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CO gas sensing properties in Pd-added ZnO sensors

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Abstract Unadded and 0.5 mol% Pd-added ZnO bulk and thin films were prepared by sintering and sputtering, respectively, and their CO gas sensing properties were investigated. The effects of Pd addition, sensing temperature (100–500 °C), and humidity on the CO gas response were discussed. In the bulk sensors, Pd-addition lowered the temperature for the maximum CO gas response (sensitivity) from 400 to 300 °C, whereas the thin film sensors (unadded and Pd-added) exhibited maximum gas response at 200 °C. The Pd-addition enhanced the CO gas response in thin film sensors, and it was also effective for reducing the interference from humidity in both bulk and thin film sensors.

Keywords CO gas sensor · ZnO · Pd-addition · Bulk · Thin film

1 Introduction

Oxide semiconductor ZnO has been extensively studied as a gas sensor detecting gases such as CH_4, CO, H_2, C_2H_5OH, Cl, and H_2S [1–9], based on the resisivity changes from adsorption/desorption and reactions with target gases. Several forms of sensors have been fabricated including single crystal [1], sintered bodies [1, 6], thick layers [8], thin films [2, 3, 5, 7], and nano structures [4, 9]. The sensing performance (magnitude of gas response (sensitivity), selectivity, sensing temperature, and so on) depends on the electronic and structural properties of the sensor materials, and a common approach to improve the sensing properties is to employ the metal additives such as Al, Sb, Cu, and Pt [5, 8, 10, 11]. Among them, Sb and Cu additives improved the CO gas sensing performance in ZnO when operated at ~350 °C. The addition of noble metal catalysts (Pt, Pd) in SnO_2 greatly enhanced the sensitivity and selectivity to CO gas [12], but a little work of Pt or Pd addition in ZnO has been performed [13, 14]. Pd added ZnO exhibited the improved sensitivity toward ethanol with short response time [14], but was insensitive to CO at low temperatures (50–75 °C) [13].

In this study, the Pd-addition effects on the CO gas sensing properties were investigated in the ZnO sintered specimens (bulk) and thin films. Special focuses were placed on the influence of Pd-addition, sensing temperature, and humidity on the CO gas sensing performance.

2 Experimental

Pd-added ZnO powders (0.5 mol%) were synthesized using a solid-state reaction of the reagent grade chemicals, ZnO (Aldrich) and $PdSO_4$ (Aldrich). The raw materials were mixed in acetone and ball milled for 48 h. The dried mixtures were calcined at 620 °C for 5 h. For the bulk specimens, the unadded (pure) ZnO and Pd-added ZnO powders were uniaxially pressed into pellets of 10 mm diameter and then cold isostatically pressed at 200 MPa. The sintering was conducted on the pressed pellets at 700 °C for 1 h.

ZnO thin films were deposited by rf magnetron sputtering of ZnO or 0.5 mol% Pd-added ZnO target on SiO_2/Si substrates. The targets were prepared by sintering the pressed pellets at 1300 °C for 5 h. Film deposition was carried out without substrate heating in an Ar environment with an rf

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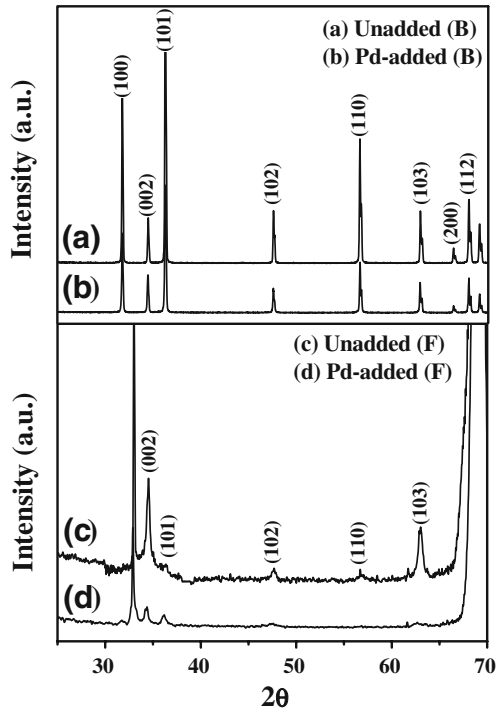

Fig. 1 XRD patterns of (**a**) unadded, bulk (*B*), (**b**) Pd-added, bulk, (**c**) unadded, thin film (*F*), and (**d**) Pd-added, thin film ZnO

power of 75 W at 5 mTorr for 10 min. For the crystallization, the samples were annealed at 600 °C for 1 h in air. The phase and orientation of the films were examined using X-ray diffraction (XRD, Model M18XHF-SRA, Mac Science, Japan). The surface morphology and cross-section of the films were characterized by field emission scanning electron microscope (FE-SEM, Model JSM-6330F, JEOL, Japan).

For the electrical measurements, a circular Pt electrode of 5 mm diameter was sputtered on both sides of the bulks, and a pair of comb-like Pt electrodes were formed by sputtering on the thin films through a mask. The Pt wires were attached to them by using a Pt paste. Thereafter, all the sensors were fired at 600 °C for 1 h in order to make the electrical contact between the paste and the Pt lead wires. The CO sensing properties were determined by measuring the changes of electric resistance between air and 1,000 ppm CO balanced with air at temperatures ranging from 200 to 500 °C. The electrical resistance was measured using a multimeter (2000 multimeter, Keithley). In this study, the magnitude of the gas response (*S*, sensitivity) was defined as the ratio (R_a/R_g) of the resistance in air (R_a) to that in a sample gas (R_g). The gas response was also measured in a wet atmosphere, which was obtained by passing the gases through a glass bubbler with distilled water kept at 50 °C. The relative humidity was 70% at the outlet of the sensing equipment measured at room temperature (~22 °C).

3 Results and discussion

The XRD patterns of the sintered specimens and deposited thin films are shown in Fig. 1. All the diffraction peaks for the sintered specimens were completely indexed based on the hexagonal wurtzite structure (Fig. 1(a) and (b)). No Pd-containing phase or compound was detected by XRD. The as-deposited films were crystalline and the annealing at 600 °C further increased the crystallinity of the films. The

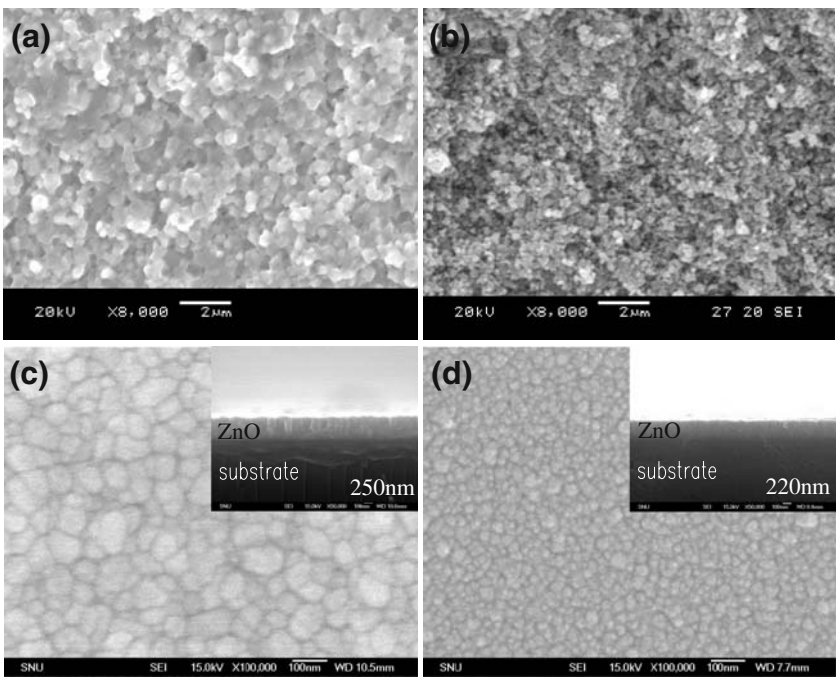

Fig. 2 SEM images of (**a**) unadded, bulk (*B*), (**b**) Pd-added, bulk, (**c**) unadded, thin film (*F*), and (**d**) Pd-added, thin film ZnO. The *inset* is the cross-section image of the film

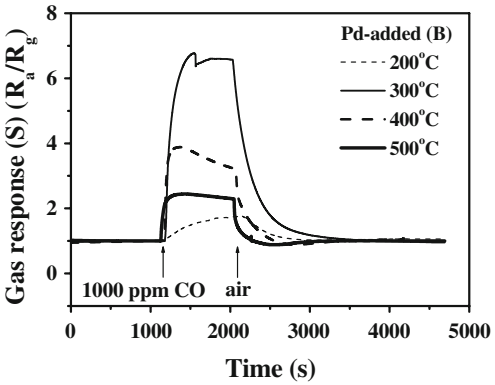

Fig. 3 Response transients of Pd-added, bulk ZnO toward 1,000 ppm CO gas as a function of the measuring temperature

unadded ZnO films exhibited a strong (002) diffraction peak, indicating a preferential orientation along *c*-axis (Fig.1(c)). Pd-addition decreased the degree of *c*-axis orientation, resulting in the less oriented films (Fig. 1(d)).

Figure 2 shows SEM images of fracture surface for the sintered specimens and of surface morphology for the thin films. Unadded ZnO was relatively well sintered at 700 °C (~93% theoretical density) and exhibited a relatively dense microstructure, composing of ~400 nm sized grains (Fig. 2(a)). Pd-addition significantly inhibited the sintering of ZnO and almost no densification was achieved, as shown in Fig. 2(b) (58% theoretical density). The deposited films were dense and polycrystalline. Pd-addition reduced the grain size and the film thickness. The cross-section image indicated that unadded ZnO films had a columnar structure, but no obvious structure was found in Pd-added films, which appears to be closely related to the film orientations, as shown in Fig. 1. It was reported that Pd exists as nanoparticles of 2–12 nm in ZnO [14], but no confirmation has been made in this study.

Figure 3 shows the typical response transients and sensing properties to 1,000 ppm CO as a function of the measuring temperature, and the obtained results were expressed in terms of the magnitude of gas response (*S*). At low sensing temperature (200 °C), the response time was prolonged and the sensing signal was not saturated within 20 min. With increasing the measuring temperature, the response and recovery time were shortened, and the magnitude of gas response increased. The ZnO sensor was operated in the temperature range of 200 and 500 °C, and exhibited the maximum gas response at the intermediate temperature, which is a typical characteristic of conventional semiconducting gas sensors. The determined magnitude of gas response to 1,000 ppm CO was shown in Fig. 4. In the bulk forms, the maximum gas sensitivity of ~7 was obtained at 400 and 300 °C for unadded and Pd-added ZnO sensors, respectively. Thus, in case of Pd-added sensor, the optimum operating temperature was reduced by 100 °C without improvement of gas sensitivity. On the other hand, the thin film ZnO sensors exhibited the maximum gas response at 200 °C, and Pd-added sensor showed the enhanced gas response at temperatures between 200 and 400 °C. In the Al-doped ZnO films, the maximum sensitivity of 61.6% (*S*~2.6) toward 1,000 ppm CO was obtained at 400 °C [15]. The shift of the response maximum toward lower temperature in the bulk sensors and the improved gas sensitivity in thin film sensors can be attributed to the smaller grain size in Pd-added sensor and/or catalytic effect of Pd [12]. Further study is required to find out which mechanism is dominant in the bulk and thin film sensors.

The effect of humidity on the CO sensing performance was investigated and the response transients in dry and wet atmospheres were shown in Fig. 5. When exposed to wet air, the resistance rapidly decreased and then stabilized. The decrease of resistance in the wet atmosphere was attributed to the adsorption of water molecules on the sensor surface acting as electron donors by forming surface hydroxyl groups [16, 17]. The magnitude of gas response was reduced in wet atmosphere, and the unadded ZnO sensors exhibited a larger decrease of gas sensitivity. Thus, the Pd-added ZnO sensors were more resistant toward humidity.

4 Conclusion

The grain size was decreased by Pd-addition in both bulk and thin film ZnO. All the ZnO sensors responded toward the

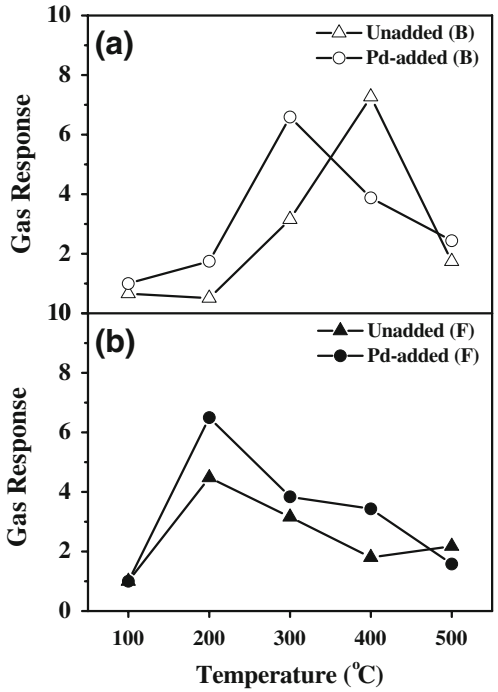

Fig. 4 Magnitude of gas response to 1,000 ppm CO in (**a**) bulk and (**b**) thin film ZnO sensors as a function of measuring temperature

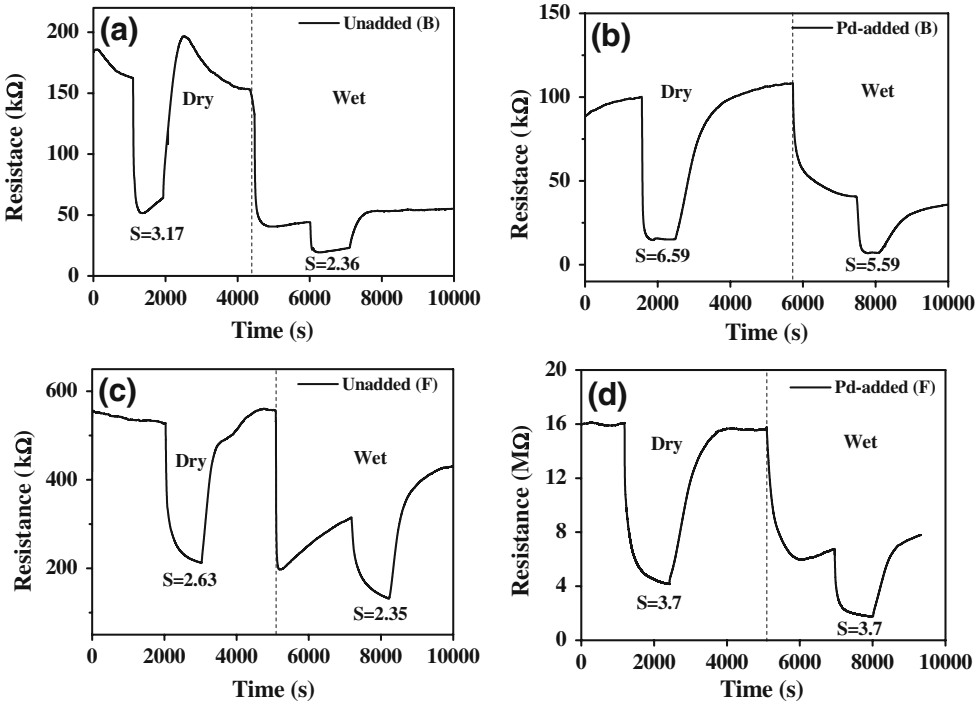

Fig. 5 Response transients of (**a**) unadded, bulk (*B*), (**b**) Pd-added, bulk, (**c**) unadded, thin film (*F*), and (**d**) Pd-added, thin film ZnO sensors under dry and wet (70% humidity) atmospheres measured at 300 °C

CO gas and had the optimum sensing temperatures. The Pd-addition decreased the operating temperature for the maximum CO gas response by 100 °C in the bulk form. The CO gas response was improved with Pd-addition by a factor of 1.5 in thin film sensors. The Pd-added ZnO sensors were less affected by humidity exposure compared to unadded sensors.

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References

1. A. Jones, T.A. Jones, B. Mann, J.G. Firth, Sens. Actuators **5**, 75 (1984)
2. U. Lampe, J. Mullwe, Sens. Actuators **18**, 269 (1989)
3. S. Basu, A. Dutta, Sens. Actuators B **22**, 83 (1994)
4. P.-S. Cho, K.-W. Kim, J.-H. Lee, J. Electroceram. **17**, 975 (2006)
5. F. Paraguay, D.M. Miki-Yoshida, J. Morales, J. Solis, W.L. Estrada, Thin Solid Films **373**, 137 (2000)
6. K.-I. Inoue, M. Miyayama, J. Electroceram. **2**, 41 (1998)
7. S. Roy, S. Basu, J. Mater. Sci. Mater. Electron. **15**, 321 (2004)
8. N.D. Jayadev, R.N. Karekar, R.C. Aiyer, S.R. Sainkar, J. Mater. Sci. Mater. Electron. **8**, 277 (2004)
9. A. Kolmakov, Y. Zhang, G. Cheng, M. Moskovits, Adv. Mater. **15**, 997 (2003)
10. H. Gong, J.Q. Hu, J.H. Wang, C.H. Ong, F.R. Zhu, Sens. Actuators B **115**, 247 (2006)
11. J. Xu, Y. Shun, Q. Pan, J. Qin, Sens. Actuators B **66**, 161 (2000)
12. N. Yamazoe, Y. Kurokawa, T. Seiyama, Sens. Actuators **4**, 283 (1983)
13. W.P. Kang, C.K. Kim, Sens. Actuators B **22**, 47 (1994)
14. C. Liewhiran, S. Phanichphant, Sensors **7**, 1159 (2007)
15. J.F. Chang, H.H. Kuo, I.C. Leu, M.H. Hon, Sens. Actuators B **84**, 258 (2002)
16. K. Ihokura, J. Watson, The Stannic Oxide Gas Sensor: Principles and Applications (CRC, Boca Raton, 1994), p. 58
17. M. Morimitsu, Y. Ozaki, S. Suzuki, M. Matsunaga, Sens. Actuators B **67**, 184 (2000)