gas sensors in the diagnosis of diabetes.

Key words: WO_3-NiO thin films, selectivity, porous structure, acetone, and gas-sensor

Introduction

Recently, the detection of acetone gas in human breath has attracted much attention because the diabetes is harmful to human health. There are about 150 million patients all over the world; also the number is continually increasing[1].According to many medical investigations, the acetone concentration in the breath from a healthy human body is lower than 0.8 ppm, while that from a diabetic patient is higher than 1.8 ppm. Therefore, the quantitative analysis of acetone in human breath is beneficial to diabetes treatment.

Over the last three decades, metal oxide semiconductors have been extensively investigated due to their applications in industrial and domestic sectors [2-3]. WO_3 is an n-type semiconductor, and it has been considered one of the best candidates among the large number of acetone sensing materials. Especially in recent years, numerous efforts have been directed to improving its sensitivity and selectivity. R.S. Khadayate *et al*. [4] have reported acetone sensing properties of WO_3 thick films prepared by standard screen-printing method. A. Teleki *et al* [5] used flame spray pyrolysis (FSP) method to prepare Cr-doped WO_3 films, which show good selectivity to acetone gas.

In this paper, Ni-doped WO_3 thin films with small grain size and porous structure were prepared by using sol-gel method. Acetone vapor sensing properties were investigated as a function of NiO content, acetone concentration, sintering temperature, and porous structure. A possible gas sensing selective mechanism was also discussed.

Experimental details

In our experiment, WO_3-NiO sol was prepared by sol-gel method using H_2WO_4 and Ni $(NO_3)_2 \cdot 6H_2O$ as raw materials, citric acid (CA) as chelating agent, and H_2O_2 as dispersant. Urea was employed as pore-forming agent to produce porous structure. A typical experimental procedure was as follows: about 0.5 g of urea and 0.0436 g of Ni $(NO_3)_2 \cdot 6H_2O$ were dissolved in 12.5 mL deionized water and 20 mL H_2O_2 solution. Then 0.015 mol of the anhydrous tungstenic acid precursor, H_2WO_4, was added into the solution with vigorously stirring. After treated by ultrasonication for 35-40 min, the pH of the solution was adjusted with $NH_3 \cdot H_2O$ aqueous solution to ca. 3-4. The mixture was then stirred at 80 °C for 3 h to get homogeneous sol. Finally, the resulting sol solution can be used to prepare thin films on Al_2O_3 ceramic tube by dip coating. The samples were sintered in oxygen atmosphere for 1 h at

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different sintering temperatures (500 °C, 600 °C and 700 °C).

Crystal phase and surface morphologies were characterized by XRD (Rigaku D/max 2500) and FE-SEM (Hitachi, S4800), respectively. The average crystal size was estimated from the Debye-Scherrer equation. Acetone sensing properties of the side-heated gas sensors were measured in a static gas system connected with a computer which was used to measure the films' resistances. The sensitivity (*S*) was defined as:

$$S = Ra / Rg \qquad (1)$$

Where *Rg*is the resistances of the films measured in test gases and *Ra* is that in air. The resistance measurements were carried out at 320 ° C operating temperature.

Results and discussion

Microstructure characterization

Fig. 1 shows X-ray diffraction patterns of 1.0 and 10 mol% Ni-doped WO_3 thin films sintered at 500 ° C for 1 h. Reflection peaks of both samples belong to orthorhombic WO_3 (JCPDS card no. 20-1324). No peaks were observed for second phase in the case of 1.0 mol% doping. However, when increasing the NiO content to 10 mol%, the second phase $NiWO_4$ (JCPDS card no. 15-0755) was detected. The average grain size of 1.0 mol% Ni-doped WO_3 is approximately 14nm.The small grain size enlarged the surface areas, which will finally help improving the gas-sensing properties.

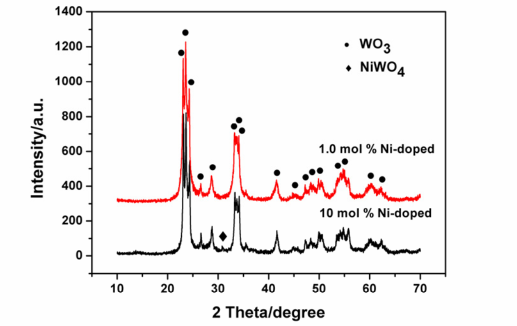

Fig. 1 X-ray diffraction patterns of 1.0 and 10 mol% Ni-doped WO_3 thin films sintered at 500 °C for 1 h.

Fig. 2 shows the surface morphologies of porous and non-porous 1.0 mol% Ni-doped WO_3 thin films sintered at 500 °C for 1 h. Fig. 2A clearly shows that the films prepared with urea exhibits a porous structure formed by nanoparticles. The pore diameters are from tens of nanometers to several microns. Therefore, the WO_3 thin films can absorb more target gases due to more exposed surface area. Besides, the microstructure of the thin film is seen to consist of large amount of small grains. The small grain size enlarged the surface areas, which improves the gas-sensing properties for oxide semiconductor materials. From Fig. 2B we can clearly see that no porous structure is observed for the films prepared without urea, and the surface is smooth. The sensitivities of the two type's films are compared, which are totally different. When the acetone concentration is 20 ppm, the measured sensitivity of porous thin film is 5.83, which is almost 4 times greater than the film with non-porous structure. T. Wagner *et al* [6] using two-step structure replication method to prepare mesoporous ZnO films, and has obtained similar result. Therefore, such a porous structure is likely to facilitate the absorption process of acetone molecules because of the capillary pore and large surface area. This implies that this type of sensor will be able to offer a good sensitivity to acetone gas.

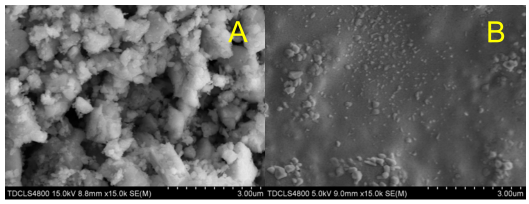

Fig.2 SEM surface morphologies of 1.0 mol% Ni-doped WO_3 thin films sintered at 500 °C for 1 h. A: porous structure B: non-porous structure.

Electrical properties

According to Whyoshup Noh *et al* [7], the electrical properties of Ni-doped WO_3 can be affected by the change in defect concentration (oxygen vacancy), the absorption and desorption of test gas on the surface of WO_3, and the formation of a second phase.

WO_3 is an n-type semiconductor after sintering because oxygen vacancies are created at low pressure of oxygen and the electron concentration increased. Acetone is a kind of reducing gases. The acetone gas (*R*) and oxygen molecules acting on the WO_3 surface can be described as:

$$1/2\ O_2 + e' \rightarrow O^- \ (ads) \qquad (2)$$

$$R\ (gas) \leftrightarrow R\ (ads) \qquad (3)$$

$$R\ (ads) + O^- \ (ads) \leftrightarrow RO\ (ads) + e' \qquad (4)$$

When in the air, electrons are removed from WO_3 conduction band by the absorbing of O_2, resulting in the formation of O^- species. When introducing reducing gas R, it reacts with O^- (ads) to form RO, and electrons are released back to WO_3 conduction band, leading to the decrease of the film's resistance.

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The resistances of Ni-doped WO_3 films as a function of NiO content were measured at 320 °C operating temperature. The resistance is slightly increased with NiO content up to 1.0 mol%, and then it is increased remarkably at 10 mol%. The defect equation as a function of NiO content in WO_3 can be written as:

$NiO + O_2 \leftrightarrow Ni_W'''' + 4h^{\cdot} + 3O_O^x$ (5)

$NiO \leftrightarrow Ni_W'''' + 2V_O^{\cdot\cdot} + O_O^x$ (6)

Reactions (5) and (6) represent the increase of hole concentration and oxygen vacancy, respectively. Because WO_3 is an n-type semiconductor, so the resistance of the films will increase. Besides, the huge increase at 10 mol% NiO content is also due to the formation of the second phase, $NiWO_4$, by the reaction of NiO and WO_3 above the solubility limit. $NiWO_4$ acts as a blocking material for electron transport, which finally increase the film's resistance.

Gas-sensing properties

The response of 1.0 mol% Ni-doped WO_3 thin films sintered at 500 °C for 1 h to acetone vapor was investigated. Fig. 3 shows the change in electrical resistance of that film to 10, 15, and 20 ppm acetone exposure. The resistance decreases at all gas concentrations, which is a typical behavior of n-type semiconductors. The sensitivities are 2.74, 3.52 and 5.83 corresponding to 10, 15 and 20 ppm of acetone, respectively. The response and recovery time (defined as the time reaching 90 % of final signal) were less than 20 and 10 s, respectively. Besides, little responses were observed forWO_3 thin films with 0.1 and 10 mol% NiO doping. Therefore, 1.0 mol% Ni-doped WO_3 thin film exhibits best gas sensing properties. This type of sensor is capable of real-time, fast response-recovery, and good sensitive detection to acetone gas. The high sensitivity for relatively low acetone concentration is attractive for practical use in breath analysis of diabetes diagnosis.

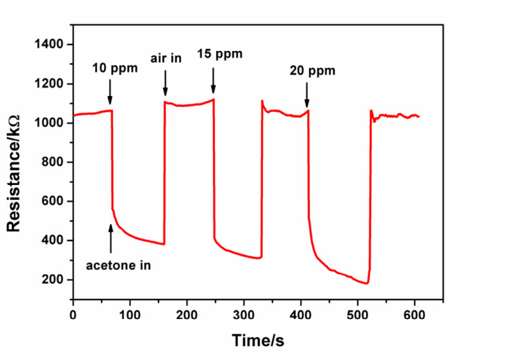

Fig. 3 Resistance response of 1.0 mol% Ni-doped WO_3 films sintered at 500 °C for 1 h at repeated exposure to 10, 15, 20 ppm acetone.

Based on Fig. 3, the sensitivity with NiO content is shown in Fig. 4.We can clearly see that the sensitivity increases up to 1.0 mol% NiO, and then it shows a decrease. The maximum sensitivity was observed in 1.0 mol% NiO. We suppose that the increment of the sensitivity may relate to a large number of active sites formed by the addition of NiO and the acceleration of the dissociation of acetone by NiO as a catalyst, which was also reported by Whyoshup Noh *et al* [7]. However, with further increasing the NiO content, the formation of second phase ($NiWO_4$) may be the reason for the decrease in sensitivity because it is likely to hinder the interaction of acetone molecules on the surface of WO_3.

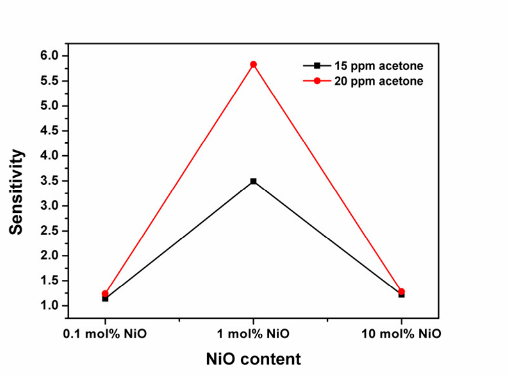

Fig. 4 Sensitivity behavior with NiO content and acetone concentration at 320 °C operating temperature. Sintering temperature 500 °C.

The effect of sintering temperature to the sensor's gas sensing properties was also investigated. The sensitivities of 1.0 mol% Ni-doped WO_3 films sintered at various temperatures (500 to 700 °C) were evaluated. The films were subjected to a few minutes of exposure to 20 ppm of acetone in synthetic air. The sensitivity decreases with increasing sintering temperature obviously. The highest sensitivity was obtained for the films sintered at 500 °C for 1 h. The sensitivity of the films sintered at 500 °C is almost 4 times greater than the films sintered at 700 °C.

Because the humidity of human breath is about 70 %, so it is necessary to discuss the influence of humidity to Ni-doped WO_3 thin films. Based on our experimental results, it is clearly that the sensor's resistance changes little in the test range (20 % - 70 % relative humidity). Especially for 0.1 and 1.0 mol% Ni-doped WO_3, the curve (which is not shown here) is approximately an unchanged straight line. Therefore, it is considered that the sensors prepared in this research are able to resist high humidity environment.

Selectivity is the ability that a sensor can distinguish different kinds of gases. Because there are hundreds of gases exhaled from human health, so the selectivity to acetone is very important. Fig. 5 shows the sensitivity of the films to various gases (such as acetone, ethanol, carbon dioxide, etc.).Compared to acetone, the sensor shows relatively lower sensitivities to other gases. Ethanol, ethylene glycol, isopropyl alcohol and methanol belong to VOCs; however, the sensor sensitivities to 20 ppm of these gases are much lower than that of acetone. Also, the sensor shows a very low response to ammonia, carbon dioxide, and methanal. The above results indicate that the sensor prepared in this research has a good selectivity to acetone gas at 320 °C operating temperature.

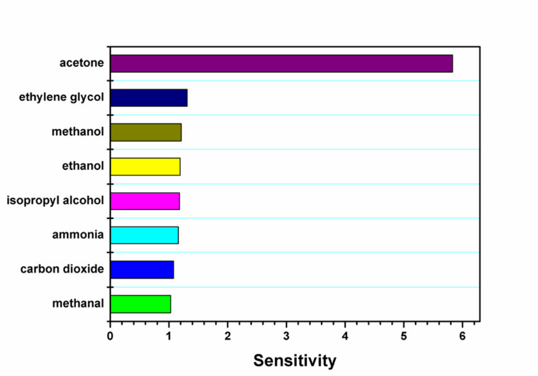

Fig. 5 Sensitivity of 1.0 mol% Ni-doped WO_3 films to 20 ppm various gases at operating temperature of 320 °C. Sintering temperature 500 °C.

A. Teleki et al [5] used flame spray pyrolysis (FSP) method to prepare Cr-doped WO_3 films, and reported that the dissymmetrical monoclinic structure is the key factor for selective acetone detection. In our experiment, similar result has also been obtained. The orthorhombic structure of WO_3 was observed from Fig. 1. It means that this sample possesses large dipole moment, which is resulting from the low structural symmetry. Besides, the appropriate addition of Ni atoms may also introduce distortion into the WO_3 matrix, and repelling tungsten atoms from centric positions in WO_6 octahedra. This can help enhance the structural dissymmetry of WO_3 thin films. Since the acetone gas also has a larger dipole moment than any other gases exhaled from human breath, so the interaction between acetone molecules and WO_3 surface is much stronger, which finally leads to a better selectivity to acetone gas. Nevertheless, over-doping of NiO is detrimental to WO_3 film's selectivity because of the formation of second phase $NiWO_4$.

Conclusions

Ni-doped WO_3 thin films were prepared by sol-gel method. The material and electrical properties were investigated as a function of NiO content, acetone concentration, sintering temperature, and porous structure. The sensitivity of Ni-doped WO_3 films increased with NiO content up to 1.0 mol%, and then it decreased. With increasing the sintering temperature, the sensitivity has a tendency to decrease. The 1.0 mol% Ni-doped WO_3 films sintered at 500 °C for 1 h show highest sensitivity and good selectivity to acetone gas among all samples. The sensitivity of this sensor to 20 ppm acetone attained 5.83. In addition, the humidity has little effect. The small grain size, porous structure and dissymmetrical orthorhombic phase with low symmetry are considered to be main reason for increasing the sensor's sensitivity and selectivity to acetone gas. As a result, the sensors prepared in this study show a fast response, high sensitivity and good selectivity to low concentrations of acetone. It can be a good candidate for diabetes diagnosis based on human breath analysis.

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