Structure and ultrafast ethanol sensing properties of In$_2$O$_3$-capped Zn-doped Fe$_2$O$_3$ nanorods

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ABSTRACT

This paper reports the facile synthesis of In$_2$O$_3$-capped Zn-doped Fe$_2$O$_3$ nanorods along with their ethanol gas sensing properties. A two-stage process involving thermal oxidation of Fe foils and Zn powders in air and the sputter-deposition of In$_2$O$_3$ was used to synthesize these nanostructures. The nanorods synthesized using this method were ~5 $\mu$m in length and 50–120 nm in diameter with a shell layer thickness of 10–15 nm. The multiple-networked In$_2$O$_3$-capped Zn-doped Fe$_2$O$_3$ nanorod sensor showed a significantly enhanced and ultrafast response to ethanol gas. The enhanced sensing performance was explained by modulation of the potential barrier height and the strong catalytic activity of In$_2$O$_3$ for ethanol oxidation.

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1. Introduction

Hematite ($\alpha$-Fe$_2$O$_3$) is an n-type semiconductor with many applications such as gas sensors, catalysts, magnetic recording media, electrode materials, and pigments owing to its high corrosion resistance, low toxicity and low cost [1,2]. The thermal oxidation of iron (Fe) in an oxidizing atmosphere has attracted considerable attention as a facile method for growing high-quality $\alpha$-Fe$_2$O$_3$ one-dimensional nanostructures over a larger area. p-type $\alpha$-Fe$_2$O$_3$ can be obtained by doping with Mg [3], Zn [4], Cu [5], and N [6]. Oxide semiconductors are used widely as sensor materials because they show good sensing properties such as high sensitivity, fast sensing and low detection limits [7]. On the other hand, oxide semiconductors also have several drawbacks, including high operation temperature, poor selectivity and unsatisfactory reliability. Several techniques, such as noble metal doping [8–10], heterostructure formation [8,9,11,12], and light activation have been developed to overcome these drawbacks [11,13,14]. In particular, the formation of a p–n heterostructure is now accepted widely as a promising strategy like catalyst metal doping [8,9,12,15]. In this study, Zn-doped $\alpha$-Fe$_2$O$_3$ and In$_2$O$_3$ were adopted as p- and n-type oxide semiconductors for the fabrication of p–n heterostructured gas sensors. The Zn-doped $\alpha$-Fe$_2$O$_3$ are hereafter called simply Fe$_2$O$_3$(Zn). This paper reports the facile synthesis of In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorods by thermal oxidation of Fe foils and zinc (Zn) powders followed by In$_2$O$_3$ sputtering and their enhanced ethanol gas sensing performance.

2. Experimental

In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorods were synthesized by the thermal oxidation of Fe foils and Zn powders in an oxidizing atmosphere, followed by the sputter-deposition of In$_2$O$_3$. First, Fe$_2$O$_3$(Zn) nanorods were synthesized using a single step process. Fe foil (2 cm × 2 cm) and Zn powders were placed individually in two alumina boats that were separated by 5 cm inside a quartz tube. The tube furnace was evacuated to 1mTorr and heated to 600 °C at a heating rate of ~5 °C/min. The samples were maintained at that temperature for 10 h in an atmosphere containing N$_2$ and O$_2$ mixture gas (N$_2$ flow rate = 80 standard cubic centimeter per minute (scm) and O$_2$ flow rate = 20 scm) and cooled to room temperature. Subsequently, the as-synthesized Fe$_2$O$_3$ nanorods were transferred to a radio frequency (RF) magnetron sputtering...
chamber to cap the nanorods with In$_2$O$_3$. The base and working pressures were 5.0 mTorr and 2.0 mTorr, respectively, and the N$_2$ gas flow rate was 20 cm$^3$/min throughout the evaporation process. The RF sputtering power and sputtering times were 50 W and 10 min, respectively.

The morphology of the products was examined by scanning electron microscopy (SEM, Hitachi S-4200, 10 kV). The crystal structure of the products was determined by glancing angle X-ray diffraction (XRD, Philips X’pert MRD diffractometer) using Cu-K$_\alpha$ radiation ($\lambda = 0.1541$ nm). Networked In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorod sensors were fabricated by connecting the synthesized Fe$_2$O$_3$(Zn) nanorods to electrodes to examine their gas sensing properties. The nanorods were dispersed ultrasonically in a mixture of deionized water (5 ml) and isopropyl alcohol (5 ml). The as-grown nanorods were placed onto 200 nm thick SiO$_2$-coated Si(100) substrates with a pair of interdigitated Ni (~200 nm)/Au (~50 nm) electrodes with a gap of 20 $\mu$m. A flow-through technique was used to measure the gas sensing properties. All measurements were taken in a temperature-stabilized sealed chamber at a constant flow rate of 200 sccm at 300 °C under 40% relative humidity (RH). The ethanol concentration was controlled by mixing ethanol gas with different amounts of synthetic air. The electrical resistance of the gas sensors was determined by measuring the electric current using a Keithley source meter-2612 with a source voltage of 1 V. Detailed procedures for sensor fabrication and the sensing test are described elsewhere [16].

3. Results and discussion

Fig. 1(a) presents a SEM image of the In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorods with a rod-like morphology grown vertically on a Fe substrate by thermal oxidation of an Fe foil. The diameters and lengths of the nanorods ranged from 50 to 150 nm and from 4 to 7 $\mu$m, respectively. The inset in Fig. 1(a) shows a typical Fe$_2$O$_3$(Zn) nanorod capped with an In$_2$O$_3$ shell where the nanorod diameter and shell layer thickness were ~70 and ~12 nm, respectively.

Fig. 1(b) presents XRD patterns of the pristine and In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorods. The former exhibited five peaks assigned to the (110), (113), (202), (214), and (300) reflections from rhombohedral $\alpha$-Fe$_2$O$_3$. In contrast, the latter exhibited three peaks assigned to the (012), (104) and (024) reflections from body-centered cubic In$_2$O$_3$ as well as the reflections from $\alpha$-Fe$_2$O$_3$. The tall reflection peaks of the In$_2$O$_3$-capped Fe$_2$O$_3$ nanorods suggest that both the Fe$_2$O$_3$(Zn) core and In$_2$O$_3$ shell are crystalline.

Fig. 2(a) and (b) show the gas response transients of the pristine and In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorod sensors, respectively, to ethanol at 300 °C. The electrical behaviors of the sensors were reversible and reproducible upon each ethanol pulse. Fig. 3(a) presents the responses of the pristine and In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorod sensors, respectively, to ethanol at 300 °C as a function of the ethanol concentration. Herein, the sensor response to ethanol gas was defined as $[R_e/R_0] \times 100($%), where $R_e$ and $R_0$ are the electrical resistances of the sensors in ethanol gas and air, respectively. Fig. 3(b) shows the response time and recovery time of the two nanorod samples to ethanol gas, which were determined from the resistance data in Fig. 2(a) and (b), respectively, as a function of the ethanol concentration. The response and recovery times were

![Fig. 1](image1.jpg) (a) SEM image and (b) XRD patterns of pristine and In$_2$O$_3$-capped Zn-doped Fe$_2$O$_3$ nanorods.

![Fig. 2](image2.jpg) Ethanol gas response transients of (a) the pristine and (b) In$_2$O$_3$-capped Zn-doped Fe$_2$O$_3$ nanorod sensors.
defined as the times to reach 90% of the resistance change upon exposure to ethanol and air, respectively. The pristine Fe2O3(Zn) nanorods showed responses of 744% to 200-ppm ethanol. In contrast, the In2O3-capped Fe2O3(Zn) nanorods showed responses of 1548% to 200 ppm of ethanol. The In2O3-capped Fe2O3(Zn) nanorod sensor also showed a more rapid response and recovery than the Fe2O3(Zn) nanorod sensor. The response and recovery times of the Fe2O3(Zn) nanorod sensor towards 100 ppm ethanol were 12.1 s and 35.8 s, respectively, whereas those of the In2O3-capped Fe2O3(Zn) nanorod sensor were 2.3 s and 30.2 s. Table 1 presents the ethanol gas sensing data of different metal oxide semiconductor sensors. The In2O3-capped Fe2O3(Zn) nanorod sensor showed shorter response and recovery times than most other metal oxide semiconductor sensors reported in the literature [17–29].

Fig. 4 shows the responses of the pristine and In2O3-capped Fe2O3(Zn) nanorod sensors to ethanol gas as a function of the operation temperature. Both sensors showed a maximum response at 300 °C. Therefore, all other sensing tests in this study were carried out at 300 °C. As the operating temperature was increased, the adsorption of oxygen molecules on the sensor surface and the oxidation of ethanol occurred more actively, leading to an enhanced response to ethanol gas. On the other hand, further increases in temperature than the optimal temperature resulted in an increase in carrier concentration, leading to a decrease in the response. Furthermore, at temperatures higher than the optimal temperature, desorption of all kinds of species will occur, which also causes a decrease in the response [30].

Fig. 5 compares the responses of the pristine and In2O3-capped Fe2O3(Zn) nanorod sensors to 200-ppm ethanol gas with those to 200 ppm of other volatile organic compounds such as methanol, acetone, benzene and toluene. Both samples showed selectivity to ethanol by showing the strongest response to ethanol. The selectivity of the sensor to ethanol over other VOC gases might be due to the higher adsorption and desorption rates of ethanol and higher oxidation rate of ethanol than those of other VOC gases at the operating temperature of 300 °C.

The sensing mechanism of the pristine Fe2O3(Zn) nanorod sensor is as follows:

Upon exposure to air, the p-type Fe2O3(Zn) interacts with oxygen. In general, the oxygen species of O2−, O−, and O2²− are stable at below 150 °C, between 150 and 400 °C, and above 400 °C, respectively [31]. Therefore, of these oxygen species, O− might form at the working temperature of 300 °C according to the following equation:

\[
\frac{1}{2}O_2(g) + O^−(ad) + h^+ \quad (1)
\]

and the holes are transferred to the valence band of the p-Fe2O3(Zn). As a result of these reactions, a hole-accumulation layer forms in the surface region of the p-Fe2O3(Zn) nanorod.

Upon exposure to ethanol, ethanol is oxidized by consuming the holes in the surface region of the p-Fe2O3(Zn) according to the following equation:

\[
C_2H_5OH(gas) \rightarrow C_2H_5OH(ads) \quad (2)
\]

\[
C_2H_5OH(ads) + 6O^−(ads) + 6h^+ \rightarrow 2CO_2(gas) + 3H_2O(gas) \quad (3)
\]

Consequently, a thin depletion layer forms in the surface region of the p-Fe2O3(Zn) nanorod.

The enhanced ethanol gas sensing performance of the In2O3-capped Fe2O3(Zn) nanorod sensors could be explained by a combination of electronic and chemical mechanisms. The electronic mechanism is associated with a modulation of the conduction channel width [32] and the potential barrier height at the Fe2O3–In2O3 interface [33,34]. Fig. 6 presents schematic diagrams showing the depletion layer, accumulation layer and potential barrier forming at the Fe2O3–In2O3 interface as well as the energy band diagrams of the Fe2O3–In2O3 binary system in air and ethanol gas.

Upon exposure to air, the n-type In2O3 capping layer interacts with oxygen in air by transferring electrons from the conduction band of In2O3 to the adsorbed oxygen atoms, according to the following equation:

\[
1/2O_2(g) + e^− \rightarrow O^−(ad) \quad (4)
\]

At this time, the capping layer might be completely depleted of carriers because the In2O3 capping layer thickness is smaller than 2λD(In2O3), where λD(In2O3) is the Debye length of In2O3 (~25 nm). On the other hand, the p-Fe2O3(Zn) nanorod core interacts with oxygen forming ionic oxygen species and producing holes according to Eq. (1). These holes are transferred to the valence band of p-Fe2O3(Zn). As a result of these reactions, an electron depletion layer and a hole-accumulation layer form on the n-In2O3 and p-Fe2O3(Zn) sides, respectively, in the Fe2O3–In2O3 interfacial region.
and a potential barrier with a height of $V_1$ forms at the interface. In this case, the hole-accumulation layer in the surface region of p-Fe$_2$O$_3$(Zn) acts as a conduction channel with a width of $W_{C1}$.

Upon exposure to ethanol, ethanol is oxidized by consuming the holes at the surface region of the p-Fe$_2$O$_3$(Zn) according to Eqs. (3) and (4). Consequently, a thin depletion layer forms on the p-Fe$_2$O$_3$(Zn) side in the interfacial region. On the other hand, in the surface region of the n-type In$_2$O$_3$ capping layer, an ethanol oxidation reaction also occurs according to the following equation:

$$C_2H_5OH(\text{ads}) + 6O^{\text{(ads)}} \rightarrow 2CO_2(\text{gas}) + 3H_2O(\text{gas}) + 6e^-.$$ (5)

As a result of Reaction 5, a part of the depleted layers is filled with electrons, leading to a decrease in the depletion layer thickness on the In$_2$O$_3$ side in the interfacial region and a thin depletion layer also forms at the outer surface of the In$_2$O$_3$ capping layer. In this case, the current flows through the central region of the nanorod except for peripheral depletion layer along its axis. Therefore, the conduction channel width will be $W_{C2}$. In addition, a potential barrier with a height of $V_2$ forms at the Fe$_2$O$_3$(Zn)–In$_2$O$_3$ interface. In other words, modulation of the conduction channel width and potential barrier height occurs at the Fe$_2$O$_3$(Zn)–In$_2$O$_3$ interfaces in the sensor accompanying the adsorption and desorption of ethanol gas. The modulation, in turn, results in a change in resistance and hence the response to ethanol gas.

The response of a sensor to ethanol gas depends on the difference in the conduction channel width between in air and in ethanol, i.e., $W_{C2} - W_{C1}$. Actually, there is little difference in $W_{C2} - W_{C1}$ between the pristine and In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorod sensors. Therefore, the effect of the modulation of the conduction channel width on the response of the sensor is insignificant. The enhanced sensing properties of the In$_2$O$_3$-capped Fe$_2$O$_3$(Zn) nanorod sensor compared to the pristine counterpart can be attributed mainly to a modulation of the potential barrier height of the two electronic mechanisms. In particular, numerous p–n heterojunctions exist in the former sensor but not in the latter sensor.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conc. (ppm)</th>
<th>Sensitivity</th>
<th>T (°C)</th>
<th>Res. time/Rec. time (sec)</th>
<th>Ref.</th>
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<tr>
<td>In$_2$O$_3$@Fe$_2$O$_3$(Zn)</td>
<td>100</td>
<td>12,160$^a$</td>
<td>300</td>
<td>2/12</td>
<td>Present work</td>
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<tr>
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<td>5</td>
<td>4,250$^a$</td>
<td>300</td>
<td>7/16</td>
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<td>22$^a$</td>
<td>200</td>
<td>70/−</td>
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<td>2.24$^a$</td>
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<tr>
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<td>71.90$^c$</td>
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<td>250</td>
<td>90/14</td>
<td>[33]</td>
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</table>

$^a$ ($R_a/R_g$, %).
$^b$ ($R_b/R_g$).
$^c$ ($[R_a - R_g]/R_g$, %).

**Fig. 4.** Responses of the pristine and In$_2$O$_3$-capped Zn-doped Fe$_2$O$_3$ nanorods to ethanol gas as a function of the operating temperature.

**Fig. 5.** Electrical responses of the pristine and In$_2$O$_3$-capped Zn-doped Fe$_2$O$_3$ nanorod gas sensors to different VOC gases. The gas concentration was fixed as 200 ppm for all VOC gas at 300 °C.
height at the Fe₂O₃–In₂O₃ interface and the strong catalytic activity of In₂O₃ for ethanol oxidation.

Acknowledgments

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References


On the other hand, the chemical mechanism is related to the catalytic activity of In₂O₃ for the ethanol oxidation reaction occurring when the sensor is exposed to ethanol [32]. The excellent catalytic property of In₂O₃ has been reported previously [35,36]. Chu et al. reported that the addition of nanoparticles In₂O₃ to Pd catalysts promoted the catalytic activity for ethanol electro-oxidation [35]. Parrondo et al. reported that the In₂O₃ supported Pt/C nanoparticles exhibited higher catalytic activity for ethanol electro-oxidation despite their lower electrochemical surface area than Pt/C [36].

4. Conclusions

In₂O₃-capped Fe₂O₃(Zn) nanorods were synthesized by a two-stage process involving the thermal oxidation of Fe foils and Zn powders in an oxidizing atmosphere and the sputter-deposition of In₂O₃. The multiple-networked In₂O₃-capped Fe₂O₃(Zn) nanorod sensor showed a significantly stronger electrical response to ethanol gas than their Fe₂O₃(Zn) nanorod counterpart. The former sensor also showed more rapid response and recovery to ethanol gas than the latter one. The enhanced sensing performance of the In₂O₃-capped Fe₂O₃(Zn) nanorod sensor towards ethanol was explained by a combination of a modulation of the potential barrier height at the Fe₂O₃–In₂O₃ interface and the strong catalytic activity of In₂O₃ for ethanol oxidation.