Effect of Annealing Temperature on the TiO_2 Nanosized Thin Films Sensing Troperties Towards Ethanol Vapor*

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Abstract: Nanosized TiO_2 thin films were prepared by the method of DC magnetron sputtering, and the films were deposited on alumina tubes and silicon substrates. After the deposition, the films were annealed at 500℃, 700℃ and 1 100℃ in a muffle respectively. The film properties such as crystal structure, grain size, phase and gas sensitivity varied on account of the annealing condition. X-ray diffraction (XRD) and gas sensing measurements were carried out to find out the relation between sensitivity and annealing temperature. Anatase occurs at annealing temperature 500℃. Sensitivity is the highest with wonderful selectivity and shortest response(recover) time for the anatase phase. After modified the surface of TiO_2 thin film, it could be concluded that the best operating temperature for the devices is 370℃. The mechanism of the gas sensing properties was also discussed.

Key words: TiO_2 thin films; Annealing temperature; Ethanol-sensing properties

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0 Introduction

The TiO_2 film has been widely used in sensors to detect various gases, such as H_2, O_2, CO and some organic vapors[1], but there were less investigations on the sensing properties towards ethanol vapor[2].

At present, SnO_2 and ZnO are the main materials to fabricate the ethanol vapor sensors, which were prepared by sol-gel method[3-5]. However, there existed a shortcoming of low selectivity. For example, they are also sensitive to gasoline and benzene, so the selectivity to ethanol in the mixing organic vapor is declined.

In this paper, we point that TiO_2 films possess preferential selected sensation towards ethanol vapor with less response and recover time about 3 seconds. In addition, TiO_2 film is not easy to be poisoned and steady in chemical property with a long life for usage.

We also pay attention to investigate the influence of the annealing temperature for samples on their gas sensitive property, because there are three crystal structures for TiO_2, such as brookite, anatase, rutile. They can transform to each other at definite temperature. There was a report[6] about the phase transition temperature of bulk TiO_2, being 600℃ for brookite, 640℃ for anatase, 1 800℃ for rutile, respectively.

In this work, TiO_2 films were prepared by the DC magnetron sputtering method, afterwards, the samples were annealed at different temperature. Then, their ethanol vapor-sensitive properties were detected with a gas-sensitive measurement instrument.

1 Experiments

The TiO_2 films were prepared by the DC magnetron sputtering equipment. The fabrication specifications were as follows: vacuum 3×10^{-3} Pa; 0.23 oxygen partial pressure for 1.6 Pa full pressure; 10 cm distance between target and substrate; 470V applied voltage with 0.2 A sputtering current. The used two substrates were respectively Si (111) wafer and Al_2O_3 ceramic tubes. The former were used for analyzing crystal structure of TiO_2 by XRD; the latter were used as gas-sensitive elements for detecting the sensitivity for varied sorts of gases. All samples were annealed respectively at different temperature during 3h. After cooling for 9 h in furnace, the samples were withdrawn out.

2 Experimental Results

2.1 The structure analysis for film samples

Fig. 1 shows the XRD measurement results for samples 1#, 2#, 3#, 4#. They were annealed respectively at 500℃ (2#), 700℃ (3#), 1 100℃ (4#), except for sample 1# without

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annealing.

It can be seen from Fig. 1 that sample 1＃ shows a amorphous structure; sample 2＃ shows anatase crystal structure with its characteristic diffraction peaks A(101), A(004), A(105) besides Si (111) diffraction peak at $2\theta=28.4°$. Sample 3＃ shows a majority of anatase phase, coexisted with a little rutile with its characteristic diffraction peak R(110). Sample 4＃ shows rutile crystal structure with its characteristic diffraction peaks R(110), R(220), R9210), R(220), R(310). It can be confirmed that anatase are formed at annealing temperature 500℃, rutile occurs beyond 700℃ and is transformed at temperature of 1 100℃ at all from anatase.

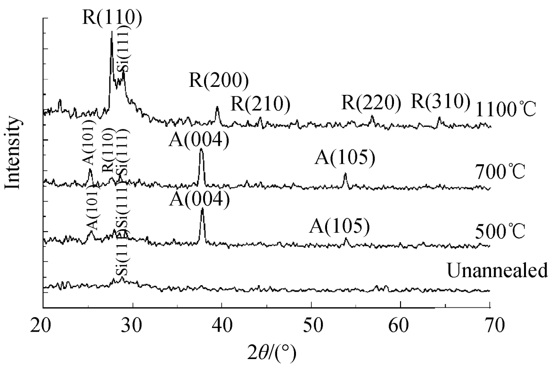

Fig. 1 The XRD of samples1＃, 2＃, 3＃, 4＃

The size of crystal grain can be estimated by following Scherrer formular for different annealing temperature

$$D=\frac{K\lambda}{\beta\cos(\theta)}$$

Where D is size of grain, λ is wave length of X ray, θ is Bragg angle, β is width of the diffraction peak for half of its hight. The average sizes of grain for sample 2＃, 3＃, 4＃ after annealing were calculated out according to Scherrer formular respectively: 10, 16, 28 nm. The size of grains increases with the annealing temperature.

2.2 Detecting the gas-sensitive properties of TiO_2 thin films towards ethanol vapor

In this experiment, the equipment of gas sensing measurement is HW-30 gas sensing system, which is the product of HanWei Electronics limited company of China. The test principle diagram of this system is as follows.

In Fig. 2, V_h is the pyrogenation voltage (V), for heating the film on tube, V_c is the applied voltage(V), R_s is the loading resistance, Vout is the output voltage. Sampling time is one second. Definition of the sensitivity is $S_r=R_{ethanol}/R_{air}$. In

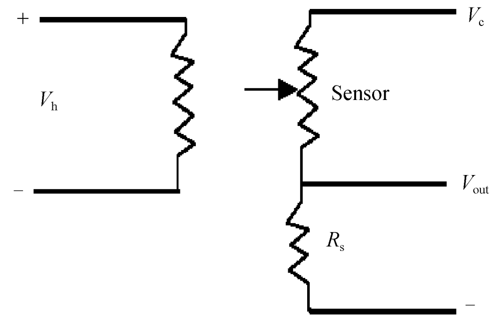

Fig. 2 The sensing system test principle diagram

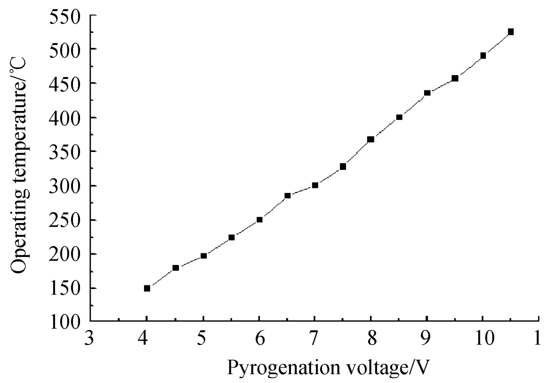

Fig. 3 The relationship between the pyrogenation voltage V_h and the thin films operating temperature

this equation, R_{air} is the resistance of thin film in the air; $R_{ethanol}$ is the resistance of thin film in the ethanol vapor. The conditions of this experiment is as follows: $R_s=100$ MΩ, $V_h=8.0$ V, one standard atmospheric pressure; the environment temperature is 28℃ and humidity is 20% RH. Fig. 3 shows the relationship between operating temperature of TiO_2 films and pyrogenation voltages.

From Fig. 4 and Table 1, it can be seen that the sensitivity of sample 2＃ is much higher than others. The best pyrogenation voltage for it is 8.0 V. So its best operating temperature is about 370℃. (Fig. 3)

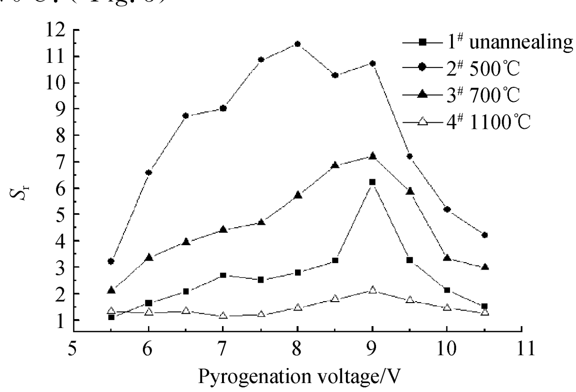

Fig. 4 Respective sensitivity(S_r) of samples 1＃、2＃、3＃、4＃ in different pyrogenation voltage(V_h)

Table 1 S_r, response time Tres(S) and recover time Trec (S) of sample 2# in different pyrogenation voltage(V_h)

V_h/V	S_r	Tres(S)	Trec(S)
5.5	3.22	45	19
6.0	6.58	26	27
6.5	8.74	15	8
7.0	9.03	10	4
7.5	10.87	6	3
8.0	11.48	2	3
8.5	10.3	8	3
9.0	10.74	8	3
9.5	7.21	10	4
10.0	5.19	23	26
10.5	4.21	37	34

Sample 2# also has an excellent selectivity, shown in Fig. 5. It can resist the interference of other familiar gases and organic vapor. In this experiment, the concentration of different testing gases is shown in the Table. 2.

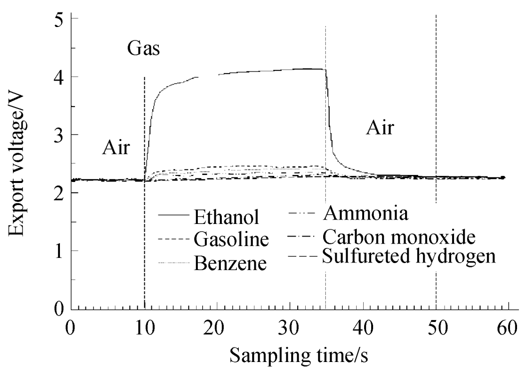

Fig. 5 Kinetic response—recovery of sample 2# towards different gas at operating temperature of 370℃

Table 2 The concentration of the used different gases and the sensitivities of sample 2# towards them

Test gas	concentration	S_r
ethanol	Volume: 20%	7.68
Gasoline	Saturated vapor	1.38
Benzene	Saturated vapor	1.17
Ammonia	Saturated vapor	1.11
CO	Volume: 20%	1.03
H_2S	Volume: 20%	1.01

2.3 Discussion

The gas-sensitive mechanism of the nanosized TiO_2 thin films toward ethanol vapor are similar to TiO_2 thin films toward oxygen[7]. When they adsorb the test gas, then the electric resistance of thin film is changed. However, the ethanol is reductive gas and the oxygen is oxygenating gas.

The complicated physic-chemical reactions were took place in the surface of the thin film of TiO_2[8-12]. Using the technique of infrared ray detecting, we compared the spectrograms of the gas component before reactions and after reactions, found out the products of the reactions. That can help us investigate the mechanism of TiO_2 thin films sensing properties towards ethanol vapor.

The method of I-R detecting is that: Took the ethanol vapor (the concentration is 20%) into the gas-cell which is make up of KBr, then did the I-R detecting (the upper line of the Fig. 6). Put the ethanol gas-element in to the gas-cell, supplying the pyrogenation voltage (V_h = 8.0 V) so as to make it work normally for 90 minutes. Finally, detected the products in the gas-cell by the I-R measure.

From Fig. 6, Two curves are very similar, but the transmittance of reacted gas in 1 694, 1 756 and 2 383 cm^{-1} is lower than the unreacted one. Those peaks are correspondingly with chemical bonds of ethanol except the peak 2 363 cm^{-1} in the upper curve. The peak 2 363 cm^{-1} is the absorbed peak of carbon dioxide in the testing gas. The testing gas contains N_2 and O_2, but they belong to symmetrical double-atom molecule, so can not absorb the I-R. We can see the bottom curve in the Fig. 6, the transmittance is lower, that shown more CO_2 was created. The peak 1 756 cm^{-1} and peak 1694 cm^{-1} are respectively the absorbed peak of group CHO and group C = C. We also can drown the conclusion from Fig. 6, H_2O was created after reactions, that made the bottom curve smoothly in the 4 000 ~ 3 800 cm^{-1}, 1 800 ~ 1 500 cm^{-1} and 650~430 cm^{-1}.

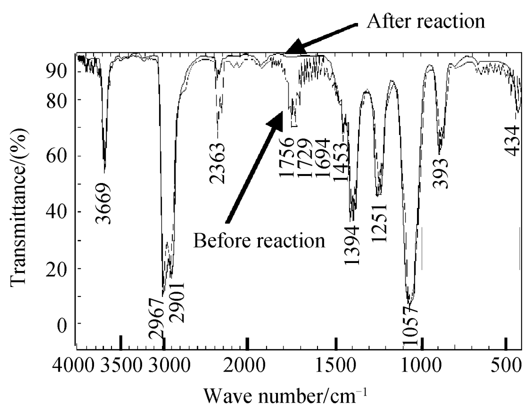

Fig. 6 The IR spectra of the detected gas

In general speaking, there are some steps occur in the surface of the TiO_2 thin film:

1) In the air environment, oxygen molecules are adsorbed on the film surface of metallic oxides, capturing great quantities of electrons from metallic oxides, so as to reduce the conductivity of the film: O_2(g) + e- = 2O-(ad).

2) The absorbed oxygen are bound to unsaturated metal sites(M+): O-(ad) + M+ = O-M.

3) Ethanol are absorbed on the film surface: $CH_3CH_2OH = CH_3CH2OH(ad)$.

4) The absorbed ethanol is dissociated as CH_3CH_2O by the catalytic function of O-M:

$CH_3CH_2OH(ad) + O\text{-}M = CH_3CH_2O + H\text{-}O\text{-}M$.

5) CH_3CH_2OH are further dissociated as water and CH_3CHO, while electrons are transformed into the film to increase the conductivity of the film:

$CH_3CH_2O + H\text{-}O\text{-}M = CH_3CHO + H\text{-}O\text{-}H + M{+} + e^-$.

6) CH_3CHO and adsorbed oxygen O-(ad) reacted, there are group C = C created, farther more, the chemical bonds between the double carbon atoms are ruptured, finally became into the water and carbon dioxide.

Our experiments indicate that these four samples have different properties toward ethanol vapor. Because the annealing temperature are different, the grain size, phases are different. According to XRD analysis results, we can know that the higher annealing temperature, the bigger grain size. So the annealing temperature have great influence on the sensing properties of the sensors. Operating temperature is also a very important parameter. An optimal operating temperature can accelerate the process of adsorption and disengagement, have shorten the response and recovery time.

Fig. 7 shows the sensing property towards ethanol vapor of sample 1#. The conditions of this experiment is as follows: $R_s = 4.7$ MΩ, $V_h = 9$ V (operating temperature is about 425℃), one standard atmospheric pressure; environment temperature is 28℃ and humidity is 20% RH. The concentration of ethanol vapor is 20%.

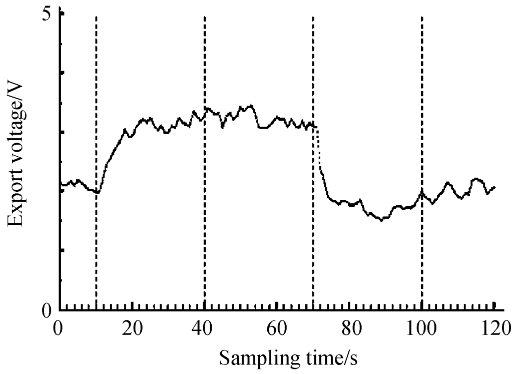

Fig. 7 Kinetic response—recovery of sample 1# towards ethanol vapor at operating temperature of 425℃

According to Fig. 7 we can see that the sensitivity at this operating temperature is much higher ($S_r = 6.12$), but the response time and recovery time are too long (Tres(S) = 20 s, Trec(S) = 35 s). Furthermore, the response-recovery curve is not smoothly. The reason is as follows: Sample1# without annealing shows a amorphous structure, when the sample1# is operating on a much higher temperature, above 425℃, it is in an unsteadiness habitus. The microstructure, phase, and the size of grain would change slightly, so the stability is much poor.

3 Conclusion

According to experiments above we can draw the conclusion as following: annealing conditions have great influence on the grain size and phase. TiO_2 thin films are an amorphism when they are not annealed. These films have a little ethanol-sensing properties, the sensors are not very stable, the response and recover time are long. Anatase occurs at annealing temperature 500℃, the films have excellent selectivity and highest sensitivity. The response and recover time are also shorter than others, Tres(S) = 2 S, Trec(S) = 3 S. The best operating temperature is 370℃ After modified the surface of TiO_2 thin film. Rutile occurs at annealing temperature 700℃, the sensitivity and selectivity appear to be descending when temperature increase. TiO_2 thin films are transformed into rutile completely when anneled at 1 100℃. These sensors have the worst sensitivity ($S_r < 1.5$) and selectivity. So the anatase phase of the TiO_2 thin films has best ethanol-sensing properties.

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退火温度对 TiO_2 纳米薄膜酒精气敏特性影响的研究

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摘　要：采用直流磁控溅射的方法在 Al_2O_3 陶瓷管、硅基片上溅射制备了二氧化钛（TiO_2）纳米薄膜材料. 将薄膜样品放入管式退火炉中分别在 500℃，700℃和 1 100℃温度下退火. 由于退火温度的不同，薄膜的晶体结构、晶粒尺寸、晶向以及气敏特性都有所不同. 利用 X 射线衍射（XRD）技术和薄膜气敏特性测试，分析了退火温度对薄膜气敏特性的影响. 分析结果表明退火温度在 500℃时，呈现锐钛矿结构，薄膜具有很好的选择性、很短的反应（恢复）时间. 对 TiO_2 薄膜表面进行修饰，发现此 TiO_2 薄膜的最佳工作温度为 370℃左右. 薄膜的气敏机理也得到了讨论.

关键词：二氧化钛纳米薄膜；退火温度；乙醇气敏特性

LI Yang was born in 1969. He received the M. S. degree and Ph. D. degree from Nankai University. Now he is engaged in the research of material and device technology for sensors.