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Detection of ethanol vapours with Al-incorporated ZnO thin films

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Al_2O_3 has been incorporated in the nanosize ZnO (Al/ZnO) thin film to enhance its sensitivity ($R_{air}/R_{C_2H_5OH}$) to C_2H_5OH vapour. It is found that the Al/ZnO thin film has a high sensitivity (>20), which is much greater than the plain ZnO by at least 50%. The speciation of zinc in the Al/ZnO thin films during detection of C_2H_5OH (200 ppm) has also been studied by in situ X-ray absorption near edge structure (XANES) spectroscopy. The least-square fitted XANES spectra indicate that the main zinc species in the thin film are bulky ZnO (>100 nm) (5%) and nanosize ZnO (95%). At the temperature of 300 K, during sensing of C_2H_5OH, a small amount of $Zn(OH)_2$ (7%) is formed in the thin film. The chemical interaction between C_2H_5OH and ZnO has also been found by *in situ* extended X-ray absorption fine structure (EXAFS) spectroscopy. The bond distance of Zn–O is decreased to 1.93 Å during sensing of C_2H_5OH, which may be caused by the electron donating to ZnO during adsorption of C_2H_5OH ($C_2H_5HO \rightarrow$ Zn–O). In the absence of C_2H_5OH, the Zn–O bond distance is restored to 1.92 Å.

Keywords: ZnO thin film; C_2H_5OH; sensor; XANES; nanostructures

1. Introduction

The concept of adsorption sensing on the semiconductor thin films was used to detect select gases in air [1]. Progressively, many comprehensive commercial semiconducting devices have been developed for detecting gases [2]. ZnO thin films have attracted considerable interest because of their good electrical and optical properties, in combination with the wide bandgap, abundance in nature and relatively less toxicity. Many applications of ZnO thin films have been found in solar cells, luminescent, electrical and acoustic devices and chemical sensors [3]. Select gases at moderate temperatures can be detected by ZnO thin films with desired stability [4]. ZnO gas sensors can be fabricated in various forms such as single crystals, sintered pellets, thick films, thin films and heterojunctions [5]. ZnO in the form of thin films has better sensitivities than the single crystal counterparts [6]. In addition, ZnO thin films can be prepared in small dimensions

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at relatively low cost, which can be applied in microelectronics, circuits and sensors [7,8]. In order to enhance gas sensitivities of ZnO thin films, metal ions were frequently doped onto ZnO thin films. For example, ZnO thin film doped with Al can detect NO_x [9]. To have a desired sensitivity to C_2H_5OH vapour, ZnO has been doped with Al, In, Cu, Fe and Sn [10].

By X-ray absorption (extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES)) spectroscopy, molecule-scale data, such as coordination number, bond distance and oxidation state of select elements in the complex matrix can be determined [11–13]. Although metal promoted ZnO thin films have been widely used in sensing of organic vapours, their sensing reaction paths are still not well understood. Thus, the main objective of the present work was to study the speciation of zinc in the Al/ZnO thin films during sensing of C_2H_5OH by in situ XANES and EXAFS.

2. Experimental procedure

The Al/ZnO sol–gels were prepared by dissolving zinc acetate [$Zn(CH_3COO_2)\cdot 2H_2O$] (Osaka) and Al_2O_3 (RDH, 98%) in 2-methoxyethanol (0.5 M) (Merck) at an Al_2O_3/zinc acetate molar ratio of 0.02, in which a surfactant, monothanolamine (MEA) (WAKO) was subsequently added. The molar ratio of MEA to zinc acetate was 0.02. The sol–gels were well stirred at 333 K for 30 min. The crystalline structures of the thin films were examined by X-ray powder diffraction (XRD) (D8 advance, Bruker) with a Cu Kα radiation. The samples were scanned from 10° to 80° (2θ) at a scanning rate of 4°/min. The images of the thin film were characterised by scanning electron microscopy (SEM, Philips, XL-FEG).

The in situ XANES spectra of zinc in the Al/ZnO thin films were recorded on the Wiggler beam line (BL17C) at the Taiwan National Synchrotron Radiation Research Center. The electron storage ring was operated at energy of 1.5 GeV (ring current = 80–200 mA). A Si(III) double-crystal monochromator was used for selection of energy. The energy resolution $\Delta E/E$ of the beamline was about 1.9×10^{-4} (eV/eV). The data were collected in the fluorescence mode with a Lytle detector. The photon energy was calibrated by the characteristic pre-edge peaks in the absorption spectrum of a zinc powder (9659 eV).

The in situ EXAFS spectra were measured on the oscillatory structure during sensing of C_2H_5OH, which appear at 50–1000 eV above the absorption edge. The EXAFS data were analysed using the UWXAFS 3.0 and FEFF 7.0 simulation programmes [14,15]. The principal component (factor) analysis was used in the data treatment to optimise the quantitative extraction of relative concentrations of zinc species in the Al/ZnO thin films. The semi-quantitative analyses of the edge spectra were conducted by the least-square fitting of linear combinations of standard spectra (ZnO, Zn and nanosize ZnO) to the spectrum of the sample.

3. Results and discussion

Figure 1 shows the XRD patterns of the ZnO and Al/ZnO thin films. The well-crystallised diffraction peaks of ZnO at $2\theta = 32°$ (1 0 0), 34° (0 0 2), 36° (1 0 1), 47° (1 0 2) and 57° (1 1 0) are observed, and their d values are in a good agreement with those given in the standard data (JCPDS, 36-1451). The average crystalline sizes of ZnO in the ZnO and Al/ZnO thin

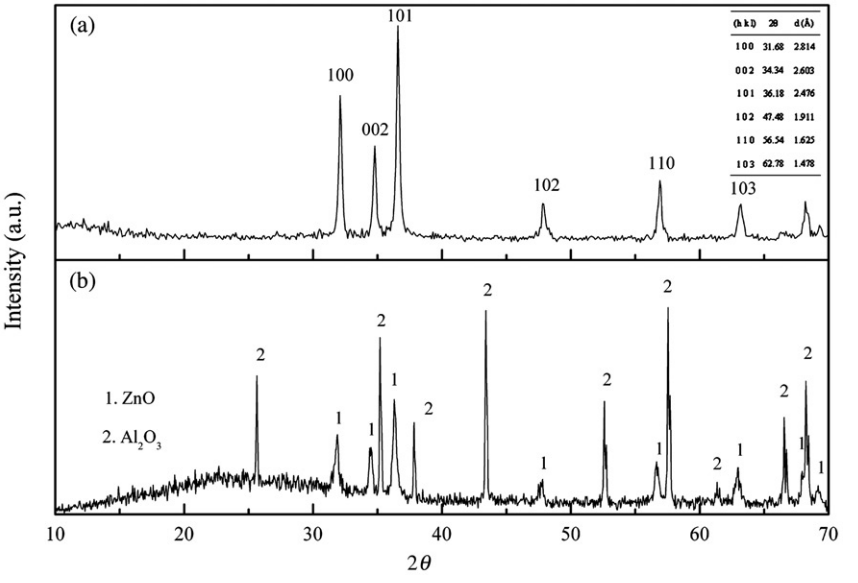

Figure 1. X-ray diffraction patterns of the (a) ZnO and (b) Al/ZnO thin films.

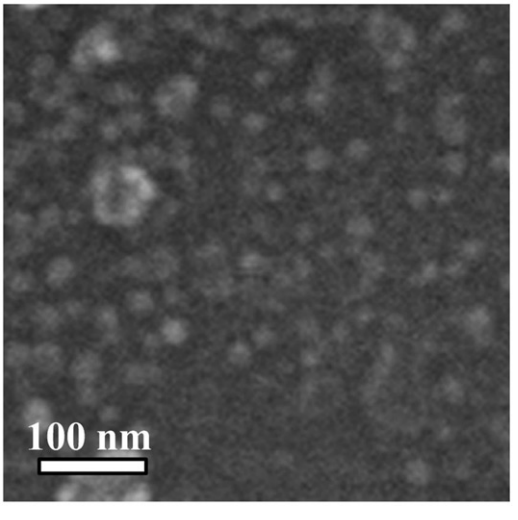

Figure 2. SEM image of the Al/ZnO thin films.

films, calculated by the Scherrer equation, are 28 and 24 nm, respectively. The Al_2O_3 crystalline is also found in the Al/ZnO thin film. In Figure 2, it is clear that the Al/ZnO thin films are consisted of mainly nanoparticles (<40 nm) that are packed closely and well distributed. A small amount of sub-micron size Al_2O_3 is also found.

At the temperature of 300 K, the sensitivities ($R_{air}/R_{C_2H_5OH}$) of the ZnO and Al/ZnO thin films to C_2H_5OH vapour (200 ppm) are shown in Figure 3. The nanosize ZnO thin

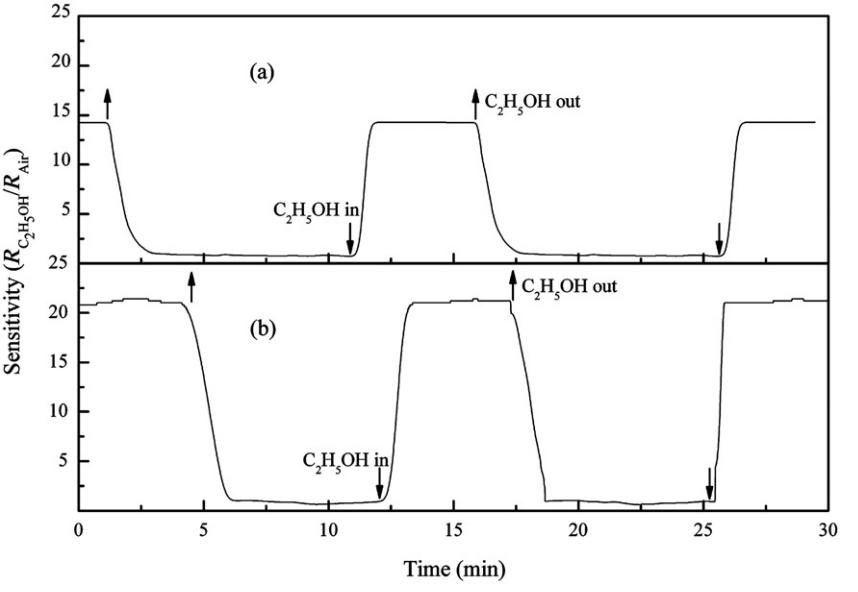

Figure 3. Sensitivities of the (a) ZnO and (b) Al/ZnO thin films to C_2H_5OH (200 ppm) at 300 K.

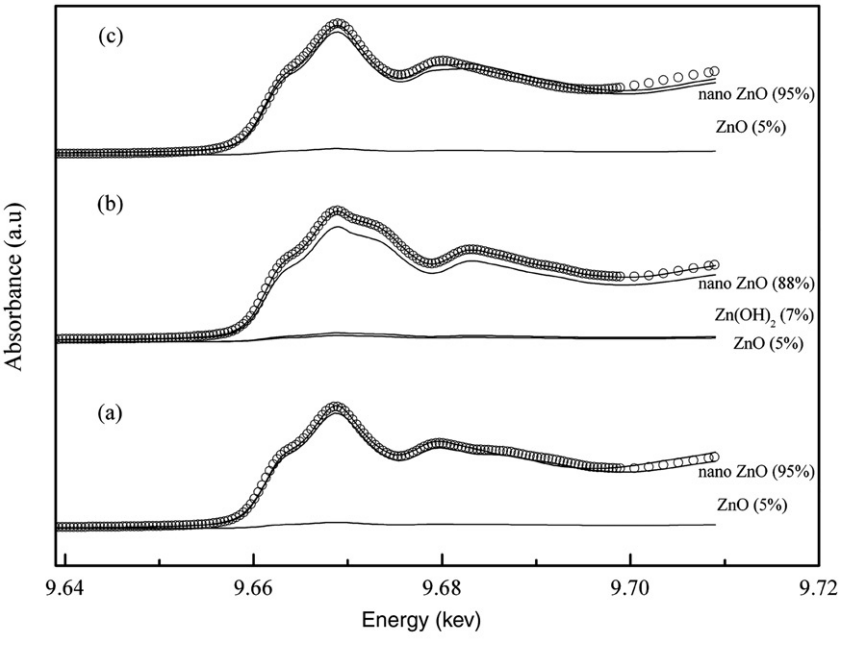

Figure 4. Component fitted XANES spectra of zinc compounds in the (a) ZnO and (b) Al/ZnO thin films during sensing of C_2H_5OH (200 ppm) at 300 K.

Table 1. *In situ* EXAFS data of zinc in the Al/ZnO thin films during sensing of C_2H_5OH (200 ppm) at 300 K.

C_2H_5OH (ppm)	Shells	Bond distance (Å)	$\Delta\sigma^2$ (Å^2)[a]
0	Zn–O	1.93	0.009
200	Zn–O	1.92	0.008
0	Zn–O	1.93	0.01

[a]Debye–Waller factor.

film has a sensitivity of 14 to C_2H_5OH with a short response time (<2 min). It should be noted that the sensitivity of the Al/ZnO thin films to C_2H_5OH is greater than 20. A good reproducibility of the sensing experiments is also observed.

The XANES spectra were expressed mathematically in an LC XANES fit vectors, using the absorption data within the energy range of 9640–9700 eV. The least-square fitted XANES spectra of zinc in the Al/ZnO thin films with model compounds (ZnO, nanosize ZnO and Zn) are shown in Figure 4. The main zinc species in the thin films are nanosize ZnO (95%) and bulky ZnO (5%). During sensing of C_2H_5OH (200 ppm) at 300 K for about 30 min, about 7% of $Zn(OH)_2$ is formed in the thin film. As expected, in the absence of C_2H_5OH, $Zn(OH)_2$ is not found in the thin films.

The in situ EXAFS spectra of zinc were also recorded and analysed in the k range of 3.5–12.5 Å during sensing. The Debye–Waller factors ($\Delta\sigma^2$) are less than 0.01 Å^2 in all EXAFS data analysis. At the temperature of 300 K, the bond distance of ZnO in the Al/ZnO thin film is 1.92 Å (Table 1). As C_2H_5OH is introduced onto the thin film, the bond distance of Zn–O is increased slightly from 1.92 to 1.93 Å. In the absence of C_2H_5OH, the bond distance of Zn–O can be restored to 1.92 Å. During sensing, C_2H_5OH may be adsorbed onto zinc of Al/ZnO. Electron donating to zinc of ZnO from C_2H_5OH ($C_2H_5HO \rightarrow$ Zn–O) may occur, which may be associated with the increase of the ZnO bond distance during sensing.

4. Conclusions

The least-square fitted XANES spectra of zinc in the Al/ZnO thin film show that nanosize ZnO (95%) and bulky ZnO (5%) are the main zinc compounds in the Al/ZnO thin films. The Al/ZnO thin film has a desirable sensitivity ($R_{air}/R_{C_2H_5OH} > 20$) to C_2H_5OH with a very short response time at 300 K. A good reproducibility for the Al/ZnO thin film in sensing of C_2H_5OH vapour has also been observed. During sensing, $Zn(OH)_2$ (7%) is formed in the thin film and the bond distance of Zn–O is increased slightly from 1.92 to 1.93 Å, suggesting the adsorption of C_2H_5OH onto ZnO via the intermediate species (i.e. C_2H_5HO–ZnO). As expected, the bond distance of Zn–O is restored to 1.92 Å in the absence of C_2H_5OH.

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