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Research Article

Sensing of Ethanol with Nanosize Fe-ZnO Thin Films

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Sensing of ethanol with iron doped ZnO (Fe-ZnO) thin films has been studied in this work. By X-ray diffraction spectroscopy, it is found that ZnO is the main compound in the low-iron (<10%) doped ZnO thin films. $ZnFe_2O_4$ is also found as 20–50% of iron are doped on the thin films. The 5% Fe-ZnO thin film has a very high sensitivity ($R_{air}/R_{ethanol} > 70$) to 1000 ppm of ethanol at 300 K. It seems that iron can promote the sensivity of the ZnO thin film. The thin film doped with a greater amount (20–50%) of iron has, however, a much less sensitivity (<15) to ethanol. The chemical interactions between oxygen of ethanol and zinc on the Fe-ZnO thin film cause changes of the bond distances of Zn–O and Fe–O in the thin films to 1.90 and 1.98 Å which can be restored to 1.91 and 1.97 Å, respectively, in the absence of ethanol.

1. Introduction

Real-time detection of toxic gases by analytical equipments such as FTIR, GC, or mass spectrometers is expensive and not practical mainly due to their bulky sizes. Metal oxide semiconductor sensors have advantages of small size, low mass, good sensitivity and low cost [1–3]. ZnO which is an n-type semiconductor (band-gap = 3.2 eV) has been widely used in sensing of gases such as H_2, H_2O, and CH_4 [1–8]. Methods of preparing ZnO thin films include spray pyrolysis, chemical vapor deposition, sputtering, electron beam evaporation, screen printing, and sol-gel methods [9–16]. However, ZnO thin films have drawbacks, for instance, the working temperature is too high (>673 K) and their sensitivities are frequently not very desired [17]. To improve sensitivity, transition metals can be doped onto ZnO thin films [18]. Generally sensors doped with transition metals may also lead to a better stability [19]. Thus the main objective of the present work was to investigate sensitivities of the ZnO thin films doped with iron (5–50%) in the presence of ethanol vapor. Nature of the sensing active species in the iron-doped ZnO (Fe-ZnO) thin films was also studied by in situ extended X-ray absorption fine structure (EXAFS) spectroscopy.

2. Experimental

The Fe-ZnO thin films were prepared by dissolving $Zn(CH_3COO)_2 \cdot 2H_2O$ (OSAKA) and $Fe(NO_3)_3 \cdot 9H_2O$ (MERCK, 99%) in 2-methoxyethanol (MERCK), to which a surfactant, monoethanolamine (MEA) (WAKO); was subsequently added. The molar ratio of MEA to $Zn(CH_3COO)_2$ was 0.02. The mole fractions of $Fe(NO_3)_3$ in the ZnO thin films were 0, 5, 10, 20, and 50%. The thin films were prepared by dip-coating on a home-made slow pulling device at a speed of 1.2 cm/d. The thin film samples were preheated at 523 K for 10 minutes to decompose organic compounds and annealed at 773 K for 60 minutes.

Chemical structure of the Fe-ZnO thin films was determined by X-ray powder diffraction (XRD) spectroscopy (D8 advance, Bruker) with a Cu Kα radiation (λ = 1.542 Å). The surface morphology of the thin films was also measured by scanning electron microscope (SEM) (S-3000N, Phillips). In situ EXAFS spectra of zinc and iron in the Fe-ZnO thin

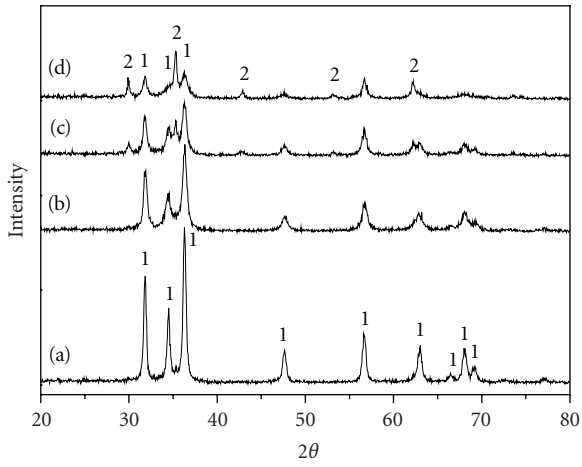

Figure 1: X-ray diffraction patterns of the Fe-ZnO thin films doped with (a) 5, (b) 10, (c) 20, and (d) 50% of iron.

films were recorded on the Wiggler beam line (BL17C) at the National Synchrotron Radiation Research Center (NSRRC), Taiwan.

3. Results and Discussion

The X-ray diffraction (XRD) patterns of the Fe-ZnO thin films are illustrated in Figure 1. For the low-iron (0–10%) doped ZnO thin films, the main compound in the thin films is ZnO. As the fractions of the doped iron are greater than 20%, in addition to ZnO, $ZnFe_2O_4$ is also observed. By SEM, it is found that the thin film is consisted of nanosize ZnO which is packed closely and well distributed (Figure 2). The mean particle size of ZnO in the thin film is in the range of 50–90 nm.

Figure 3 shows the sensitivities ($R_{air}/R_{ethanol}$) of the ZnO and Fe-ZnO-Fe thin films in the presence of 1000 ppm of ethanol at 300 K. The sensitivity and response time of the ZnO thin film to ethanol are about 50 and 2.5 minutes, respectively. Interestingly, it is found that the 5% Fe-ZnO thin film has a relatively higher sensitivity (>70) and shorter response time (one minutes). Increasing the amount (>10%) of iron doped on the ZnO thin films leads to a rapid decrease of the sensitivity to less than 15.

It seems that a small amount (e.g., 5%) of iron can promote the sensitivity of the ZnO thin film to ethanol. The thin film doped with greater amount (20–50%) of iron has, on the contrary, a much less sensitivity to ethanol ($R_{air}/R_{ethanol} < 15$). To obtain a better understanding of interactions involved during sensing, the thin films have also been studied by in situ EXAFS spectroscopy. During sensing of ethanol, the chemical interactions between oxygen of ethanol and zinc on the Fe-ZnO thin film can be observed by EXAFS. An over 99% reliability of the EXAFS data fitting for zinc and iron species in the Fe-ZnO thin films is shown in Table 1. Their Debye-Waller factors ($\Delta\sigma^2$) were less than

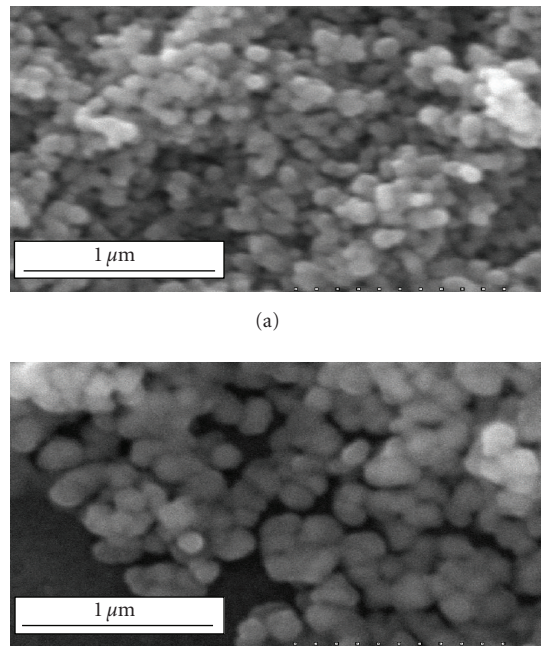

Figure 2: SEM morphologies of the Fe-ZnO thin films doped with (a) 5 and (b) 10% of iron.

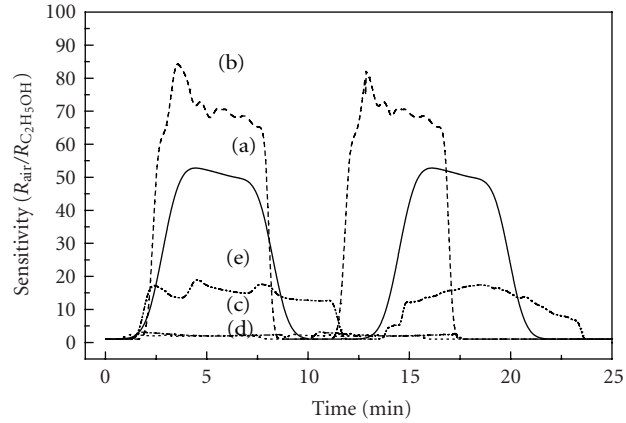

Figure 3: Dependence of time on sensitivities of the Fe-ZnO thin films doped with (a) 5, (b) 10, (c) 20, and (d) 50% of iron to 1000 ppm of ethanol at 300 K.

0.01 ($\Delta\sigma < 0.1$ Å in general). Adsorption of ethanol on the 5% Fe-ZnO has caused changes of bond distances of Zn-O and Fe-O in the thin films to 1.90 and 1.98 Å and restored to 1.91 and 1.97 Å, respectively, in the absence of ethanol. The thin films doped with excess (>20%) iron have less amount of sensing active ZnO species which are consumed in formation of $ZnFe_2O_4$.

4. Conclusions

at the ambient temperature (e.g., 300 K), it is found experimentally that iron can promote the sensivity of the ZnO thin

Table 1: In situ EXAFS data of zinc and iron in the 5% Fe-ZnO thin film during sensing of ethanol at 300 K.

Ethanol (ppm)	Shells	Bond distance (Å)	σ^2 (Å^2)
0	Zn–O	1.91	0.008
0	Fe–O	1.97	0.008
1000	Zn–O	1.90	0.008
1000	Fe–O	1.98	0.008

σ^2: Debye-Waller factor.

film, for instance, the thin film doped with 5% of iron has a relatively higher sensitivity (>70) and shorter response time (one minutes) when sensing of 1000 ppm of ethanol vapor. On the contrary, the thin films doped with 20–50% of iron have a very low sensitivity to ethanol ($R_{air}/R_{ethanol} < 15$). By in situ EXAFS, it is found that sensing of ethanol on the Fe-ZnO has caused changes of bond distances of Zn–O and Fe–O in the thin films to 1.90 and 1.98 Å and restored to 1.91 and 1.97 Å, respectively in the absence of ethanol. It is clear that the thin films doped with excess (>20%) iron have less amount of sensing active ZnO species which are consumed in formation of $ZnFe_2O_4$.

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