Enhanced acetone gas sensing performance of the multiple-networked Fe2O3-functionalized In2O3 nanowire sensor

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ABSTRACT

In2O3 nanowires functionalized with Fe2O3 nanoparticles were synthesized by the thermal evaporation of In2S3 powders in an oxidizing atmosphere followed by the solvothermal deposition of Fe2O3 and their acetone gas sensing properties were examined. The pristine and Fe2O3-functionalized In2O3 nanowires exhibited responses of 141±390% and 298±960%, respectively, to 10–500 ppm acetone at 200 °C. The Fe2O3-functionalized In2O3 nanowire sensor showed stronger electrical response to acetone gas at 200 °C than the pristine In2O3 nanowire counterpart. The former showed more rapid response but slower recovery than the latter. Both the pristine and Fe2O3-functionalized In2O3 nanowire sensors showed the strongest response to acetone gas at 200 °C. The underlying mechanism for the enhanced sensing performance of the Fe2O3-functionalized In2O3 nanowire sensor towards acetone gas is discussed.

1. Introduction

Oxide semiconductors have attracted considerable attention for gas sensing owing to their high sensitivity, fast sensing, simple and cheap fabrication [1,2]. On the other hand, enhancing their sensing properties further is still a challenge. Several techniques such as noble metal doping [3–5], heterostructure formation [6–11] and UV irradiation [6,12,13] were developed for this purpose. Heterostructure formation can be achieved by forming a core-shell structure [6–8] or functionalizing one type of oxide semiconductor nanostructure with another type nanoparticles [9–11]. The largest portion of recent studies on oxide-functionalized gas sensors deal with n-type oxide semiconductor nanostructures functionalized with p-type oxide semiconductor nanoparticles. On the other hand, far fewer studies have made on n-type oxide-functionalized n-type oxide semiconductor sensors compared to p-type oxide-functionalized n-type oxide semiconductor sensors despite their remarkable sensing properties.

In2O3 is an n-type wide direct bandgap semiconductor (Eg = 3.55–3.75 eV) [14]. In2O3 showed excellent response to several gases such as O3, NO2, CO and H2 [15–19]. On the other hand, hematite (α-Fe2O3), which is the most stable iron oxide, with n-type semiconducting properties under ambient conditions, has been extensively used as a gas sensor, catalyst, and pigment owing to its low cost and high resistance to corrosion [20–23]. Regarding the sensing performance of α-Fe2O3-n-type oxide semiconductor heterostructured sensors, several study results have been reported previously. Zhao et al. reported that In2O3/α-Fe2O3 heterostructure nanotubes showed a high sensitivity to ethanol with a short response/recovery times, and the performance was stable at a low operating temperature [24]. Chen and Zhu reported that the α-Fe2O3/SnO2 core–shell nanorods and α-Fe2O3/ZnO heterostructures exhibited significant improvements in ethanol sensing characteristics compared to pure α-Fe2O3 nanorods [25,26]. Jin et al. showed the excellent response and selectivity of the Fe2O3-decorated V2O5 nanotubes to the ethanol gas [27]. Lou et al. demonstrated the excellent sensing performances of the α-Fe2O3/TiO2 heterostructures sensor towards trimethylamin gas compared with α-Fe2O3 nanorods and TiO2 nanofibers sensors [28]. In this study, the acetone gas sensing properties of the multiple-networked Fe2O3-functionalized In2O3 nanowire sensor were examined. The underlying mechanism for the enhanced sensing performance of Fe2O3-functionalized In2O3 nanowires towards acetone compared to the pristine In2O3 nanowires is discussed.
2. Experimental

Pristine and Fe$_2$O$_3$-decorated In$_2$O$_3$ nanowires were prepared by thermal evaporation of In$_2$S$_3$ powders in an oxidizing atmosphere followed by a solvothermal method. First, Au-coated (0001) Al$_2$O$_3$ substrates were used for growing In$_2$O$_3$ nanowires. A 3-nm Au thin film was sputter-deposited on the (0001) Al$_2$O$_3$ substrates. A quartz tube was mounted horizontally inside a tube furnace. An alumina crucible containing 99.99% pure In$_2$S$_3$ powders was placed on the lower holder at the center of the quartz tube, while an Au-coated Al$_2$O$_3$ substrate was placed on the upper holder, approximately 5 mm away from the crucible. The furnace was heated to 800 °C and maintained at that temperature for 1 h in a N$_2$/O$_2$ atmosphere with constant N$_2$ and O$_2$ flow rates of 100 and 0.1 standard cubic centimeters per minute (sccm), respectively. The total pressure was set to 1.0 Torr. On the other hand, 50-mM Fe$_2$O$_3$ precursor solution was prepared by dissolving 0.1 M FeCl$_3$ in isopropyl alcohol. The Fe$_2$O$_3$ precursor solution was dropped onto the In$_2$O$_3$ nanowires on a substrate and the substrate was rotated at 1000 rpm for 1 min for Fe$_2$O$_3$ coating. After the spin-coating process, the Fe$_2$O$_3$ functionalized In$_2$O$_3$ nanowire sample was dried at 150 °C for 1 min and then annealed in air at 600 °C for 1 h in a N$_2$/O$_2$ atmosphere with constant N$_2$ and O$_2$ flow rates of 190 and 10 sccm, respectively. We made an Fe$_2$O$_3$ thin film sample on a Si (100) substrate using the same solvothermal method as used in this study and performed Hall measurement on our nanowire samples and confirmed that they showed n-type characteristics (Electron concentration: $7.3 \times 10^{17}/\text{cm}^3$).

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). To measure the sensing properties of the grown nanowires pristine and multiple-networked Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire sensors were prepared as follows: Each nanowire sample was dispersed ultrasonically in a mixture of deionized water (5 ml) and isopropyl alcohol (5 ml). The as-grown nanowires were placed onto a 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 μm. The flow-through technique was used to measure the gas sensing properties. All the measurements were performed in a temperature-stabilized sealed chamber with a constant flow rate of 200 cm$^3$/min at 200 °C under 40% RH. The acetone concentration was controlled by mixing acetone gas with synthetic air with different ratios. The electrical resistance of 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 sensing test are described elsewhere [29].

3. Results and discussion

Fig. 1(a) and (b) show the pristine and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowires, respectively, with a rod-like morphology synthesized in this study. The diameters and lengths of the nanowires ranged from 30 to 80 nm and from 10 to 30 μm, respectively.

A comparison of the insets of Fig. 1(a) and (b) revealed that the functionalized nanowires were ~20% larger in diameter than the pristine ones, suggesting that the thickness difference is big enough to affect the response of the sensors to acetone gas. Fig. 1(c) exhibits a high density of Fe$_2$O$_3$ nanoparticles with diameters of 10–30 nm
precipitated on a bent In$_2$O$_3$ nanowire. Fig. 1(d) presents the XRD pattern of the pristine and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowires. Most peaks in the XRD pattern were assigned to the body-centered cubic-structured In$_2$O$_3$ with lattice constants of $a = 1.011$ nm (JCPDS No. 89–4595). In addition, several reflections from the (012), (014), (116), and (300) lattice planes of rhombohedral-structured Fe$_2$O$_3$ with lattice constants of $a = 0.504$ nm, $c = 1.375$ nm (JCPDS No. 89–2810) were identified, suggesting that the Fe$_2$O$_3$ nanoparticles were also crystalline.

Fig. 2(a) and (b) show the gas sensing transients of the pristine and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowires, respectively, to 10–500 ppm of acetone gas at 200 °C. The electrical behavior of the sensors was reversible and reproducible upon each acetone pulse. The responses, response times and recovery times of the two nanowire samples to acetone gas at different concentrations at 200 °C determined from the data in Fig. 2(a) and (b) are plotted as a function of acetone concentration in Fig. 3(a), (b) and (c), respectively. In this study, the sensor response to acetone gas is defined as $[R_a/R_g] \times 100\%$, where $R_a$ and $R_g$ are the electrical resistances in the sensors in air and acetone gas, respectively. The response time and recovery time were defined as the times to reach 90% variation in resistance upon exposure to acetone and air, respectively. The pristine In$_2$O$_3$ nanowires showed responses of approximately 141–390% to 10–500 ppm of acetone. In contrast, the Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowires showed responses of approximately 278–960% to 10–500 ppm of acetone. The two nanowire sensors showed rapid response and slow recovery. It is not clear why the response time is shorter than the recovery time. The authors surmise that the rapid response is due to the higher solid solubility and diffusivity of acetone in In$_2$O$_3$ and Fe$_2$O$_3$ than those of oxygen. The Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire sensor also showed more rapid response but slower recovery than the pristine In$_2$O$_3$ nanowire sample regardless of acetone concentration. The more rapid response of former than the latter can also be explained by the electronic and chemical effects similarly to the explanation for its stronger response. On the other hand, the origin of the slower recovery of the former than the latter is not clearly understood at present.

Table 1 compares the response of the sensors to acetone obtained in this study with those of other metal oxide semiconductor gas sensors [30–38]. The responses of the pristine and Fe$_2$O$_3$-decorated In$_2$O$_3$ nanowires are significantly stronger than those of other oxide semiconductor gas sensors in the literature. Fig. 4(a) shows the responses of the pristine and Fe$_2$O$_3$-decorated In$_2$O$_3$ nanowires to 500-ppm acetone as a function of operation temperature. Both the two nanowire samples showed the highest response at 200 °C. The stable oxygen ions are O$_2$ below 100 °C, O$^-$
between 100 and 300 °C, and O₂ above 300 °C. As the temperature increases from 200 °C to 225 °C to 250 °C, the adsorption of O₂ increases and the adsorption of oxygen on the sensor surface occurs more actively, and thereby oxidation of acetone occurs more actively, leading to enhanced response to ethanol gas. Further increases in temperature than the optimal temperature will also result in an increase in carrier concentration, leading to a decrease in Debye length [39]. Furthermore, desorption of all kinds of adsorbed species will occur, aggravating the response. For these reasons, the response of ZnO sensor decreases at 200–250 °C.

Fig. 4(b) compares the responses of the pristine and Fe₂O₃-functionalized In₂O₃ nanowire sensors to various gases. Both the pristine and Fe₂O₃-functionalized In₂O₃ nanowire sensors showed selectivity to acetone over other gases including ammonia, CO, NO₂ and H₂ except ethanol. Fig. 5(a) and (b) show the cycle test data of the pristine and Fe₂O₃-functionalized In₂O₃ nanowire gas sensors. Both sensors exhibited stable sensing behaviors.

Both In₂O₃ and Fe₂O₃ are n-type semiconductors. When In₂O₃ nanowires or Fe₂O₃ nanoparticles are exposed to air at 200 °C, the nanowires interact with oxygen by transferring electrons from the conduction band to the adsorbed oxygen atoms, forming ionic species such as O⁻, O²⁻ and O₂ depending on temperatures. In particular, among these oxygen species, O⁻ is known to predominant in the temperature range of 100–300 °C [40]. A depletion layer is created in the surface region of the In₂O₃ nanowire due to the consumption of electrons in the In₂O₃ nanowire. Upon exposure to acetone gas, acetone molecules are adsorbed by the In₂O₃ nanowire surface, and electrons are released back to the conduction band of In₂O₃ nanowire as shown in the following reactions [41]:

\[
\text{CH₃COCH₃ (gas)} + 2O^{-} \rightarrow \text{CH₃CO} + \text{CH₃O}^{-} + 2e^{-} \quad (1)
\]

\[
\text{CH₃CO} \rightarrow \text{CH₃} + \text{CO} \quad (2)
\]

### Table 1

<table>
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<tr>
<th>Materials</th>
<th>T (°C)</th>
<th>Acetone concentration (ppm)</th>
<th>Response (%)</th>
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Fig. 4. (a) Electrical responses of the pristine and Fe₂O₃-functionalized In₂O₃ nanowire gas sensors to 500-ppm acetone gas as a function of operation temperature. (b) Electrical responses of the pristine and Fe₂O₃-functionalized In₂O₃ nanowire gas sensors to various gases at 500 ppm.

Fig. 5. The cycle test data of the (a) pristine and (b) Fe₂O₃-functionalized In₂O₃ nanowire gas sensors.
The release of electrons will decrease the depletion layer width, resulting in a decrease in the resistance of the nanowire sensor.

On the other hand, the acetone gas sensing mechanism of the Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire sensors can be explained using a combination of electronic and chemical mechanisms. Firstly, the electronic mechanisms include the surface-depletion mechanism [42] and potential barrier-controlled carrier transport mechanism [43,44]. One of the most important differences between the pristine and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowires is the existence of In$_2$O$_3$–Fe$_2$O$_3$ interfaces in the latter (Fig. 6(a)). Fig. 6(b) shows the energy band diagrams of the In$_2$O$_3$–Fe$_2$O$_3$ binary system in air and acetone [45–49]. Upon exposure to air, a depletion layer with a width of $W_{D1}$ forms near the In$_2$O$_3$–Fe$_2$O$_3$ interface and a potential barrier with a height of $E_1$ forms at the interface. On the other hand, upon exposure to acetone, an electron accumulation forms at the interface, so that the depletion layer shrinks to $W_{D2}$ and the potential barrier height changes to $E_2$. In other words, the modulation of the depletion layer width and potential barrier height at the n–n junction occurs in the sensor accompanying the adsorption and desorption of acetone gas, which results in increased resistance change and thereby enhanced sensitivity. More importantly, as can be seen by comparison of the pristine and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowires in Fig. 6(a), the conduction path widths in the functionalized nanowire in air and acetone gas, respectively: $W_{C1}(F)$ and $W_{C2}(F)$ are smaller than those in the pristine nanowire in air and acetone, respectively: $W_{C1}(P)$ and $W_{C2}(P)$. Secondly, a chemical mechanism is related to the creation of active adsorption sites by the incorporation of Fe$_2$O$_3$. Precipitation of Fe$_2$O$_3$ nanoparticles on the In$_2$O$_3$ nanowires creates crystallographic defects at the Fe$_2$O$_3$–In$_2$O$_3$ interface due to the lattice mismatch between the two materials [50], which provides preferential adsorption site for acetone and oxygen molecules. The sensing performance of the Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire sensor is believed to be enhanced by the combination of these effects. Actually, it is not easy to conclude which mechanism is dominant between the two, but we would say that the electronic mechanism is predominant over the chemical mechanism because the lattice mismatch between Fe$_2$O$_3$ and In$_2$O$_3$ is not very big.

4. Conclusions

Multiple-networked Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire sensors showed far stronger electrical response to acetone gas than pristine In$_2$O$_3$ nanowire sensors. The former showed more rapid response but slower recovery to acetone gas. The optimal operation temperature of the two sensors was found to be 200°C. The enhanced sensing properties of the Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire sensor towards acetone can be explained by a combination of electronic and chemical mechanisms. The electronic mechanism is a combination of modulation of the interface potential barrier and the depletion layer width, whereas the chemical mechanism is creation of active adsorption sites by incorporation of Fe$_2$O$_3$. We believe that this study shows a possibility of realizing high-performance gas sensors using n–n heterostructure formation technique and elucidate the underlying mechanism for the enhanced sensing performance of the n–n heterostructured gas sensors.

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