ISSN 1726-5749

SENSORS & TRANSDUCERS

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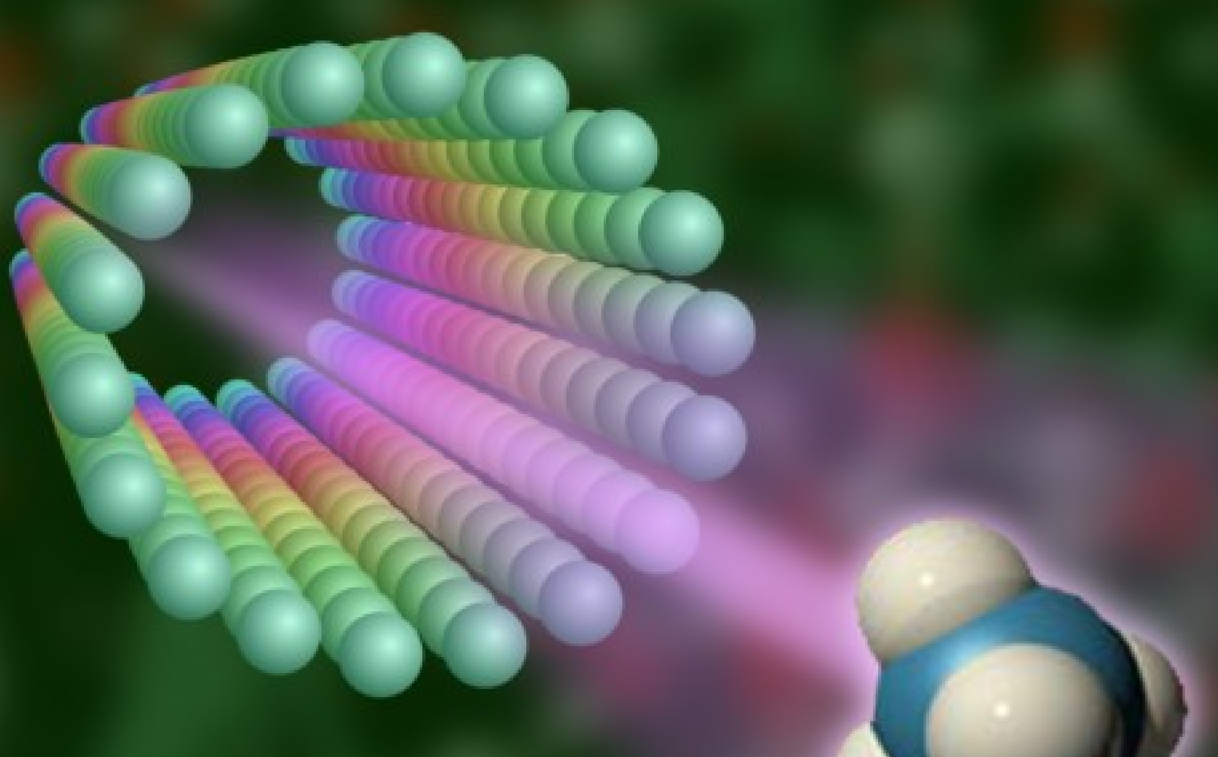
vol. 73



Nanosensors and Nanodevices

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 73
Issue 11
November 2006

www.sensorsportal.com

ISSN 1726-5479

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Sensors & Transducers Journal, Vol.73, Issue 11, November **2006,** *pp.819-825*

Sensors & Transducers

ISSN 1726-5479

http://www.sensorsportal.com

Effective Factors on Methane Sensing of Tin-Oxide Activated by Palladium in Sol-Gel Process

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Received: 8 October 2006 /Accepted: 30 November 2006 /Published: 4 December 2006

Abstract: Stannic oxide thin films activated by palladium were prepared by sol-gel method. The morphology of the layers and the size of the particles were investigated by scanning electron microscopy and atomic force microscopy. Investigations showed that the number of coating, annealing procedure and the viscosity of the sol, affect structure and thickness of the layers. These different preparing conditions result in different change in resistivity of the samples toward methane gas. In addition to these parameters, the Pd/Sn atomic ratio in the sol is another effective factor on sensitivity of methane.

Keywords: Methane sensor, SnO_2 nanoparticle, Palladium, Sol-gel

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1. Introduction

Methane is the principle component of natural gas and when it burns, is a cleaner source of energy than coal and oil. In Iran, this gas is used in various fields especially for domestic application for heating and cooking extensively. Therefore, methane leak should be avoided because concentrations of methane in dry air exceeding 5% are easily flammable and highly explosive. Consequently, detection and monitoring of this gas in the vicinity of methane pipes in homes by a low cost sensor has received more attention.

Metal oxide semiconductor gas sensors have been largely employed for the detection of toxic and explosive gases in air. Among the metal oxides, tin oxide (SnO_2) is the most used material in chemical gas sensors due to its high sensitivity at relatively low operating temperature. In fact, commercially available gas sensors are mainly based on this material. Moreover, it has been shown [1-3] that sensing material in the nanoparticle phase improves the sensitivity of chemical sensors. Among the several techniques for the preparation of thin film tin-oxide (e.g. RF sputtering, electron gun evaporation, PVD, RGTO, etc.) as a gas sensor, sol-gel technology has won the scientific interest because of its advantages mainly related to the low cost of nanoparticles production [3-11].

In this work, we produced sol-gel derived SnO_2 thin-films. Since the introduction of small quantities of Pd to tin-oxide increases the sensitivity to methane and the sensor can be operated at lower sensing temperature [7, 12], we added palladium to the sol. The effect of number of coating, annealing procedure, concentration of the palladium in the sol and viscosity of the sol on the film sensitivity toward methane were investigated.

2. Experiment

Pure SnO_2 sols were prepared starting from anhydrous $SnCl_4$ (99% Merck), water, propanol (C_3H_7OH), isopropanol ($2\text{-}C_3H_7OH$), in the following molar ratios: $SnCl_4/H_2O/C_3H_7OH/2\text{-}C_3H_7OH=1:9:9:6$. For this purpose, $SnCl_4$ was dropped into two-third of the total amount of propanol. An exothermic reaction took place. After cooling down the solution, one third of the total water was dissolved in the remaining propanol and added dropwise for prehydrolisis of the Sn precursor. The prepared sol was stirred with stirrer for 1h. Then this sol was mixed with a solution that it was prepared with the remaining amount of water dissolved in tatal amount of isopropanol, followed by 1h stirring. For the activation process, the palladium acetate dissolved in acetone added to the pure sol with different Pd/Sn atomic ratio and for preparing sol with different viscosity, acetone was added to the sol.

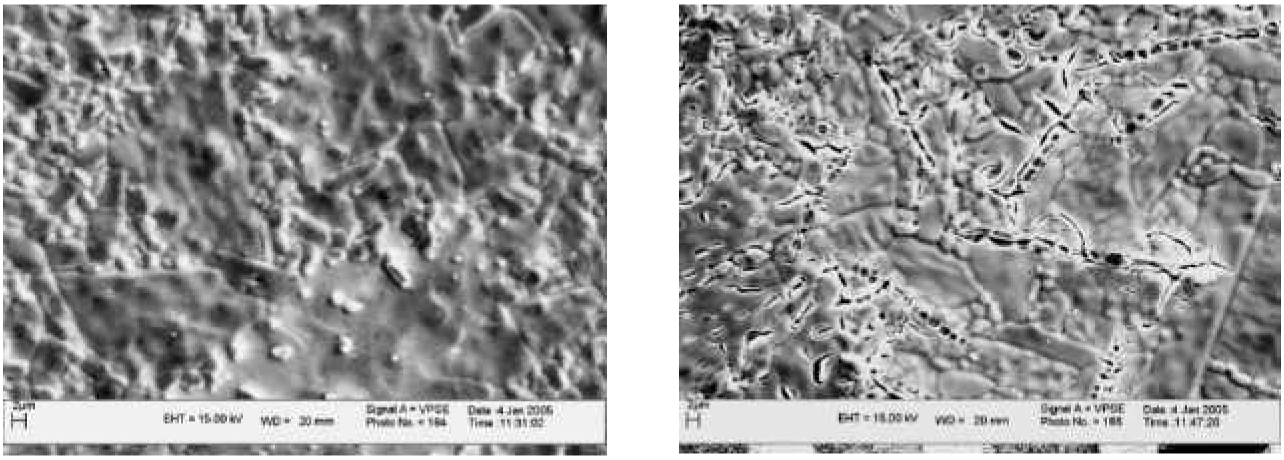
After a suitable cleaning procedure on Al_2O_3 substrates (10×10 mm^2), the prepared sol was deposited by spinning at 3000rpm. After the deposition, the sensitive layer was dried for 20 min at 100^oC and was annealed at 600^oC for 1h. For deposition of more layers, two procedures were used. In procedure A, after the layer deposition and drying for 20 min at 100^oC, the subsequent layers were deposited and dried. Annealing at 600^oC for 1h was done in this procedure as a final sequence. In procedure B, each layer was deposited, dried for 20 min at 100^oC and annealed at 600^oC for 1h and this sequence repeated for subsequent layers.

Atomic force microscopy (AFM) was done in the ambient atmosphere (Autoprobe CP, Vecco company) with a Si cantilever. Scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDAX) were performed in a SEM1455 (VP, LEO company) microscope. For viscosity measurement an Ostwald viscometer was used.

For measuring the sensitivity toward methane, diluted gas with dry air was utilized. Samples with Ti/Au interdigitated electrodes were placed in a test chamber and diluted gas with the rate of 250 sccm was passed over them. During operation, the sensors were heated to a desired temperature. For measuring sensitivity a 100-10000 Ù resistor was connected in series with the sensor along with a constant dc voltage supplier and a 2 V voltage was applied between the sensors and resistor. The sensitivity defined as $S=(V_{r,g}/V_{r,a})-1$ that $V_{r,a}$, $V_{r,g}$ are the resistor voltage in the absence and presence of gas, respectively.

3. Results and Discussion

Fig.1 shows the SEM images of SnO_2–Pd (Pd/Sn =0.02) thin films after two-layer deposition by procedure A (Fig.1a) and procedure B (Fig.1b). Both images illustrate a rough surface. However, the roughness of these two surfaces is lower than the roughness of alumina substrate. Moreover, it can be observed that procedure A causes many cracks on the surface. EDAX investigations were made in order to get semi-quantitative information on the film composition. Fig. 2 reports an EDAX spectrum which was taken from the sample of Fig.1b.This spectrum shows the presence of C, O, Al, Pd and Sn. The Al and C peaks come from the alumina substrate and contamination respectively.



a) b)

Fig. 1. SEM image of two-layer SnO_2-Pd (Pd/Sn=0.02) after annealing by procedure a) A, b) B.

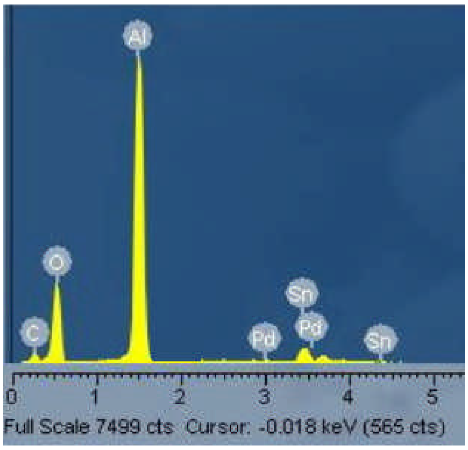


Fig. 2. EDAX spectrum of the sample in Fig. 1b.

Atomic Force Microscopy gives us information about the grain size of the particles in the layer. Fig. 3 illustrates one of the AFM images from the SnO_2–Pd (Pd/Sn =0.02) surface after the deposition of two layers by procedure B. “Scanning Probe Image Processor” (SPIP) software helped us to derive the average size of SnO_2 particles in Fig. 3. By taking image from different parts of the surface and deriving the average size of particles in each image by foregoing software and averaging over these sizes, the average size of SnO_2 particles in each sample was calculated. Table 1 shows these averages for some samples. It can be seen that the average size of the grains increases by increasing the number of layers in procedure A. However, in procedure B, this size remains nearly constant by increasing the number of layers, changing the palladium concentration in the sol and viscosity.

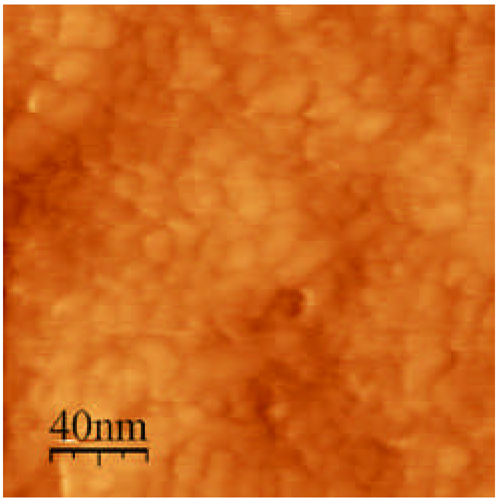


Fig. 3. AFM image of the sample in Fig. 1b.

Table 1. Average particle size for some samples calculated by SPIP software.

Sample	Number of layers	Annealing procedure	r =Pd/Sn	Viscosity (cP)	Particle size (AFM results) (nm)
S1	1	---	0.02	---	15.5
S2	2	A	0.02	---	22.0
S3	2	B	0.02	---	15.7
S4	3	A	0.02	---	31.0
S5	3	B	0.02	---	15.4
S6	2	B	0.05	3.15	15.6
S7	2	B	0.05	2.72	15.9
S8	2	B	0.05	2.15	16.0
S9	2	B	0.05	1.05	16.0

Fig. 4 illustrates the change in voltage of the resistor, which was serried by a one-layer SnO_2–Pd (Pd/Sn =0.02) obtained with 1000ppm CH_4 at 350°C. After exposure to methane, the resistivity of thin film sensor decreases and consequently the voltage of serried resistor increases and reaches a saturation value. When dry air is introduced, the voltage approaches to the original values. The response time (time to reach 90% of change in voltage) and recovery time (time for reach 60% of change in voltage) to this concentration of methane are 100s and 20s respectively.

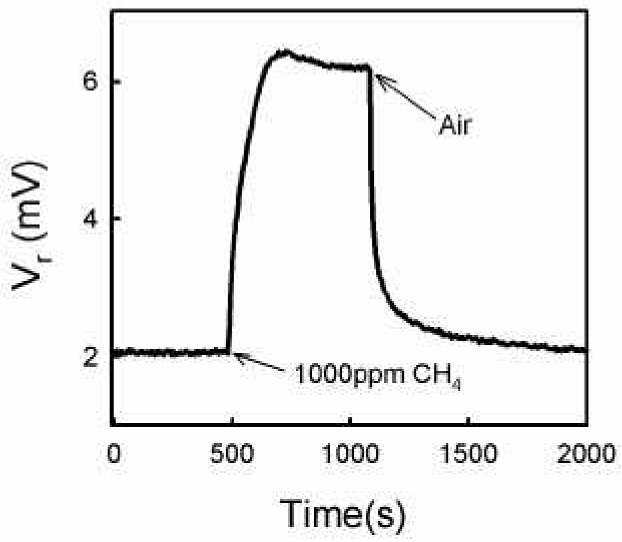


Fig. 4. The voltage of the serried resistor with a one-layer SnO_2-Pd (Pd/Sn=0.02) toward 1000 CH_4 at 350°C.

Fig. 5 compares the sensitivity of SnO_2–Pd (Pd/Sn =0.02) samples, which have different number of layers or different annealing procedure toward 1000ppm CH_4 at different temperatures. All samples have sensitivity to methane that increases with increasing temperature up to 350°C, and decreases for temperature higher than this value. This result is in harmony with the observations of Cabot et al. that the Pd-SnO_2 has the maximum sensitivity to methane at around 330°C [7, 13]. Furthermore, the figure demonstrates that adding the number of layers by procedure A decreases the sensitivity. It is likely related to the grain size of particles. As it was extracted from AFM images (Table 1), adding the number of layers by procedure A increases the grain size of particles and it is well known that the reduction of particle size in SnO_2 layer, leads to improvement in sensitivity of samples [1-3]. Therefore, we can relate the decrease in sensitivity in these series of samples to the increase of particle size. However, this growth of the grain size is not due to adding the number of layers in procedure B (Table1). It seems that in this series two-layer sample has the optimum thickness for sensing methane gas.

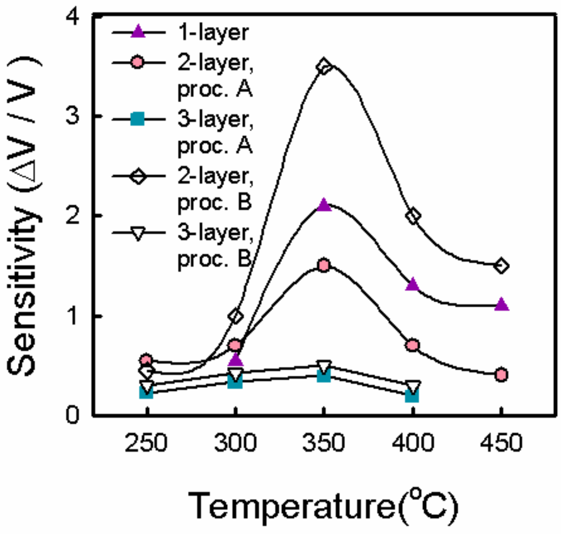


Fig.5. Sensitivity of SnO_2–Pd (Pd/Sn =0.02) samples, which have different number of layers or different annealing procedure toward 1000ppm CH_4 at different temperature.

The sensitivity of samples with different amount of Pd in their sol toward different concentration of CH_4 at 350°C is shown in Fig. 6. These data demonstrate that the introduction of 5% of Pd to tin-oxide is the optimum value for increasing sensitivity.

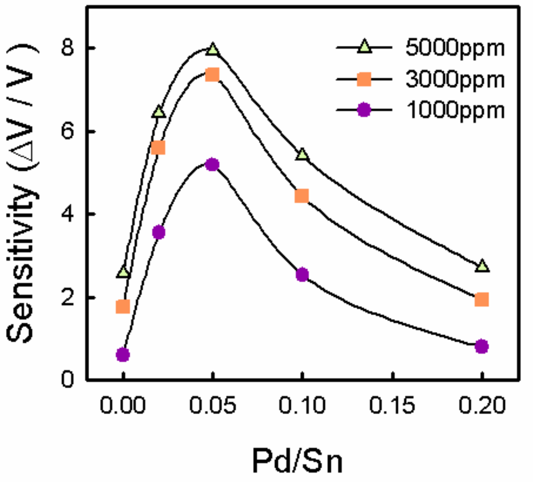


Fig. 6. Sensitivity of SnO_2–Pd samples toward different concentration of CH_4 at 350°C versus the Pd/Sn atomic ratio in the sol.

Our investigations demonstrated that the viscosity of the sol is another effective factor on sensitivity. Fig. 7 illustrates the sensitivity of samples, which were prepared with different sol viscosity toward different concentration of methane at 350°C. At first by decreasing the sol viscosity from 3.15cP to 2.15cP, the sensitivity of samples increases and reaches the maximum. By decreasing this value more, the sensitivity decreases. Since the grain size of these samples is nearly the same (Table 1), the origin of different sensitivity is important to understand. In addition to sensitivity, the resistance of these samples in dry air at 350°C is shown in Fig. 7. As illustrated, the resistance increases by decreasing the viscosity. It seems that this phenomenon arises from the decrease in thickness of layers. To confirm this idea, we determined the thickness of the film by using the AFM scratch test. The results of these tests showed that by decreasing the sol viscosity from 3.15 cP to 1.05 cP, the thickness of the film decreased from 633nm to 481nm. Thus, the maximum sensitivity versus viscosity is likely related to the optimum thickness of the layer.

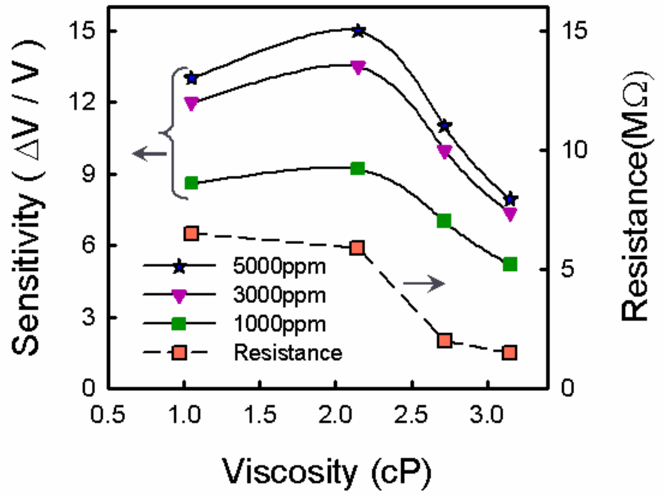


Fig. 7. The Sensitivity and resistance of SnO_2–Pd (Pd/Sn=0.05) samples toward different concentration of CH_4 at 350°C versus the viscosity of their sol.

4. Conclusions

Stannic oxide thin films samples activated by palladium were prepared by sol-gel method. AFM images showed that the size of the particles is about 15-30nm. Investigations demonstrated that the number of coating, annealing procedure and the viscosity of the sol, which affect on the size of particles or thickness of the layer, are effective factors on sensitivity toward methane. Moreover, the Pd/Sn atomic ratio in the sol is another important factor to specify the responses to this inflammable gas.

Acknowledgements

The authors thanks from High tech. Center, Ministry of industries and Mines for financial supports.

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