

## Effect of surface modification layer thickness on the gas sensitivity of SnO<sub>2</sub> films

Y.H. Xiong\*, L. Wang, X.Y. Wei, G.R. Qin, C.H. Mao and J. Du

*Institute of Advanced Electronic Materials, General Research Institute for Nonferrous Metals, Beijing 100088, China*

Nickel was used as a surface modification material to enhance the gas-sensing properties of SnO<sub>2</sub> films. The thickness of the Ni modification layer was controlled by the sputtering time. The surface morphology and surface chemical composition of the surface modification layers of different thicknesses were analyzed by Field Emission Scanning Electron Microscopy (FESEM) and X-ray Photoelectron Spectroscopy (XPS), respectively. The gas sensitivity to clean air with a low hydrogen concentration of 1000 ppm of the modified tin dioxide thin films was investigated at temperatures from 20°C to 100°C. The results show that the thickness of the modification layer plays an important role in the enhancement of the gas-sensing properties and surface electric properties of SnO<sub>2</sub> films. A Ni modification layer with a thickness of 50 nm on the surface of a SnO<sub>2</sub> film can improve the hydrogen gas sensitivity of a SnO<sub>2</sub> film up to 112%, and reduce the response time to 80s.

**Key words:** SnO<sub>2</sub>, thin film, surface modification, gas-sensing properties.

### Introduction

Semiconductors are widely used in the field of gas sensors, whereas their selectivity and sensitivity to a flammable gas may not meet the application requirements. Many methods including semiconductor doping, surface modification, and metal catalysts have been tried to improve the gas sensitivity and selectivity of a semiconductor. In particular, a surface modification technique combined with a modern MEMES (Micro-electromechanical Systems) technique has attracted much attention in the field of mini-semiconductor sensors [1]. According to the effect of the surface modification layer, modification materials may be divided into catalysts and semiconductor modification layers. Presently, Pd with a catalytic effect is utilized as the commonest surface modification material for SnO<sub>2</sub> films [2]. In recent studies, metals Pt, Ru, Fe, and Au [3-6] and some metal oxides with semiconductor characteristics including CuO, AgO, and MoO<sub>3</sub> [7-9] have been used as modification materials for enhancing selectivity and sensitivity of SnO<sub>2</sub> films to H<sub>2</sub>. With an investigation of the surface and interface of the film, it is found that the surface morphology, composition, and methods of deposition of films have a significant effect on gas sensitivity [10]. Therefore, recently much attention is paid to the effects of the size, distribution and composition of surface modification materials on gas sensitivity.

In the present study, Ni metal from the VIII B group of the periodic system of elements with a catalytic

effect was selected as the modification material for SnO<sub>2</sub> films. SnO<sub>2</sub> films and Ni surface modification layers were prepared by DC magnetron sputtering. The size and thickness of the Ni layers were controlled by the sputtering parameters. The effects of the Ni modification layer thickness on the gas sensitivity of SnO<sub>2</sub> films were studied.

### Experimental

Sputtering was made in a JPG-5 type multiple-targets magnetron sputtering system. 99.95% purity Sn and Ni targets with a diameter of 60 mm and with a thickness of 3 mm were used. The base pressure was maintained at  $5 \times 10^{-5}$  Pa. High purity argon and oxygen were introduced into the sputtering chamber through two Mass-Flow-Meters (MFC) to keep the total gas pressure approximately 2.0 Pa and a desired mixture composition ratio of O<sub>2</sub>/Ar=1:3. The Si (100) substrates kept at 180°C have been used in this study. The deposition rate was 10 nm/minute. A Pt film electrode was deposited on the SnO<sub>2</sub> films for testing their electrical resistance conveniently. The thickness of the Ni modification layer was controlled by adjusting the sputtering time.

The surface morphology of nickel modified SnO<sub>2</sub> films was studied by Field Emission Scanning Electron Microscopy (FESEM). The variation in chemical composition of the modification layer and SnO<sub>2</sub> film was studied by XPS experiments which were performed in a Mark II spectrometer with a discharge capacity of 1486.6 eV. All the peak sites were calibrated with C<sub>1s</sub> peak of 286.4 eV.

The surface electrical resistance was measured with a four-point method. The gas-sensing properties of samples were tested through a stationary gas-sensing system.

\*Corresponding author:  
Tel : 8610 82241236  
Fax: 8610 62001412  
E-mail: yuhua\_xiong@sina.com

**Table 1.** Effect of Ni modification layer thickness on the sensitivity and response time of SnO<sub>2</sub> films

	SnO <sub>2</sub>	1 minute	3 minutes	5 minutes	10 minutes
electrical resistance in air (KΩ)	2.28	41.71	47.67	30.28	30.97
sensitivity (%)	18	28.1	60.6	112	6.7
response time (s)	600	350	120	80	220

The gas flux was controlled by a MFC. The testing ambient temperature was adjustable in the range of room temperature to 100°C. The relative humidity (HR) was maintained at 25%. The gas sensitivity was estimated from  $(R_{\text{air}} - R_{\text{gas}})/R_{\text{gas}}$ , where  $R_{\text{air}}$  and  $R_{\text{gas}}$  are the electrical resistance of a film exposed to air and to the testing gas mixture with a H<sub>2</sub> concentration of 1000 ppm (parts per million), respectively.

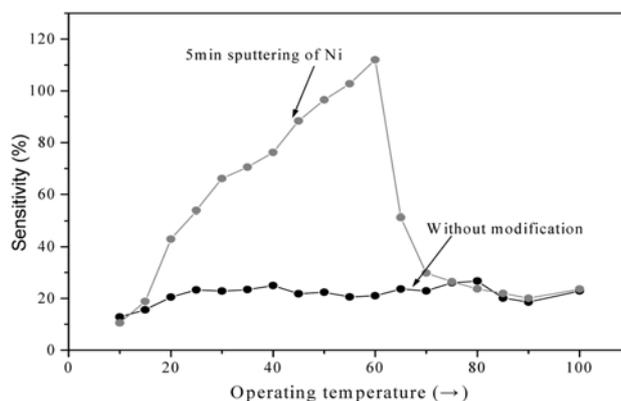
## Results and Discussion

### Gas sensitivity

At first, a 400 nm thick SnO<sub>2</sub> film was prepared on the clean silicon wafer. Then, Ni modification layers with different thicknesses were deposited on the SnO<sub>2</sub> film by controlling the sputtering time. After that, the H<sub>2</sub> sensitivity of these samples was measured at 60°C. The experimental results are shown in Table 1. It can be seen that a suitable Ni modification layer thickness could improve the H<sub>2</sub> sensitivity of samples. A Ni film with 30–50 nm thickness, namely 3–5 minutes sputtering of Ni will greatly increase the sensitivity and decrease the response time of SnO<sub>2</sub> film. However, when the sputtering time of Ni is 10 minutes, the hydrogen sensitivity reduces to 6.7%.

### Temperature dependence

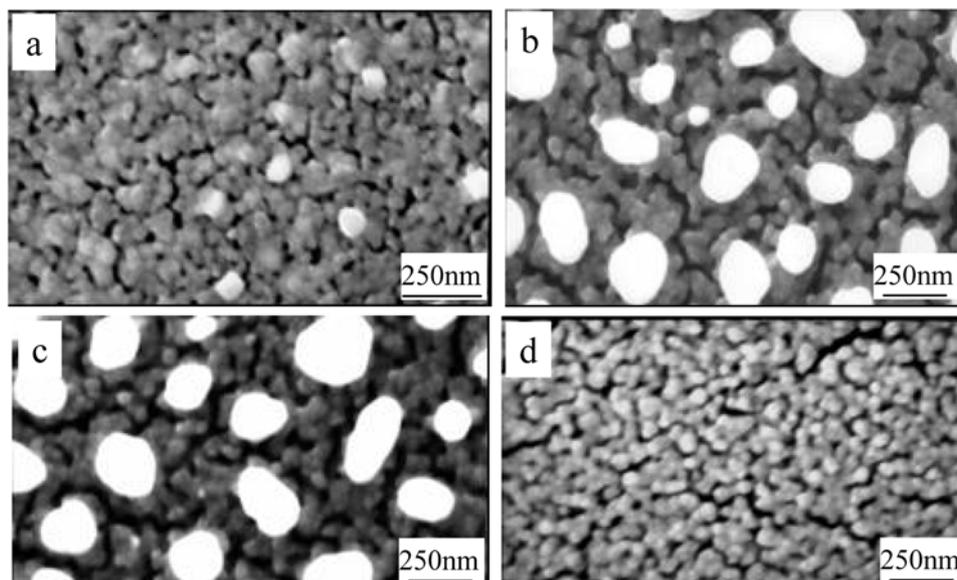
The temperature dependence of a modified SnO<sub>2</sub> sample with a 50 nm thick Ni layer and an unmodified

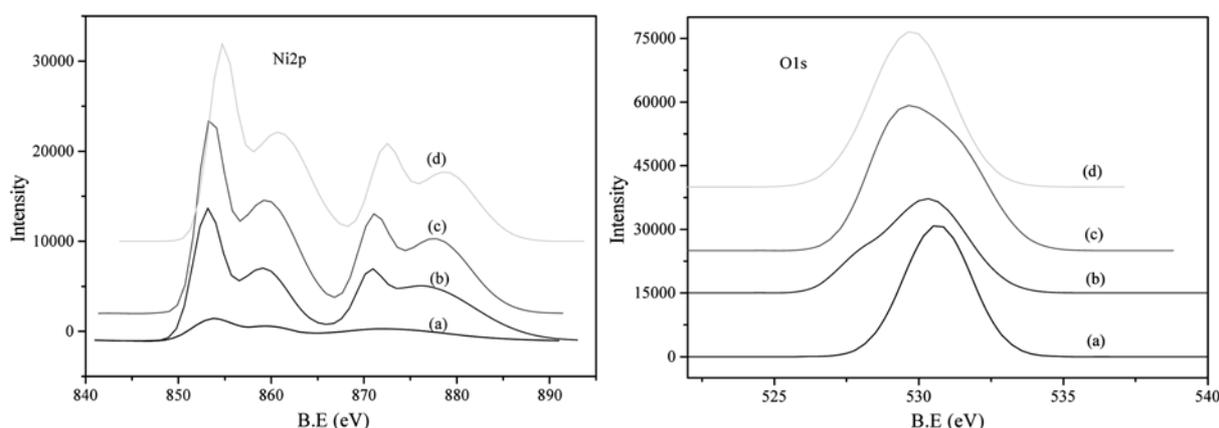
**Fig. 1.** Temperature dependence of the modified and unmodified SnO<sub>2</sub> samples.

SnO<sub>2</sub> sample was measured under the same atmosphere. Up to 100°C, the H<sub>2</sub> sensitivity of the unmodified SnO<sub>2</sub> sample changes very little with the ambient temperature, as shown in Fig. 1. However, the modified SnO<sub>2</sub> film with 5 minutes sputtering of Ni shows a sensitivity peak at 60°C, indicating that it has a temperature dependence.

### Surface morphology and composition analysis

The surface morphology of SnO<sub>2</sub> films with different modification layer thicknesses was observed with FESEM, as illustrated in Fig. 2. One can see that Ni on the surface of SnO<sub>2</sub> appears in a spherical island struc-

**Fig. 2.** FESEM observation of SnO<sub>2</sub> films with different Ni sputtering time. (a) 1 minute; (b) 3 minutes; (c) 5 minutes; (d) 10 minutes



**Fig. 3.** The Ni<sub>2p</sub> and O<sub>1s</sub> profiles of the SnO<sub>2</sub> based gas sensors with different Ni sputtering time. (a) 1 minute; (b) 3 minutes; (c) 5 minutes; (d) 10 minutes

ture. With an increase of the sputtering time, both the size and percentage coverage of the island increase. Combined with the results in Table 1, it can be concluded that a suitable modification layer thickness will increase the porosity on the surface of the SnO<sub>2</sub> film, thus enhancing the contact area between SnO<sub>2</sub> and H<sub>2</sub>, which helps to improve the sensitivity and reduce the response time. Whereas, when the sputtering time increases up to 10 minutes, the surface of SnO<sub>2</sub> was completely covered by the Ni modification layer, which may be the reason that the H<sub>2</sub> sensitivity reduces sharply with the large increase in the modification layer thickness. It is believed that besides the catalytic effect, Ni has an additional effect to improve sensitivity, which relates to a change in composition of the surface modification layer.

In this paper, core-level XPS analysis for SnO<sub>2</sub> samples with different Ni thicknesses was carried out. The Ni<sub>2p</sub> and O<sub>1s</sub> spectra were collected and the variation of the surface chemical composition of SnO<sub>2</sub> samples with different Ni thicknesses is displayed in Fig. 3.

It can be seen that the peak sites and intensity of Ni<sub>2p</sub> and O<sub>1s</sub> change markedly with the Ni modification layer thickness. It is known that the binding energy of metallic Ni<sub>2p</sub> is 852.7 eV and that of Ni<sub>2p</sub><sup>2+</sup> is in the range 853.8-854.3 eV. According to the change of Ni<sub>2p</sub>, for 1 minute sputtering of Ni, Ni is still in a metallic state and the Ni intensity on the surface of the SnO<sub>2</sub> is very weak. With an increase in the sputtering time, the increase in Ni layer thickness on the surface of the SnO<sub>2</sub> enhances the intensity of Ni<sub>2p</sub>. At the same time, it can be noticed that the peak site of Ni<sub>2p</sub> moves to a higher binding energy, indicating that Ni and Ni<sup>2+</sup> appear on the surface of the SnO<sub>2</sub> simultaneously with the increase in the Ni thickness. For the SnO<sub>2</sub> sample with 10 minutes sputtering of Ni, the binding energy of Ni<sub>2p</sub> is 853.6 eV, meaning that the surface oxidation becomes more and more obvious. In order to further testify to the existence of Ni<sup>2+</sup>, O<sub>1s</sub> spectrum of modified SnO<sub>2</sub> samples with different Ni thicknesses was

analyzed. For unmodified SnO<sub>2</sub> and NiO, the binding energy of O<sub>1s</sub> are 530.6 eV and 529.6 eV, respectively. With the increase in Ni thickness, the binding energy of O<sub>1s</sub> moves from 530.6 eV to 529.6 eV, suggesting the formation of NiO on the surface of SnO<sub>2</sub> with increasing sputtering time.

It is known from the above-mentioned analysis that 3-5 minutes sputtering of Ni will lead to the formation of a definite amount of NiO on the surface of SnO<sub>2</sub>. Since SnO<sub>2</sub> is an n-type semiconductor, and NiO is a p-type one, some amount of nanosized NiO particles will promote the formation of p-n junctions on the surface of the n-type semiconductor film. When a reducing gas such as H<sub>2</sub> touches the surface of a SnO<sub>2</sub> sample, a reaction similar to a destroy reaction of p-n junction in the p-n junction system will take place [11-12], which results in an enormous change of the surface electrical resistance of the film, thus improving the gas sensitivity of sample. Therefore, the thickness of modification layer plays an important role in controlling the gas sensitivity of sample. A suitable thickness of the Ni modification layer, 30-50 nm is helpful to improve gas sensitivity.

## Conclusions

Surface modification will enhance the gas sensitivity of SnO<sub>2</sub>-based gas sensors. A Ni modification layer with a thickness of 50 nm on the surface of a SnO<sub>2</sub> film can improve the hydrogen sensitivity up to 112%, and reduce the response time to 80s. Furthermore, the thickness of the modification layer not only changes the surface morphology of the SnO<sub>2</sub>, but also causes the formation of compound layer.

Due to the appearance of Ni<sup>2+</sup>, there maybe exists a p-n junction effect on the surface of the SnO<sub>2</sub>. The p-n junction is destroyed on contact with the H<sub>2</sub>, leading to a change in surface electrical resistance and improvement in the H<sub>2</sub> sensitivity of the SnO<sub>2</sub>.

### Acknowledgement

This work was supported by Technical Innovation Program of GRINM. Grant 82248.

### References

1. I. Lundström, A. Spetz, F. Winqvist, U. Ackelid, and H. Sundgren, *Sensors and Actuators B*. 1[1-6] (1990) 15-20.
2. B. Chadwick, and M. Gal, *Applied Surface Science* 68[1] (1993) 135-138.
3. T. Maosong, D. Guorui, G. Dingsan, *Applied Surface Science*. 171[3-4] (2001) 226-230.
4. Y. Okayama, T. Nomura, H. Yajima, T. Ishii, in *Proceedings of the International Meeting on Chemical Sensors*, September 1986, edited by Denki Kagaku 54 (Fukuoka, Japan, 1986) 777-782.
5. C.P. Li, J.F. Wang, W.B. Su, H.C. Chen, W.L. Zhong, and P.L. Zhang, *Ceramics International* 27[6] (2001) 655-659.
6. G. Sulz, G. Kühner, H. Reiter, G. Uptmoor, W. Schweizer, H. Low, M. Lacher, and K. Steiner, *Sensors and Actuators B*. 16[1-3] (1993) 390-395.
7. T. Kololuoma, A.H.O. Kärkkäinen, Tolonen A, and J.T. Rantala, *Thin Solid Films*. 440[1-2] (2003) 184-189.
8. J. Tamaki, T. Maekawa, N. Miura, N. Yamazoe, *Sensors and Actuators B*. 9[3] (1992) 197-203.
9. E. Gaigneaux, D. Herla, P. Tsiakavas, U. Roland, P. Ruiz, and B. Edlmon, *Journal of American Chemical Society* 27(1996) 330-345.
10. A. Galdikas, S. Kačiulis, G. Mattogno, A. Mironas, A. Napoli, D. Senulienė and A. Šetkus, *Sensors and Actuators B*. 58[1-3] (1999) 478-485.
11. J. Bandara, C.M. Divarathne, S.D. Nanayakkara, *Solar Energy Materials & Solar Cells*. 81[1-4] (2004) 429-437.
12. A. Khanna, R. Kumar, and S.S. Bhatti, *Appl. Phys. Lett.* 82[24] (2003) 4388-4390.