Synthesis and ethanol sensing properties of CuO nanorods coated with In$_2$O$_3$

Sunghoon Park$^a$, Hyunsung Ko$^a$, Soyeon An$^a$, Wan In Lee$^b$, Sangmin Lee$^c$, Chongmu Lee$^{a*,n}$

$^a$Department of Materials Science and Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea
$^b$Department of Chemistry, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea
$^c$Department of Electronic Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea

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Abstract

CuO/In$_2$O$_3$ core–shell nanorods were fabricated using thermal evaporation and radio frequency magnetron sputtering. X-ray diffraction and transmission electron microscopy showed that both the cores and shells were crystalline. The multiple networked CuO/In$_2$O$_3$ core–shell nanorod sensors showed responses of 382–804%, response times of 36–54 s and recovery times of 144–154 s at ethanol (C$_2$H$_5$OH) concentrations ranging from 50 to 250 ppm at 300°C. These responses were 2.3–2.8 times higher than those of the pristine CuO nanorod sensor over the same C$_2$H$_5$OH concentration range. The origin of the enhanced ethanol sensing properties of the core–shell nanorod sensor is discussed.

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1. Introduction

Cupric oxide (CuO) with a band gap of approximately 1.2–1.9 eV is one of the few metal oxides with p-type semiconducting properties [1,2]. These properties make CuO suitable for catalysis [3], lithium–copper oxide electrochemical cells [4], field emission device [5], gas sensors applications [6], high temperature superconductors [7], magnetic storage media [8], photovoltaics [9], infrared photodetectors, and heterogeneous catalysts [10]. A range of CuO nanostructures, such as nanoparticles, nanoribbons, plates and nanowires have been reported to be sensitive to humidity, HCOH, C$_2$H$_5$OH, NO$_2$, H$_2$S and CO [11–16]. One-dimensional (1D) CuO nanostructures have been synthesized using wet chemical methods, room-temperature liquid–solid growth, low-temperature solid-phase processes, or anodic aluminum oxide (AAO) template-assisted electrodeposition, liquid–liquid methods and catalyzed synthesis [17–24]. These methods have difficulty in controlling the diameters and composition of nanowires, and are unsuitable for mass production. On the other hand, CuO 1D nanostructures can also be synthesized on copper substrate using simple thermal oxidation processes [20].

In recent years, one-dimensional (1D) nanostructure-based sensors have become a subject of intense research effort because of the higher sensitivity, superior spatial resolution and rapid response associated with individual nanowires due to the high surface-to-volume ratios compared to thin film gas sensors [25–27]. Nevertheless, enhancing their sensing performance and detection limit is still a challenge. Core–shell 1D nanostructures has been fabricated to improve the sensitivity, stability and response speed of the 1D nanostructure-based sensors [28–30]. This paper reports the synthesis of CuO/In$_2$O$_3$ core–shell nanorods by the direct heating of Cu sheets in air followed by radio frequency (rf) magnetron sputtering of In$_2$O$_3$ as well as their enhanced ability to detect ethanol (C$_2$H$_5$OH) gas. The origin of the enhanced sensing properties of CuO/In$_2$O$_3$ core–shell nanorods is also discussed.

2. Experimental

The CuO/In$_2$O$_3$ core–shell nanorods were synthesized using thermal evaporation and sputtering methods. First,
the CuO nanorods were synthesized in a quartz tube furnace by the thermal oxidation of a copper sheet at 500 °C in air without a metal catalyst or the supplying of any other gas. The thermal oxidation process was carried out for 2 h and the furnace was cooled to room temperature. Subsequently, the CuO nanorods were coated with a thin In2O3 layer by conventional radio frequency (rf) magnetron sputtering. The base pressure, working pressure and Ar gas flow rate were 5.0 × 10⁻⁶ Torr, 2.0 × 10⁻² Torr and 20 sccm, respectively. The rf sputtering power and sputtering time was 100 W and 10 min, respectively. The substrate temperature was maintained at room temperature.

Scanning electron microscopy (SEM, Hitachi S-4200), transmission electron microscopy (TEM, Philips CM-200), energy-dispersive X-ray spectroscopy (EDXS), and X-ray diffraction (XRD, Philips X'pert MRD diffractometer) were performed on the nanorod samples collected. The crystallographic structure was determined by glancing angle XRD using Cu Kα radiation (0.15406 nm) at a scan rate of 4°/min and at a glancing angle of 0.5° with a rotating detector.

The electrical and gas sensing properties of the plain and CuO/In2O3 core–shell nanorods were measured using a home-built computer-controlled characterization system consisting of a test chamber, sensor holder, Keithley sourcemeter-2612, mass flow controllers and data acquisition system. A given amount of ethanol (> 99.99%) gas was injected into the testing tube through a microsyringe, and the output resistance across the sensor was monitored. The resistance of the sensor in dry air or in a test gas was measured from this voltage.

The response of the CuO nanorod sensors was defined as $R_a/R_g$ for C₂H₅OH, where $R_a$ and $R_g$ are the electrical resistances in the sensors in air and target gas, respectively. The response time is defined as the time needed for the change in electrical current to reach 90% of the equilibrium value after injecting the gas. The recovery time is defined as the time needed for the sensor to return to 90% of the original current in air after removing the gas.

3. Results and discussion

XRD was conducted to determine the crystal structure of the nanorods. The XRD pattern of CuO/In₂O₃ core–shell nanorods suggested that both CuO cores and In₂O₃ shells were crystalline (Fig. 1). Most XRD peaks of the core–shell nanorods were assigned to the planes of end-centered monoclinic-structured CuO with the following lattice constants: $a = 0.4689$ nm, $b = 0.3420$ nm, $c = 0.5130$ nm and $\beta = 99.57$ (JCPDS no. 89-5899). Only three tall peaks were assigned to the (111), (110), and (200) reflections of simple cubic structured-Cu₂O with a lattice constant of $a = 0.4267$ nm (JCPDS no. 89-5899). Four peaks were assigned to the reflections of body-centered cubic (bcc)-structured In₂O₃ with lattice constants of $a = 1.011$ nm (JCPDS no. 89-4595). The thermal oxidation of Cu in air converts the metal to Cu₂O first and then into CuO [22,31]:

$$4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O} \quad (1)$$

$$2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO} \quad (2)$$

CuO is known to form at ~270 °C. Nevertheless, XRD of the copper oxide nanorods synthesized by heating at 500 °C in air for 2 h showed the coexistence of both monoclinic CuO and simple cubic Cu₂O phases. Reaction (2) does not appear to have been complete, even at a high temperature of 500 °C.

Fig. 2 shows a SEM image of the CuO/In₂O₃ core–shell nanorods prepared by thermal oxidation followed by sputtering. Each 1D nanostructure exhibited a rod-like morphology as can be seen in the enlarged SEM image of a typical 1D nanostructure (inset in Fig. 2). SEM also showed that the synthesis scheme adopted in this study can grow CuO nanorods with diameters of 50–100 nm and lengths up to a few tens of micrometers. The low-magnification TEM image of a typical core–shell nanorod showed a CuO core with a diameter of ~80 nm at the central region and In₂O₃ shells at the two edge regions of
the nanorods with thicknesses of 5 nm and 15 nm (Fig. 3(a)). The high resolution TEM (HRTEM) image revealed fringe pattern both in the core and shell regions. The clear spotty patterns in the corresponding selected area electron diffraction (SAED) pattern was fitted to monoclinic structured-CuO (JCPDS no. 89-5899) (Fig. 3(c)). On the other hand, the dim spotty and concentric ring pattern was fitted to simple cubic Cu$_2$O with a lattice constant of $a=0.4267$ nm and bcc In$_2$O$_3$ with a lattice constant of $a=1.011$ nm (JCPDS no. 89-4595), respectively. The core in the core–shell nanorod contains both single crystal CuO and Cu$_2$O phases, while the shell contains polycrystalline In$_2$O$_3$ phase from the SAED pattern.

EDX of the nanorods (Fig. 4(a)) revealed the presence of Cu, In and O, which concurs with the XRD results (Fig. 1). The Ni and C in the spectra were assigned to the TEM grid. EDXS suggested that the CuO/In$_2$O$_3$ core–shell nanorods had been synthesized successfully by indicating a higher CuO concentration in the central region and a higher In$_2$O$_3$ concentration at both edge regions of the nanorod (Fig. 4(b)).

Fig. 5(a) shows the transient response of the pristine CuO nanorods and CuO/In$_2$O$_3$ core–shell nanorods, to C$_2$H$_5$OH at an operating temperature of 300 °C. The sensors were exposed to successive pulses of C$_2$H$_5$OH with concentrations ranging from 50 to 250 ppm. The response was reversible, i.e., the nanorod sensors showed the same resistance before and shortly after each ethanol pulse. Fig. 5(b) and (c) show an enlarged part of the data in Fig. 5(a) measured at a C$_2$H$_5$OH concentration of 250 ppm for the pristine CuO nanorods and CuO/In$_2$O$_3$ core–shell sensors, respectively, to reveal the moments of gas input and gas stop. The response of the CuO nanorods showed responses of approximately 163, 192, 226, 242 and 291% at C$_2$H$_5$OH concentrations of 50, 100, 150, 200 and 250 ppm, respectively (Table 1). In contrast, the CuO/In$_2$O$_3$ core–shell nanorods showed responses of 382, 473, 618, 727 and 804% at C$_2$H$_5$OH concentrations of 50, 100, 150, 200 and 250 ppm, respectively (Table 1). The core–shell nanorod sensors showed ~2.3, 2.5, 2.7, 3.0 and 2.8 times higher responses than those of the pristine CuO nanorod sensors at C$_2$H$_5$OH concentrations of 50, 100, 150, 200 and 250 ppm, respectively (Table 1).

Fig. 5(d) shows the responses of the pristine CuO nanorods and CuO/In$_2$O$_3$ core–shell nanorods as a function of the C$_2$H$_5$OH concentration. The response of an oxide semiconductor is commonly expressed as $R=A [C]^n + B$, where A and B are constants, and n and [C] are the exponent and target gas concentration, respectively. Data fitting provided the following equations: $R=0.610 [C] + 132$ and $R=2.19 [C]+ 271$ for the pristine CuO nanorod and CuO/In$_2$O$_3$ core–shell sensors, respectively. The response of the core–shell nanorod sensor increased more rapidly with increasing C$_2$H$_5$OH gas concentration than that of the pristine nanorod sensor. Although the response of the core–shell nanorods was examined only at C$_2$H$_5$OH concentrations of 50–250 ppm, the results suggest that the response of the former would be far higher than that of the latter at high C$_2$H$_5$OH gas concentrations such as a few thousand ppm of C$_2$H$_5$OH. On the other hand, the response and recovery times of the core–shell nanorods were similar to those of the pristine CuO nanorods.

Table 2 lists the responses of the CuO/In$_2$O$_3$ core–shell nanorod sensor fabricated in this study toward C$_2$H$_5$OH gas along with those of the other reported nanomaterial sensors. Overall, the sensing properties of the CuO/In$_2$O$_3$ core–shell nanorod sensor fabricated in this study were comparable to those of the other competing nanomaterials (Table 2) [32–46]. The C$_2$H$_5$OH concentration and test temperature used in this study were lower than those in previous studies. The response of the CuO/In$_2$O$_3$ core–shell nanorods was far higher than that of the TiO$_2$ nanotubes despite the far lower C$_2$H$_5$OH concentration and test temperature [32]. Compared to CoFe$_2$O$_4$ nanopowders, the CuO/In$_2$O$_3$ core–shell nanorods showed a somewhat lower response to C$_2$H$_5$OH gas and larger response and recovery times at the same temperature [39]. On the other hand, a comparison of the CuO/In$_2$O$_3$ core–shell nanorods with Co-doped ZnO nanorods measured at a similar C$_2$H$_5$OH concentration suggests that the response of the former was higher than that of the latter.
In particular, the response of the CuO/In$_2$O$_3$ core–shell nanorods is higher than that of plain In$_2$O$_3$ nanorods and nanocrystals despite the lower C$_2$H$_5$OH concentration.

CuO and In$_2$O$_3$ in the core–shell nanorods are p-type and n-type semiconductor oxides, respectively, and the sensing mechanism of the core–shell nanorods is based on a surface reaction. In this study, the CuO/In$_2$O$_3$ core-shell nanorods showed a considerably enhanced sensor response to ethanol gas. The surface of the sensor material is covered with chemisorbed oxygen ions such as O$^-$, O$^{2-}$ and O$_2^-$, according to the following reactions [47]:

\[ \text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{ads}) \]  \hspace{1cm} (3)

\[ \text{O}_2(\text{ads}) + e^- \rightarrow \text{O}_2^-(\text{ads}) \]  \hspace{1cm} (4)

\[ \text{O}_2^- (\text{ads}) + e^- \rightarrow 2\text{O}^- (\text{ads}) \]  \hspace{1cm} (5)

\[ \text{O}^- (\text{ads}) + e^- \rightarrow \text{O}^{2-} (\text{ads}) \]  \hspace{1cm} (6)

These adsorbed oxygen ions create a space charge region near the film surface by extracting electrons from the surface of the sensor. The adsorbed ethanol molecules react with these ionic oxygen species and produce electrons via the following two reactions: (Reaction 7) dehydrogenation of ethanol to an aldehyde and (Reaction 8) dehydrogenation of ethanol to an alkene on basic and acidic oxides,

![Fig. 4. (a) EDX spectrum of the CuO/In$_2$O$_3$ core–shell nanorods and (b) EDXS line scanning concentration profiles.](image-url)
respectively [48].

$$C_2H_5OH(g) \rightarrow CH_3CHO(g) + H_2(g) \quad (7)$$

$$C_2H_5OH(g) \rightarrow C_2H_4(g) + H_2O(g) \quad (8)$$

The enhanced sensor response of the CuO/In$_2$O$_3$ core–shell nanorods to ethanol compared to that of the pristine CuO nanorods might be due to the enhanced absorption and dehydrogenation of ethanol (Reaction 7) because of the basic properties of In$_2$O$_3$ [48,49]. The CH$_3$CHO is then oxidized by the chemisorbed oxygen ions according to the following equation:

$$CH_3CHO(ad) + 5O^\cdot \rightarrow 2CO_2 + 2H_2O + 5e^- \quad (9)$$

In addition to the enhanced absorption and dehydrogenation of ethanol mentioned above, the enhanced response might be attributed partly to the modulation of electron transport by the In$_2$O$_3$–In$_2$O$_3$ homojunction at the interface of nanorods with an adjustable energy barrier height. An energy barrier exists at the In$_2$O$_3$–In$_2$O$_3$ homojunction formed at the crossing point of the two core–shell nanorods. Electron transport is modulated by the homojunction with an adjustable energy barrier height. Therefore, the homojunction acts as a lever in electron transfer through which electron transfer is facilitated or restrained, resulting in enhanced sensing properties of the nanorod sensor.

On the other hand, the enhanced sensor response of the core–shell nanorods might not be due to the changes in resistance due to CuO–In$_2$O$_3$ heterojunction barrier in each core–shell nanorod [50,51]. The width of the surface layer is in the order of the Debye length $\lambda_D$, which can be
expressed as \[ \lambda_D = \frac{e k T}{q^2 n_c}^{1/2}, \] (10)

where \( \varepsilon \) is the static dielectric constant \((8.9 \times 8.85 \times 10^{-12}\) F/m in In\(_2\)O\(_3\)), \( k \) is the Boltzmann constant \((1.38 \times 10^{-23}\) J/K), \( T \) is the absolute temperature \((573\) K), \( q \) is the electrical charge of the carrier \((1.6 \times 10^{-19}\) C) and \( n_c \) is the carrier concentration \((9.5 \times 10^{18}\) /cm\(^3\); the value obtained by Hall measurements of a 200 nm In\(_2\)O\(_3\) thin film deposited on a Si (100) substrate by sputtering). For the In\(_2\)O\(_3\) layer on the core–shell nanorods fabricated in this study, the calculated \( \lambda_D \) value at 300 \(^\circ\)C was approximately 1.6 nm. This means that C\(_2\)H\(_5\)OH molecules cannot donate/accept electrons to/from the CuO core but only to/from the In\(_2\)O\(_3\) shell layer, the width of which is approximately 5–15 nm. Therefore, the heterojunction barrier at the interface of the two nanorods does not need to be considered in this core–shell nanorod system.

## 4. Conclusions

CuO/In\(_2\)O\(_3\) core–shell nanorods were synthesized using a two-step process: the synthesis of CuO nanorods using a thermal evaporation method and the subsequent deposition of In\(_2\)O\(_3\). The cores and shells of the nanorods were single crystal CuO and polycrystalline In\(_2\)O\(_3\), respectively. The responses of the CuO nanorods were improved approximately 2–3 fold at each C\(_2\)H\(_5\)OH concentration as a result of the sheathing with In\(_2\)O\(_3\). The responses of the core–shell nanorods to C\(_2\)H\(_5\)OH gas were also far superior to those of the other material nanosensors reported previously. The improvement in the response of the CuO nanorods to C\(_2\)H\(_5\)OH gas by sheathing them with In\(_2\)O\(_3\) might be due to the enhanced absorption and dehydrogenation of ethanol. In addition, the enhanced sensor response of the core–shell nanorods was attributed partly to changes in resistance due to the potential barriers built at the In\(_2\)O\(_3\)–In\(_2\)O\(_3\) homojunction at the interface of the two nanorods.

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## References


