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The Research of Micro-structure and Gas Sensitivity of SnO_2

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Abstract: This paper adopts Sol-gel method and solid state reaction to make SnO_2 matrix material and Sb_2O_3 is used as zuji to make SnO_2 gas sensor under different sintering temperature. XRD analysis, SEM analysis and response time restoration test of working voltage sensitivity are choose to research SnO_2 gas sensor constituents and influence factor on sensing properties by processing. Experiment results show that when the SnO_2 make by sol-get method and Sb_2O_3 take up 2 %, Polyvinyl alcohol as an organic binder, platinum as catalyst, SnO_2 gas sensor can get optimal integral sensing properties. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: SnO_2, Gas sensitive character, Microstructure.

1. Introduction

Since the early 1930s, the finding of phenomenon that Cuprous oxide conductivity values change by water vapor adsorption, people conduct a series of in-depth and widely research on sensitivity material properties such as Gas sensing, thermal, humidity and pressure sensitivity. Metal oxidize gas sensor common adopts SnO_2 base material and can detect different gas constituent and concentration [1]. Due to the better gas sensitivity and selecting ability, better response-recovery time and long lifetime, so it is used widely to detect different poisonous gas, combustible gas, industry and environment pollution gas. In order to enhance the gas sensor sensitivity, selecting ability and application range, Sberveglieri G. proposed Rheotaxial Growth and Thermal Oxidation technology which adopt Magnetron sputtering to form 150 nm Sn film when the temperature reach 232 degree [2]. Then the Sn film conduct thermal oxidation reaction and SnO_2 film is produced. Some people believed that the SnO_2 film make by RGTO has good properties such as highly porous, loose, good sensitivity and stability [3]. Therefore, the development of high-performance SnO_2 gas sensor has important theoretical and practical value.

2. Theory and Preparation

2.1. The Theory of SnO_2 Gas Sensor

SnO_2 belongs to N type semiconductor which has Oxygen vacancies or gap iron and gas sensitivity is obvious [4]. Gas sense theory has many models and generally considered that it controlled by surface adsorption which means barrier is built in material crystal borders when heated in clean air. Then the barrier limits the electron drift in electric field and Make it difficult to pass through the barrier. Therefore the material conductivity is decreasing. But the measured gas reacts or exchanges position with adsorbed oxygen in reducing atmosphere, which makes adsorption oxygen desorption, surface barrier decreasing and material conductivity increasing. According to the change of material conductivity, gas detection is completed.

2.2. SnO_2 Gas Sense Material Preparation

Sol - gel method and solid state reaction method are adopted respectively, SnO_2 base material are prepared by anhydrous stannic chloride and sodium. Zuji uses Sb_2O_3, catalyst using chloroplatinic acid and gold chloride acid, adhesives using pickling asbestos, SiO_2 and Al_2O_3.

2.2.1. Sol-gel Method

Sol - gel method fundamental theory is that metal alkoxide or inorganic salts hydrolysisted to form sol or deagglomeration to form sol. Then the solute polymerized Gelation. By controlling the gelled process, Spherical particles of gel are got, and the required powder is made by certain temperature sintering [5].

The experiment make weighed Tin tetrachloride in beaker and add deionized water to form a solution of desired concentration. The $SnCl_4$ solution mixed with 1 % Citric acid water and uniform drop 28 % concentrated ammonia until overdose. Stirring was continued for 1 hour or more so as to form uniform and stable sol. Later the sol is filtered and cleaned by water bath until the $AgNO_3$ solution drop in the filtrate can't form deposition, which prove that Cl^- is disappear. Cleaned and purified sol stored for 12 hours to form gel. The gel is evaporated and dried, and the dried deposition is pestle by agate mortar. Then heat treatment is done with the temperature 400~800 ºC for 3 hours and the SnO_2 Ultrafine powder is get.

2.2.2. Solid State Reaction

Get a certain amount of tin tetrachloride and sodium carbonate (molar ratio 1:2), put in an agate mortar, fixed completed, grind to reacting completed, washing drying, 400~800 ºC calcined 1h, fully grind to obtain product.

2.2.3. Main Performances Parameters

1. Fixed resistor R_0.

Resistor of the gas sensor in normal condition called static resistor.

2. Working resistor R_S.

Resistor of gas sensor in certain concentration measured gas.

3. Sensitivity.

When gas sensor works in normal optimized condition, the ratio of R_0 and R_S under different gas concentration is called device sensitivity.

4. Response time and recovery time.

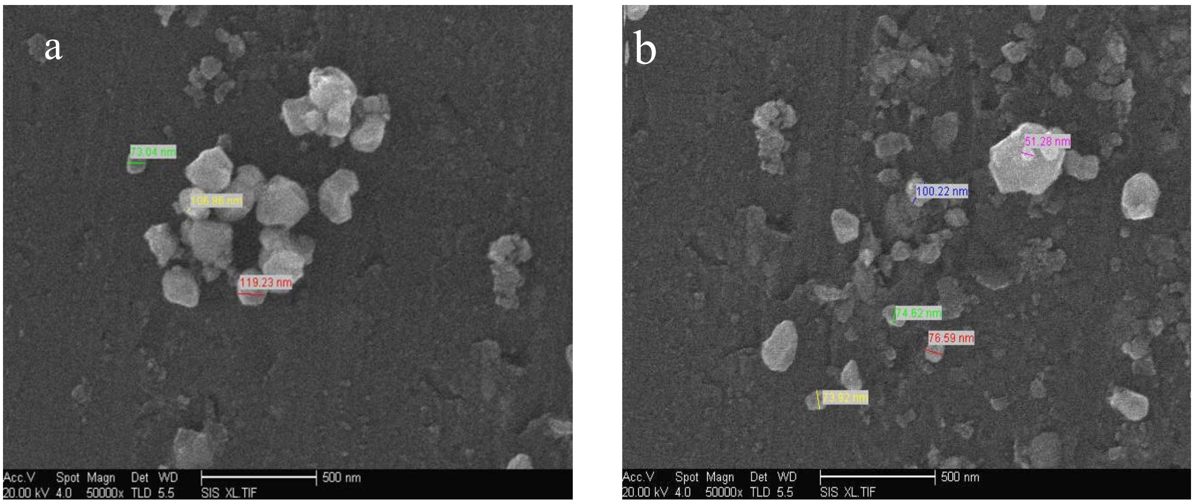
When the gas suddenly changes from one concentration to another concentration, the device resistance change quickly early and tend to stable later. General, the time of reaching 90 % of stable value is called response time. And the time of the concentration change to 10 % of original concentration is called recovery time.

3. Experimental

3.1. Contrast Between Sol-gel Method and Solid State Reaction

3.1.1. The SEM of SnO_2 Film Micro Structure

The Fig. 1 is the morphology figure of SnO_2 grain made by solid state reaction and sol-gel way.



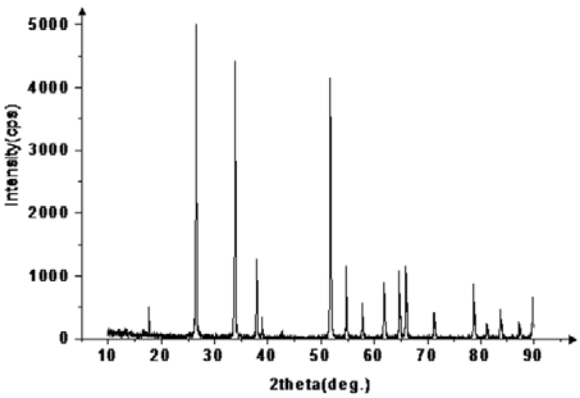
(a) sol-gel (b) solid state reaction

Fig. 1. SnO_2 grain morphology made by two ways.

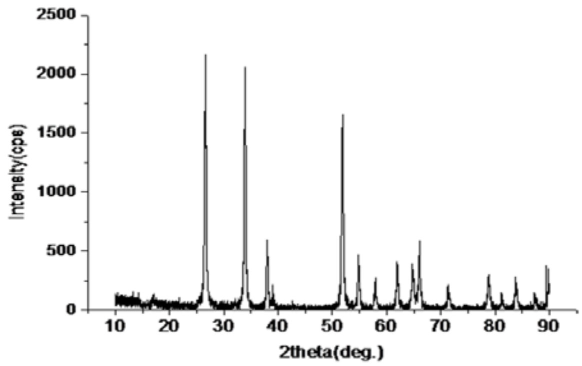
From the figure, we can know that the SnO_2 grain has irregular shape, different diameter that from 50 nm to 300 nm. But the SnO_2 made by solid state reaction has uniform small diameter about 70 nm, spherical shape, good dispersion and small change. From the requirement of gas sensor performance, the SnO_2 made by sol-gel way is more suitable for gas sensor devices base material.

3.1.2. X-ray Analysis

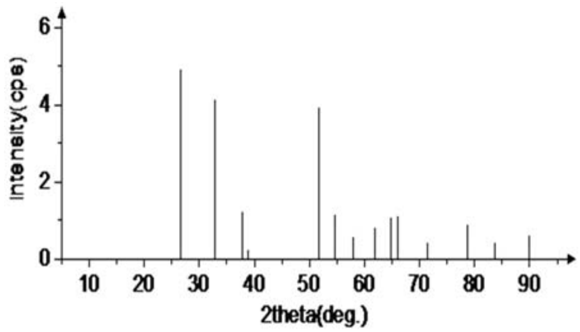
This paper adopts X-ray diffractometer to analyses SnO_2 base material made by sol-gel and solid state reaction. The results are shown in Fig. 2.



(a) Solid reactivity method



(b) Sol-gel method



(c) Standard spectrum of JCPDS

Fig. 2. XRD spectrum of gas sensitive materials prepared by different methods.

By contrasting the powder X-ray diffraction and JCPDS (21-1250) standard atlas, we can know that the powder made by two ways has consistent diffraction peak position and SnO_2 standard peak position. And the results show that the two kind powders are SnO_2 which structure is rutile. The gas sensor made by solid state reaction and sol-gel has no miscellaneous peak which explains that every kind chemical composition has reacted completed. And the SnO_2 has high purity. Compared with solid state reaction way, nano micro crystal diffraction peak made by sol-gel has wide range. By using Scherrer formula, the SnO_2 diameter is estimated as Table 1 and Table 2 shown.

Table 1. Particle diameter by sol-gel method.

β/rad	2θ/o	d/nm	mean/nm
0.0047	26.56	32.2	32
0.0067	33.86	24.64	
0.0037	51.76	40.16	

Table 2. Particle diameter by solid reactivity method.

β/rad	2θ/o	d/nm	mean/nm
0.0022	26.56	65	70
0.0041	33.86	52	
0.0019	51.76	81	

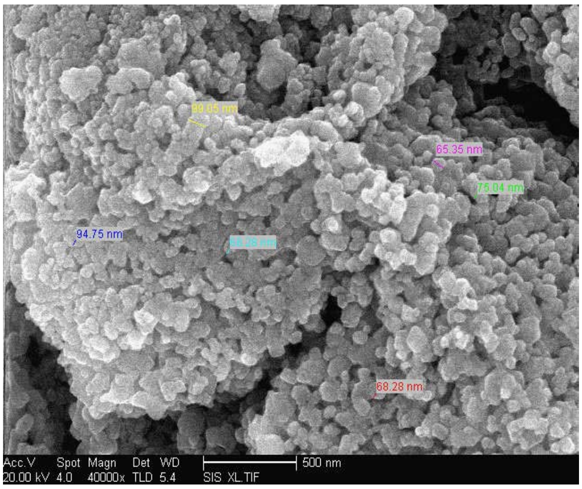
It can be seen from the Table 1 and Table 2, the SnO_2 base material made by Sol-gel way has tiny grain diameter that distributes from 24 to 40 nm. And the grain made by solid state reaction is in the range of 50-80 nm. Above all the grain made by sol-gel way has relative small diameter.

From the above analysis, we can know that the SnO_2 grain made by sol-gel way is more suitable for gas sensor base material. Next, the research is focus on the affect to the performances and SnO_2 grain morphology in other environment conditions.

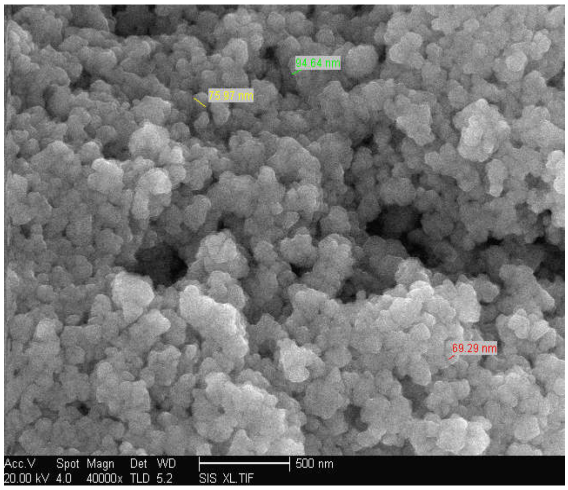
3.2. The Affect to SnO_2 Grain Morphology in Different Conditions

3.2.1. Influence on Granularity by Sinsering Temperature

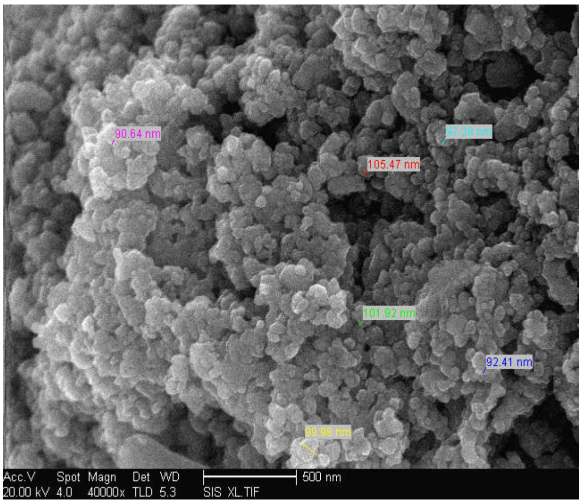
When the dioxide gas sensor is made, the grain need to sinter, which is aim to crystallization well and has a good connection with metal plate. In this process, the sintering temperature is an important parameter. The Fig. 3 is the SnO_2 grain morphology made by different sintering temperature. The Fig. 4 is the cure of SnO_2 crystal grain diameter and different sintering temperature.



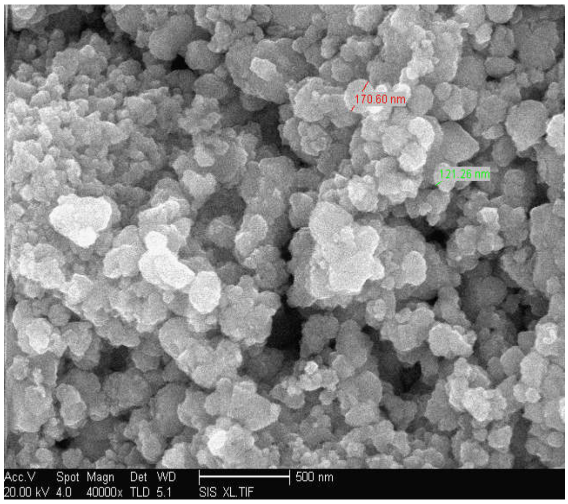
(a) at 400 °C



(b) at 500 °C



(c) at 600 °C



(d) at 700 °C

Fig. 3. The surface morphology of the film at different sinter temperature.

It can be seen from the Fig. 3 clearly, the sintering temperature has a big effect to the grain diameter. And the changing law is as Fig. 4 shown.

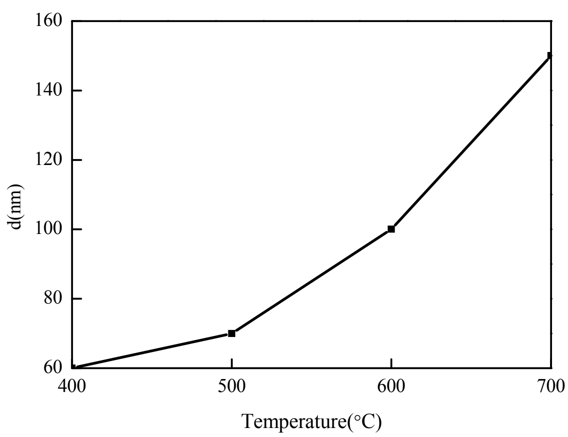
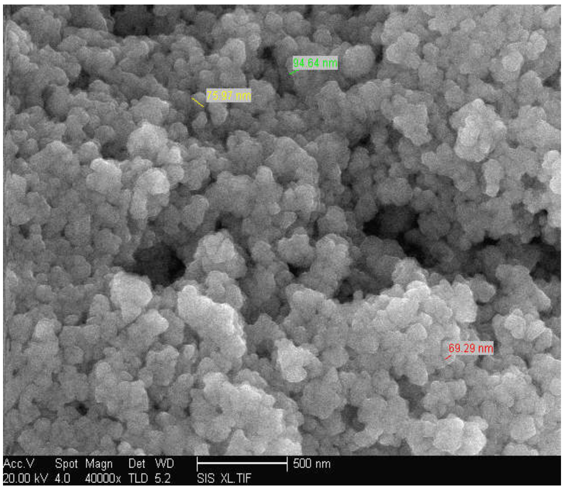


Fig. 4. Curve of SnO_2 crystal particle size at different temperatures.

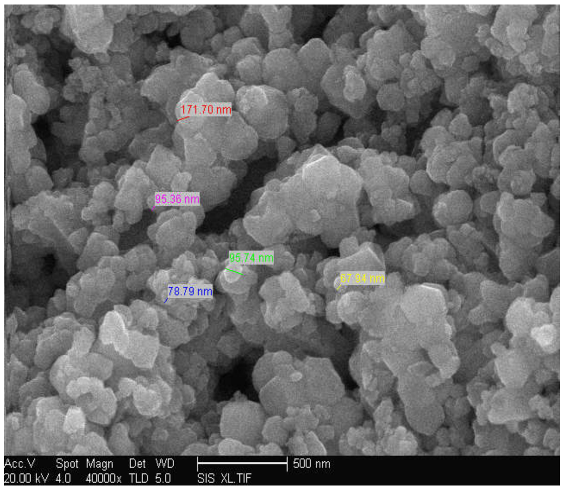
The SnO_2 crystal diameter is becoming bigger as the temperature increasing. When the sintering temperature is 400 degree, the SnO_2 diameter can reach to 60 nm. When the temperature is 500 degree, the diameter can reach to 100 nm. When the temperature is 700 degree, the diameter can reach to 150 nm. Considering the SnO_2 rutile structure can change in the 460 degree condition and gas sensor base material can burst in the 700 degree condition. So this paper adopts 500 degree sintering temperature to get smaller SnO_2 crystal grain.

3.2.2. The Influences on Granularity by Doping Antimony Trioxide

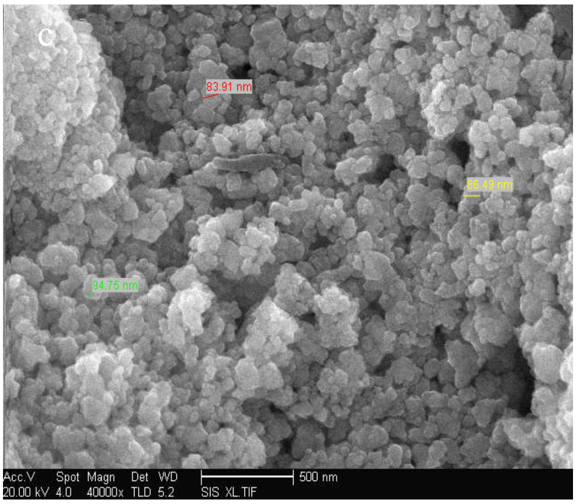
The Fig. 5 is the SnO_2 grain surface morphology when doping different concentration Antimony trioxide. And the base grain changes are as Fig. 6 shown.



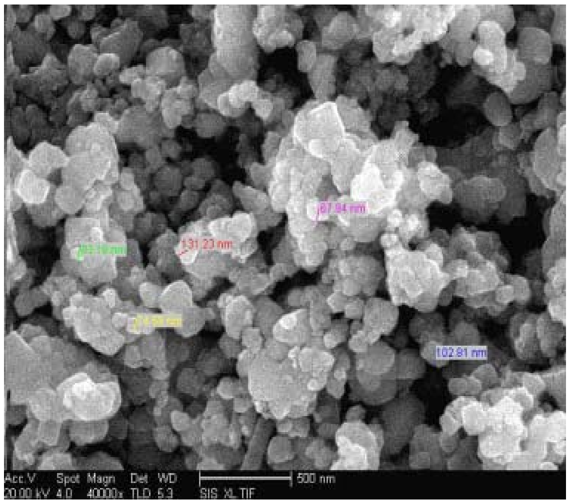
(a) 0 % Sb_2O_3



(b) 1 % Sb_2O_3



(c) 2 % Sb_2O_3



(d) 3 % Sb_2O_3

Fig. 5. Curve of SnO_2 crystal particle size at different doping Sb_2O_3.

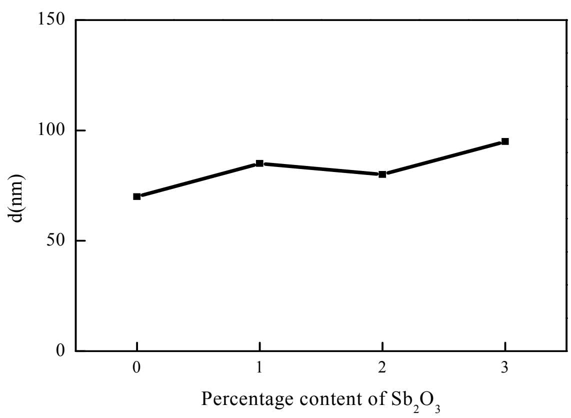
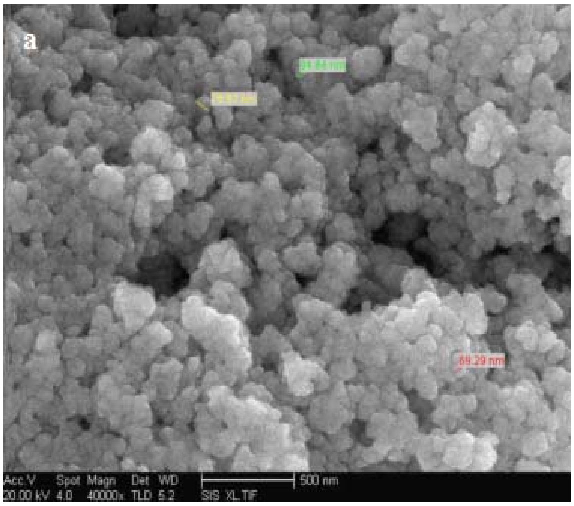


Fig. 6. Curve of SnO_2 crystal particle size at different doping Sb_2O_3.

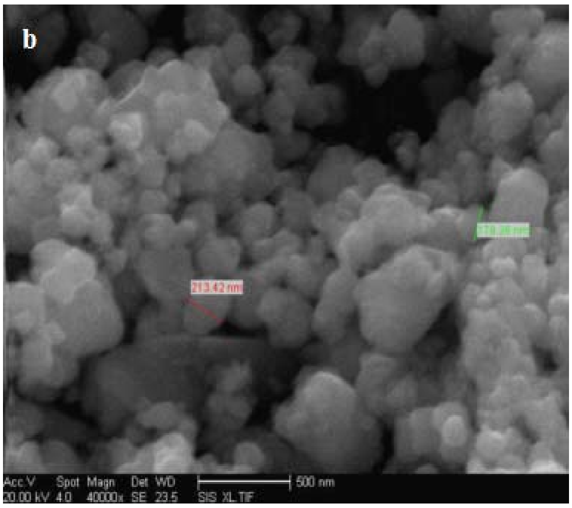
From the Fig. 5 and Fig. 6, it can be seen that the antimony trioxide can control the SnO_2 diameter. When not doping antimony trioxide, SnO_2 grains have agglomeration phenomenon, the smallest grain diameter is about 70 nm and with small porosity. When doping antimony trioxide, the agglomeration decreasing. crystallization getting uniform, porosity increases. When doping 2 % of antimony trioxide, grain size is about 80 nm. Above all, doping antimony trioxide has impact on the grain size, but little.

3.2.3. The Influences on Granularity by Doping Adhesives

It can be seen from the Fig. 7, the SnO_2 crystal grain made by organic adhesive is Spherical and uniform. The average size is 70 nm and it has many blowholes. And the SnO_2 crystal grain made by inorganic adhesive has different sizes and fewer blowholes. Due to the factor that organic adhesive reacts and volatilizes with no residual impurities and condensation centers left in high temperature condition. Besides, the organic adhesive adopts liquid penetrating with a uniform distribution.



(a) Organic felted solution



(b) Inorganic felted solution

Fig. 7. SEM image of SnO_2 at different felted solution.

Because of the volatile gas, uniform gas holes are easy to form. Above all, the SnO_2 crystal grain made by organic adhesive has characters of small size, uniform gas holes which benefit to recovery time decreasing compared to SnO_2 made by non-organic adhesive.

4. Conclusions

This paper researches the different constitutions and process influences on the SnO_2 crystal grain dimension and gas performance. The XRD analysis show that solid state reaction and sol-gel way can get high purity SnO_2 base material. The SnO_2 crystal grain dimension made by solid state reaction is about 70 nm and sol-gel way can get 30 nm dimension. SEM test results show that the SnO_2 crystal grain made by solid state reaction has irregular morphology and different sizes that from 50 nm to 300 nm. And the SnO_2 crystal grain made by sol-gel has the characteristics of small size, uniform dimension about 70 nm, spherical and dispersed well.

The optimum process of the SnO_2 gas sensor made by sol-gel is: 500 ºC sintering temperature, sintering 1h, Sb_2O_3 as Zuji, 2 % doping dose, 0.2 % Platinum catalyst and Polyethylene as organic adhesive. Besides, the sensor working resistor is 200 Ω~500 Ω which is suitable for following circuit design and the response time is 3 seconds. Analysis prove that the adhesive can increase SnO_2 grain dimension by doping metal ion to form condense center and attract positive and negative ion. At the same time, the metal ion both act as condensation centers and catalytic to improve sensitivity.

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