Sintering Time Effect on Ethanol Sensor Based on ZnO:Au Nanostructures

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ABSTRACT

In this study, ZnO with 5 % Au by weight nanostructures were prepared by thermal oxidizing technique and employed as an ethanol sensor. The mixture powder of ZnO and Au of 5% by weight was screened as a thick film onto alumina substrate. The thick films were sintered at 700°C under oxygen atmosphere for various times from 6, 12 and 24 hours. The wire-like and belt-like nanostructures were observed outward from microparticles. It was found that the diameter of ZnO nanostructures depended on the sintering time. Moreover, the ethanol sensing properties of ZnO:Au sensors as a function of sintering time at ethanol concentration of 1000 ppm and at various operating temperatures were studied. It was found that the sensor sensitivity of ZnO:Au depended on sintering time.

Key words: Zinc oxide, Nanostructure, Ethanol sensor, Gas sensor

INTRODUCTION

The gas sensing materials have been widely investigated in order to achieve highly sensitive and selective long-term-operating sensors. Zinc oxide (ZnO) is one of the gas sensing material that has caught much attention. ZnO has a wurtzite hexagonal structure and possesses various interesting properties including wide band gap semiconducting property of 3.3 eV and having a large exciton binding energy of 60 meV. Moreover, ZnO nanostructures have gained attention due to their huge surface-to-volume ratios which are expected to exhibit better sensing properties than gas sensors based on bulk or thin films. Previous researches have established that the ZnO nanostructures could be synthesized by many techniques, such as hydrothermal hot-press method, evaporation of pure Zn in the gas flow, sol-gel, spray pyrolysis, vapour phase oxidation and wet oxidation (Xu et al., 2006, Xiangfeng et al., 2005, Kim et al., 2003, Zhu et al., 2005 and Li et al., 2007). The oxidation technique is a simple, low-cost and thus, it is commonly used for the preparation of ZnO nanostructures. In addition, the metal doping such as Au, Pt or Pd etc. in semiconductor is a typical method used to enhance sensing properties. The metal dopant acts as a catalyst to modify surface reactions of metal oxide

semiconductor toward sensing gases. In this work, the effect of sintering times on the gas sensing properties of ZnO:Au nanostructures was systematically investigated.

MATERIALS AND METHODS

Zinc powder and gold powder of 5% by weight were mixed and grounded. Then, polyvinyl alcohol was added into the mixture to form the paste. The paste was screened as a thick film onto alumina substrate. Thick films were sintered at temperature of 700°C under oxygen atmosphere with flow rate of 500 ml/min at sintering time of 6, 12 and 24 hours. The Au-doped ZnO nanostructures were characterized by using the field emission scanning electron microscopy (FE-SEM) for the morphology. The ethanol vapor sensors based on the Au-doped ZnO nanostructures were fabricated by putting silver-gold interdigital electrode on the top of surface and nickel-chromium coil was used as a heater and put underneath of the alumina substrate. The ethanol sensing properties of the sensor were observed under ethanol vapor concentration of 1000 ppm and at operating temperature of 260-380°C. The response and recovery characteristics were monitored and recorded through interfaced computer.

RESULTS AND DISCUSSION

The color of the thick film of the mixer of zinc powder and gold after sintering at temperature of 700°C for 6, 12 and 24 hours changed from grey to white. FE-SEM images of the morphologies of 5% Au-doped ZnO nanostructures on the surface sintered at different sintering times were shown in Figure 1. The wire-like and belt-like nanostructures were observed outward from microparticles. The nanostructures sintered for 6 hours have a diameters between 250-750 nm and the length about 1.7-7.0 μm, the average diameter is 500 nm. For sintering time of 12 and 24 hours, diameters are in range of 110-660 nm and 170-500 nm with the lengths about 0.8-8.2 and 2.0-7.0 μm, respectively. It can be seen that the diameter decreases at higher sintering time but the length is about the same value for all sintering time. Moreover, we have also characterized Au-doped ZnO nanostructures with Raman spectroscopy (not shown here) and the results confirmed that nanostructure is wurtzite hexagonal ZnO.

The sensors were tested under ethanol concentration of 1000 ppm at different operating temperature. The sensitivity of the sensor in this work is defined as R_a / R_g where R_a is the electrical resistance of sensor in air and R_g is the electrical resistance of sensor in ethanol-air mixed gas. The response and recovery curves of thick films based on 5% Au-doped ZnO nanostructures at different sintering times were shown in Figure 2. The resistance of the sensors decreases under ethanol atmosphere. Clearly, the sensing characteristics of sensors depended on the operating temperatures and sintering time. Also, the sensitivity of 5% Au-doped ZnO nanostructures sensors as a function of operating temperature with different sintering times varied as 6, 12 and 24 hours was plotted in Figure 3.

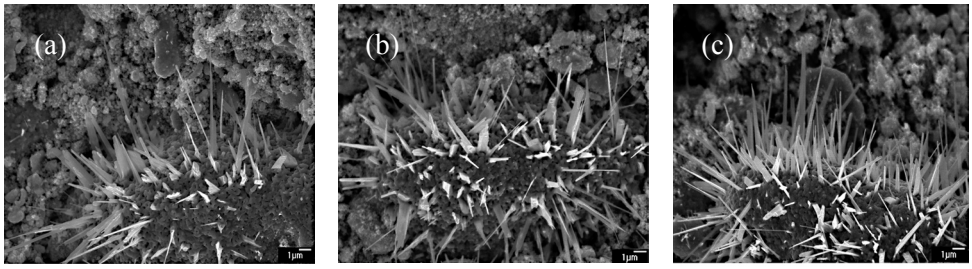

Figure 1. FE-SEM images of 5% Au-doped ZnO nanostructures growth at 700°C for (a) 6 hours (b) 12 hours and (c) 24 hours.

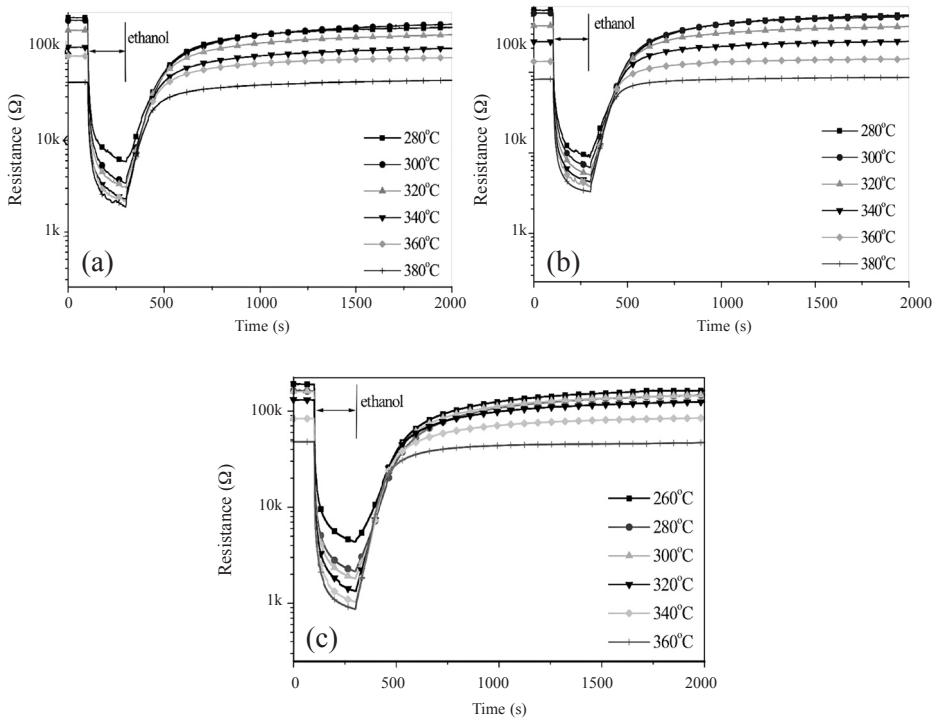

Figure 2. The response and recovery curves of the sensors at sintering times of (a) 6 hours (b) 12 hours and (c) 24 hours.

As shown in Figure 3, the optimum operating temperature of 5% Au-doped ZnO nanostructures sensors are at 300°C for sensor sintered with 6 and 12 hours but the optimum operating temperature of sensor sintered at 24 hours is 320°C corresponded to the highest sensitivity of 59, 83 and 98, respectively. The highest sensitivity at an elevated temperature for the sensor sintered at 24 hours may be due to the enhanced reaction between the ethanol and the adsorbed oxygen at an optimum temperature. The summary of sensitivity of 5% Au-doped ZnO nanostructures sensors under 1000 ppm ethanol vapour with different operating temperatures from 260-380°C was showed in Table 1. It can be seen that the sensitivity depended on the sintering time and the highest sensitivity obtained from this work was at sintering time of 24 hours.

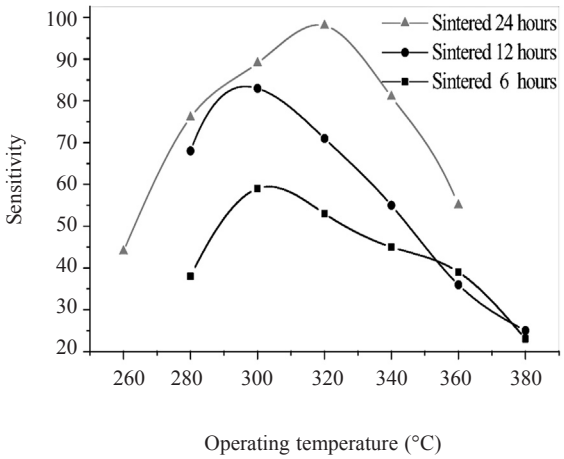

Figure 3. Plot of the 5% Au-doped ZnO nanostructures sensors as a function of operating temperature.

The sensitivity dependence on sintering times could be explained by the higher effective surface area. At longer sintering times, the diameter of nanostructure was smaller as seen from FE-SEM results. Thus, the effective area for gas sensing of Au-doped ZnO nanostructures were higher at longer sintering times and resulted in higher sensitivity. For comparison, the sensitivity of ZnO nanorods was reported to be 293 for 1000 ppm ethanol at 450°C (Li et al., 2007). The sensitivity of ZnO nanobelts gas sensor for 1000 ppm ethanol at 220°C was 23 (Hongsith et al., 2005 and Choopun et al., 2007). The sensitivity of ZnO nanorods sensor was reported to be 40 for 1000 ppm ethanol at 332°C (Jiaqiang et al., 2007) and the sensitivity of the three-dimensional network of tetrapod was ≈ 20 for 50 ppm ethanol at 400°C (Delaunay et al., 2007).

Table 1. Summary of the sensitivity as a function of operating temperature at different sintering times.

Operating temperature (°C)	**Sensitivity**		
	6 hours	12 hours	24 hours
260	-	-	44
280	38	68	76
300	59	83	89
320	53	71	98
340	45	55	81
360	39	36	55
380	23	25	-

CONCLUSION

The sensors based on ZnO nanostructures with 5% Au have been prepared by oxidation reaction at 700°C for 6, 12 and 24 hours. The Raman spectroscopy result indicated that crystal structure of nanostructure is wurtzite hexagonal. The response and recovery characteristics of the sensors were tested under ethanol concentration of 1000 ppm and at operating temperatures from 260-380°C. It was found that the sensitivity of sensor based on 5% Au-doped ZnO nanostructures depended on sintering time. The 5% Au-doped ZnO nanostructures sensors with sintered for 24 hours showed the highest sensitivity of 98 at operating temperature of 320°C.

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