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Study on nickel nanoparticles surface-modified SnO_2 film

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Abstract: SnO_2 film is widely used as a gas sensor, whereas, its gas sensitivity at low temperature is not satisfactory. Surface modification is an effective way to enhance sensitivity of SnO_2 which is closely related to the surface morphology and microstructure of SnO_2. In this paper, nickel nanoparticles surface-modified SnO_2 films were prepared by D. C. magnetron sputtering. The effects of distribution and morphology of Ni particles on the surface of SnO_2 on hydrogen sensitivity were studied. The results show that the sputtering time of Ni influences gas sensitivity of SnO_2. With increasing the annealing temperature, Ni particles separate from SnO_2 particles and gradually aggregate into spherical particles distributing uniformly on the surface of SnO_2 film. The particle size, porosity, and specific surface area of Ni influence the gas sensitivity of SnO_2 directly. Gas sensitivity examination indicates that the spherical Ni particles in a diameter of 100nm lead to the best modification. After heat treated at 800℃ for 3 hours, SnO_2 film with 30s sputtering of Ni shows a gas sensitivity of 112% for 4000 ppm H_2 at a operating temperature of 60℃.

Key words: SnO_2; Film; Gas sensor; Surface-modification

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1 Introduction

In the field of gas examination, selectivity, sensitivity and response speed are the important parameters for gas sensors. Semiconductor with gas sensitivity is beneficial for the micromation and integration of gas sensors, which is suitable for the IC industry.

At present, a N-type semiconductor oxide- SnO_2 film with a broad forbidden band is widely used in the gas sensors. For the gas sensors using semiconductor oxides, surface modification is an effective way to improve their gas sensitivity[1]. Pd[2] with catalysis is utilized as modification material for SnO_2 film. In the recent studies, metal Pt, Ru, Fe, and Au[3-6] and some metal oxides including CuO, AgO, and MoO_3[7-9] are used as modification materials for enhancing hydrogen selectivity and sensitivity of SnO_2 film. Commonly, the selection of surface modification materials is mainly from the VIIIB group of the periodic system of elements. Researchers initially believed that surface modification materials change gas sensitivity of SnO_2 film by means of changing the surface electrical resistance or electric conductance. With the profound inves-

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tigation on surface and interface of film, it is found that the surface morphology, component, and deposition methods have a significant effect on gas sensitivity[10]. As a result, much attention is paid recently to the effects of the size, distribution and component of surface modification materials on gas sensitivity.

In the present study, metal Ni from VIIIB group was selected as modification material for SnO_2 film. SnO_2 films and Ni surface modification layers were prepared by a dc magnetron sputtering. Ni layers with different size and thickness were obtained by controlling sputtering parameters. The effects of grain size and thickness of Ni on gas sensitivity of SnO_2 films were studied.

2 Experimental procedure

Sputtering was operated in a JPG-5 type multiple-targets magnetron sputtering system. Both Sn and Ni with 99.95% purity were used to prepare the targets in a diameter of 60 mm and with a thickness of 3 mm. The background vacuum was maintained at 5×10^{-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 of $O_2/Ar=1:3$. The Si (100) substrates kept at 180℃ have been used in this study. The deposition rate was about 10nm/min. The SnO_2 films were heat treated in an oxidizing atmosphere at 400℃, 600℃, and 800℃ for 3 hours. Pt electrode was prepared on the SnO_2 films in order to test electric resistance conveniently.

The surface morphology of nickel modified SnO_2 films was studied by Field Emission Scanning Electron Microscopy (FESEM). The surface electric resistance was tested with a four-point method. The gas-sensing properties of samples were tested through a stationary gas-sensing system. The gas flux was controlled by a MFC. The ambient temperature and relative humidity (HR) were kept at 30℃ and 25%, respectively. The gas sensitivity was estimated with Rgas/Rair, where Rgas and Rair are the electric resistance of film exposed to the testing gas mixture to air, respectively.

3 Results and discussion

3.1 Influence of Ni modification layer on the gas sensitivity of SnO_2 film

The thickness of Ni on the surface of SnO_2 film was controlled by the sputtering time. Table 1 lists the gas sensitivity of SnO_2 film with different Ni sputtering time for 1000 ppm H_2. It could be found that the electric resistance of SnO_2 film after Ni modification increases. The gas sensitivity of SnO_2 film with 30 s and 60 s Ni sputtering increases greatly. However, when the sputtering time of Ni is 5 min, the hydrogen sensitivity reduces again. In such a case, it could be considered from the variation in surface chemical component. Due to the increase in Ni overlays the gas-sensing layer of SnO_2, leading to the decrease in the contact between the reducing gas H_2 and SnO_2, which subsequently results in the reduction in chemical adsorbed oxygen participating in the reducing reaction. Fig. 1 illustrates the surface morphology of SnO_2 films with different Ni thickness observed with FESEM. The above mentioned explanation could be testified from the morphology of film surface. Fig. 1(a) shows that the surface of SnO_2 without modification appears in an uneven structure of cauliflower. After 60s Ni sputtering, Ni appears in spherical particles and distributes on the surface of SnO_2, leading to the increase of the specific surface area. With the elongation of Ni sputtering, as shown in Fig. 1(c), the overall surface of SnO_2 was overlaid by irregular Ni particles in a size of 50 nm. In this case, the contact between the reducing gas H_2 and SnO_2 was greatly reduced, leading to the decrease in gas sensitivity of SnO_2.

Table 1 Hydrogen sensitivity of SnO_2 modified by different thickness Ni

	SnO_2 without modification	Ni surface-modified SnO_2		
		30 s Ni sputtering	60 s Ni sputtering	5 min Ni sputtering
Surface resistance/kΩ	2.28	47.67	30.28	30.97
Sensitivity/%	26	60.6	58.3	22.4

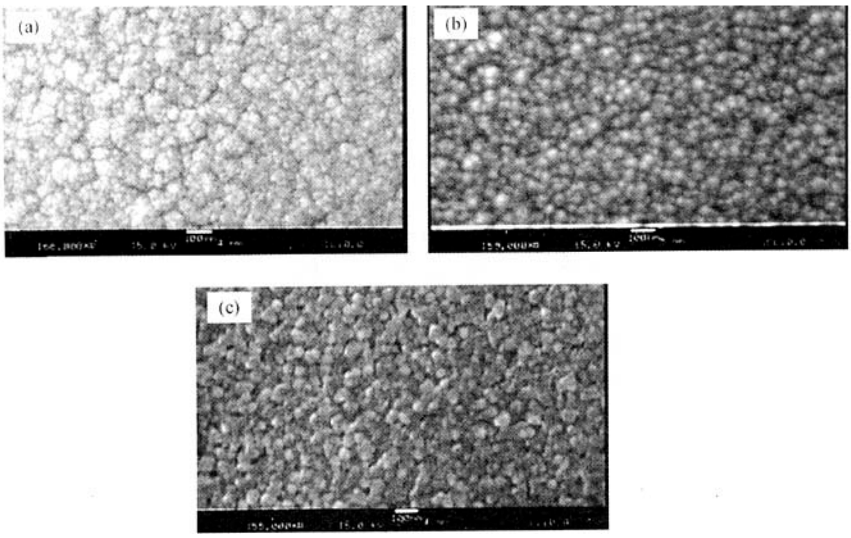

Fig. 1 FESEM micrographs of SnO_2 modified by different thickness Ni
(a)—without Ni modification; (b)—1 min sputtering of Ni; (c)—10 min sputtering of Ni

3.2 Annealing treatment

As for the surface treatment for films, annealing is the most effective and direct means to change surface morphology and component. In order to study the effect of Ni morphology on the gas sensitivity of SnO_2, SnO_2 films with 60 s sputtering of Ni were heat treated at 400℃, 600℃, and 800℃ for 3 hours in an oxidizing atmosphere. It can be seen that the surface morphology of film changes obviously as demonstrated in Fig. 2. It appears in a porous structure after 400℃ annealing treatment (see Fig. 2(a)). Ni could not be found on the surface of SnO_2, but distributes in a spheric shape among the gaps of SnO_2 particles. When the annealing temperature reaches 600℃, Ni particles rise gradually onto the surface of SnO_2 and their size increases to about 70nm. Here, the surface pore reduces owing to the glomeration, oxidation and growth of Ni. When the annealing temperature is 800℃, Ni particles with a size of 50-120nm will float completely onto the surface of SnO_2 and distribute uniformly. Gas sensitivity tests show that SnO_2 film after annealing treatment at 800℃ has the greatest hydrogen sensitivity of 112% for 4000 ppm H_2 at 60℃. The reason is that after a higher temperature annealing, Ni particles distributing in the gaps of SnO_2 move onto the surface of SnO_2 and distribute uniformly on the surface of SnO_2, which provides the maximum surface adsorbed oxygen sites and is helpful to the adsorption reaction of the reducing gas H_2.

3.3 Temperature dependency and H_2 sensitivity of Ni modified SnO_2 films

SnO_2 films with different Ni thickness were prepared and annealed at 800℃ for 3 hours in an oxidizing

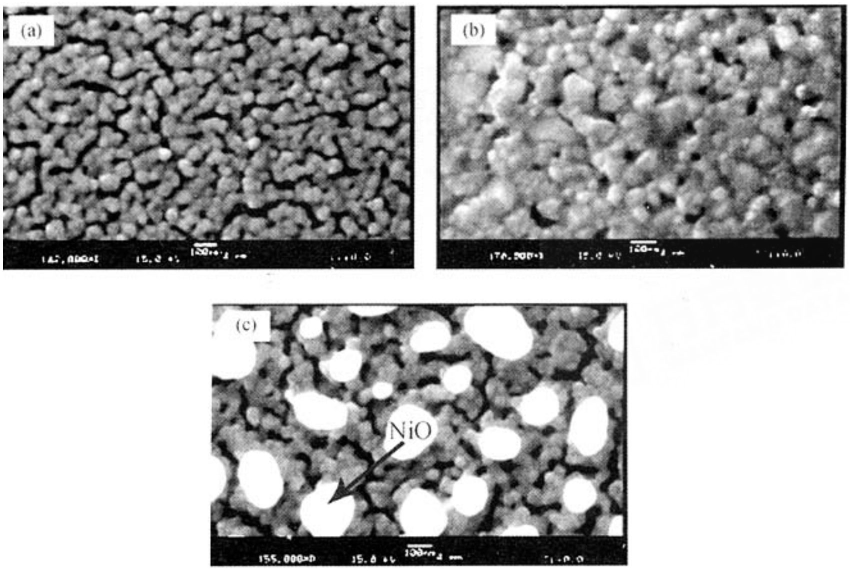

Fig. 2 FESEM micrographs of Ni－SnO_2 films under annealing treatment at different temperatures
(a)—400℃; (b)—600℃; (c)—800℃

atmosphere. After that, the temperature dependence and gas sensitivity to different hydrogen concentration of them were studied. For the 4000 ppm H_2, the gas sensitivity of SnO_2 with different Ni thickness varies dramatically in the operating temperature range of 20-100℃, as shown in Fig. 3.

It can be found from Fig. 3 that both the Ni-modified SnO_2 films show higher sensitivity compared to the unmodified one in the whole operating temperature range. Unmodified SnO_2 film has no temperature dependence, however, both Ni modified SnO_2 film have good temperature dependence. SnO_2 film with 30s sputtering of Ni has the best gas sensitivity at 60℃, while SnO_2 film with 60s sputtering of Ni shows two sensitivity peaks at 55℃ and 85℃. Since two Ni modified SnO_2 films have sensitivity peak at about 60℃, the operating temperature of 60℃ was selected. At this temperature, the effects of Ni thickness on H_2 sensitivity of SnO_2 films for different H_2 concentration were studied. The results are shown in Fig. 4. Both the Ni-modified films show higher sensitivity as compared to the unmodified SnO_2 film. Above 3000 ppm H_2 gas mixture atmosphere, the SnO_2 film with 30 s sputtering of Ni is more sensitive than the others. These results indicate that the sputtering of Ni could promote the hydrogen sensitivity of SnO_2 film.

4 Conclusions

The thickness and morphology of Ni influence the gas sensitivity of SnO_2 markedly. For the 1000 ppm H_2, gas sensitivity of SnO_2 without annealing treatment will increase from 26% without modification to 60.6% after 30s sputtering of Ni. The difference in size and distribution of Ni leads to different gas sensitivity of SnO_2 with annealing treatment. After Ni-SnO_2 film annealing treated at 800℃ for 3 hours, the spherical Ni particles in a size of 50－120nm distribute homogenously on the surface of SnO_2, which makes SnO_2 film have good temperature dependency and hydrogen sensitivity in a large hydrogen concentration range. 30s sputtering of Ni is suitable which makes SnO_2 film obtain gas sensitivity of 112% for 4000 ppm H_2 while operated at 60℃.

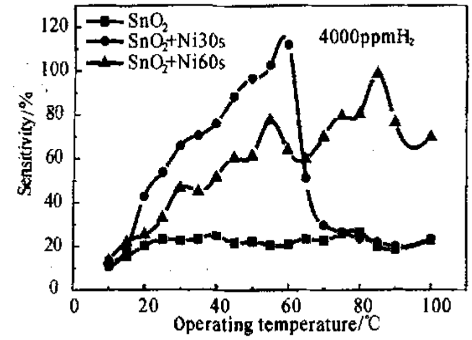

Fig. 3 Temperature dependence of Ni-SnO_2 films

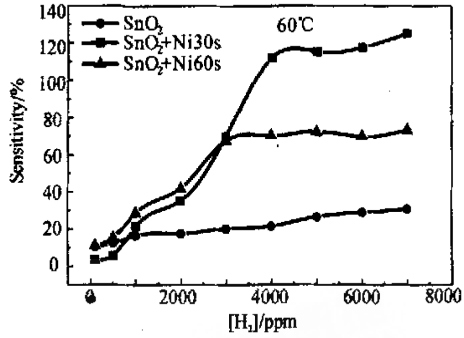

Fig. 4 H_2 sensitivity of Ni-SnO_2 films for different H_2 concentration at 60℃

References

[1] Tong M S, Dai G R, Gao D S. Surface modification of oxide thin film and its gas—sensing properties[J]. Applied Surface Science, 2001, 171,(3-4): 226-230.

[2] Yamazoe N. New approaches for improving semiconductor gas sensors[J]. Sensors and Actuators B, 1991, 5: 7-19.

[3] Safonova O V, Rumyantseva M N, Kozlov R I, *et al*. Two successive effects in the interaction of nanocrystalline SnO_2 thin films with reducing gases[J]. Materials Science and Engineering B, 2000, 77(2): 159-166.

[4] Masatsugu Morimitsu, Yasutaka Ozaki, Sachiyo Suzuki, *et al*. Effects of surface modification with platinum and ruthenium on temperature and humidity dependence of SnO-based CO gas sensors[J]. Sensors and Actuators B, 2000, 67(1-2): 184-188.

[5] Egdell R G, Rastomjee C S, Dale R S, *et al*. An Investigation of doping of SnO by ion implantation and application of ion—implanted films as gas sensors[J]. Thin Solid Films, 1996, 279(1-2): 98-105.

[6] Nomura K, Shiozawa H, Takada T. Gas—sensor properties of SnO films implanted with gold and iron ions[J]. J Mater Sci Mater Electron, 1997, 8: 301—306.

[7] Malyshev V V, Pislyakov A V. SnO-based thick-film-resistive sensor for H_2S detection in the concentration range of 1—10 mg^2/m^3[J]. Sensors and Actuators B, 1998, 47: 181—188.

[8] Ivanovskaya M, Lutynskaya E, Bogdanov P. The influence of molybdenum on the properties of SnO ceramic sensors[J]. Sensors and Actuators B, 1998, 48(1-3): 387-391.

[9] Galdikas A, Mironas A, Senulienè D, *et al*. Copper on-top-sputtering induced modification of tin dioxide thin film gas sensors[J]. Sensors and Actuators B, 1999, 58(1-3): 330-337.

[10] Hotovya I, Huran J, Spiess L, *et al*. The influence of process parameters and annealing temperature on the physical properties of sputtered NiO thin films[J]. Vacuum, 2003, 69: 237-242.