Enhanced Gas Sensing Properties of Bi$_2$O$_3$-Core/In$_2$O$_3$-Shell Nanorod Gas Sensors

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The Bi$_2$O$_3$ nanowires are highly sensitive to low concentrations of NO$_2$ in ambient air and are almost insensitive to most other common gases. However, it still remains a challenge to enhance their sensing performance and detection limit. This study examined the influence of the encapsulation of β-Bi$_2$O$_3$ nanorods with In$_2$O$_3$ on the NO$_2$ gas sensing properties. β-Bi$_2$O$_3$-core/In$_2$O$_3$-shell nanorods were fabricated by a two-step process comprising the thermal evaporation of Bi$_2$O$_3$ powders and sputter-deposition of In$_2$O$_3$. Multiple networked β-Bi$_2$O$_3$-core/In$_2$O$_3$-shell nanorod sensors showed the responses of 12-156% at 1-5 ppm NO$_2$ at 300 °C. These response values were 1.3-2.7 times larger than those of bare β-Bi$_2$O$_3$ nanorod sensors at 1-5 ppm NO$_2$. The enhancement in the response of β-Bi$_2$O$_3$ nanorods to NO$_2$ gas by the encapsulation by In$_2$O$_3$ can be accounted for based on the space-charge model.

Key Words: Bi$_2$O$_3$, In$_2$O$_3$, Nanorods, Sensor, NO$_2$

Introduction

Bismuth oxide (Bi$_2$O$_3$) is an important wide band gap semiconductor material with four main crystallographic polymorphs denoted by α-, β-, γ-, and δ-Bi$_2$O$_3$. Of these polymorphs, β-Bi$_2$O$_3$ is an n-type semiconductor, whereas δ-Bi$_2$O$_3$ is a p-type semiconductor. Due to its unique physical properties such as a large energy band gap, a high refractive index, a dielectric permittivity and a high oxygen conductivity, as well as remarkable photoconductivity and photoluminescence, β-Bi$_2$O$_3$ has been extensively investigated for a range of applications in gas sensors, photovoltaic cells, optical coatings, fuel cells, supercapacitors, photocatalysts, etc. Particularly regarding the gas sensor application, nanowires are expected to have significantly enhanced performance due to their ultrahigh surface-to-volume ratios and their dimensions comparable to Debye length, which makes their electrical properties extremely sensitive to surface-adsorbed species. Bismuth oxide nanowires have been prepared using a range of techniques such as metal-organic chemical vapor deposition (MOCVD), chemical methods, and an oxidative metal vapor transport deposition technique, a solution chemical method, and a stress-induced method. However, the vapor-liquid-solid (VLS) method has not been reported to synthesize Bi$_2$O$_3$ nanowires, yet. It is widely known that VLS process is the most successful for generating nanowires with single crystalline structures and in relatively large quantities among all vapor-based methods.

The Bi$_2$O$_3$ nanowires are highly sensitive to low concentrations of NO$_2$ in ambient air and are almost insensitive to most other common gases. However, it still remains a challenge to enhance their sensing performance and detection limit. Several techniques, such as surface functionalization, doping, and heterostructure formation, have been developed to enhance the sensing performance, detection limit and operation temperature of 1D nanostructure sensors. Among these techniques, the heterostructure formation method was used to enhance their sensing performance and detection limit further in this study. The β-Bi$_2$O$_3$-core/In$_2$O$_3$-shell nanorod sensors were fabricated and their NO$_2$ gas sensing properties were examined.

Experimental

The β-Bi$_2$O$_3$-core/In$_2$O$_3$-shell nanorods were synthesized using a two-step process: thermal evaporation of Bi powders in an oxidizing atmosphere and sputter-deposition of In$_2$O$_3$. First, Au-coated Si was used as a substrate for the synthesis of Bi$_2$O$_3$ nanostructures. Au was deposited on a (100) Si substrate by direct current (dc) magnetron sputtering. A quartz tube was mounted horizontally inside a tube furnace. 99.999% pure and bismuth (Bi) powders were placed on the lower holder at the center of the quartz tube. An Au-coated Si substrate was placed on the upper holder, approximately 5 mm apart from the source powders. The furnace was heated to 650 °C and maintained at that temperature for 1 h in a N$_2$/O$_2$ atmosphere with constant flow rates of oxygen (3 sccm) and N$_2$ (300 sccm). The total pressure was set to 1 Torr. Subsequently, the as-synthesized Bi$_2$O$_3$ nanorods were coated with an In$_2$O$_3$ thin film using a radio frequency (RF) magnetron sputtering technique. The target used in this study was sintered stoichiometric In$_2$O$_3$. The sputtering was conducted in an Ar atmosphere (flow rate: 20 sccm). The vacuum chamber was evacuated to $1.0 \times 10^{-6}$ Torr before introducing Ar. The substrate temperature, sputtering power, working pressure, and process time were 25 °C, 100 W, 2.0 × 10$^{-2}$ Torr, and 15 min, respectively.

The morphology of the products was examined by field emission scanning electron microscopy (FESEM, Hitachi S-4200). The microstructures and compositions of the nanorod samples were characterized further by transmission electron
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Results and Discussion

Figure 1 shows a SEM image of the β-Bi$_2$O$_3$-core/In$_2$O$_3$-shell 1D nanostructures synthesized in this study. The nanorods ranged from 100 to 300 nm in diameter and from a few tens to a few hundreds of micrometers in length (Figure 1). An enlarged SEM image of a typical 1D nanostructure showed that it had a rod-like morphology (Inset in Figure 1). The EDX spectrum (Figure 2(a)) confirms that the core-shell nanorod contained elemental Bi, In and O. The Au in the spectrum is due to the Au used as a catalyst for the VLS growth of the Bi nanorods. The Cu and C are due to the grid used for TEM sample preparation. On the other hand, figure 2(b) confirms that the core and shell of a core-shell nanorod consist of β-Bi$_2$O$_3$ and In$_2$O$_3$, respectively. The In detected in the central (core) region of the nanorod is due to the overlapping of the front and rear regions of the In$_2$O$_3$ shell with the Bi$_2$O$_3$ core from the viewpoint of the X-ray beam source used in the EDXS measurement.

Figure 3(a) shows a low-magnification TEM image of a typical as-synthesized core-shell nanorod, indicating that the thickness of the shell layer in the core-shell nanorod was approximately 8 nm. Figure 3(b) presents the local high-resolution TEM (HRTEM) image enlarging the core-shell interface area of the nanorod. The resolved spacings between the two neighboring parallel fringes in the core region corresponding to the tetragonal Bi$_2$O$_3$ (201) and (220) planes were approximately 0.32, and 0.27 nm, respectively. The corresponding selected area of the electron diffraction (SAED) pattern (Figure 3(c)), which was recorded perpendicular to the long axis, can be indexed for the [112] zone axis of Bi$_2$O$_3$. The strong reflection spots in the corresponding selected area electron diffraction (SAED) pattern (Figure 3(c)) were assigned to the (201), (220), and (421) reflections of tetragonal-structured β-Bi$_2$O$_3$ with lattice constants, indicating that the β-Bi$_2$O$_3$ nanorod in the TEM image is a
Figure 3. (a) Low-magnification TEM image of a typical β-Bi2O3-core/In2O3-shell nanorod. (b) Local HRTEM image of the nanostructure at the core-shell interface region. (c) SAED pattern of the [T12] zone axis of the nanomaterial at the same region shown in the HRTEM image.

Figure 4. Patterns of β-Bi2O3-core/In2O3-shell nanorods.

Figure 5(a) shows the dynamic responses of bare β-Bi2O3 nanorods and β-Bi2O3-core/In2O3-shell nanorods at 300 °C to a typical oxidizing gas NO2. The resistance increased upon exposure to NO2 and decreased even though it was not recovered completely to the initial value upon the removal of NO2. Figures 5(b) and 5(c), respectively, show the enlarged part of the data in Figure 5(a) measured at a NO2 concentration of 5 ppm for bare β-Bi2O3 nanorods (red line) and β-Bi2O3-core/In2O3-shell nanorods (black line) to reveal the moments of the gas input and gas stop. The bare β-Bi2O3 nanorods showed responses in a range of approximately 4-99% at the NO2 concentrations of 1-5 ppm (Table 1). In contrast, the β-Bi2O3-core/In2O3-shell nanorods showed responses in a range of approximately 12-156% at the NO2 concentrations of 1-5 ppm, respectively (Table 1). Therefore, the responses of the nanorods were improved by approximately 1.3-2.7 times at NO2 concentrations of 1-5 ppm through the encapsulation of β-Bi2O3 nanorods with In2O3. Figure 5(d) shows that both the bare β-Bi2O3 nanorod sensor and the β-Bi2O3-core/In2O3-shell nanorod sensor tend to increase in response as the concentration of the NO2 increases. This result agrees well with the general tendency that the response of a sensor increases with increasing the concentration of the target gas. The core-shell nanorods showed a higher increasing rate of the response with the NO2 concentration than the bare β-Bi2O3 nanorod sensor.

The NO2 gas sensing mechanism of the bare β-Bi2O3 nanorods can be depicted as follows: At this point, it is worthy of remembering that both β-Bi2O3 and In2O3 are n-type semiconductors. Upon exposure of the Bi2O3 nanorods to a strong oxidizing gas NO2, NO2 molecules are adsorbed by the Bi2O3 surface. The adsorption of NO2 on the surface of the β-Bi2O3 nanorods results in an increase in resistivity, which can be explained by the following reactions:24,25

\[
\text{NO}_2(g) + e^- \leftrightarrow \text{NO}_2^-(ads) \quad (1)
\]

\[
\text{NO}_2(g) + e^- \leftrightarrow \text{NO} (g) + \text{O}^-(ads) \quad (2)
\]

Both these reactions take electrons from the conduction band of β-Bi2O3, resulting in an increase in resistivity.

On the other hand, the substantial improvement of the...
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response of the β-Bi$_2$O$_3$ nanorods to NO$_2$ gas by encapsulating them with In$_2$O$_3$ can be explained by the space-charge model. NO$_2$ is a strong oxidizing gas. Upon exposure to NO$_2$ gas, the NO$_2$ gas is adsorbed by the core-shell nanorod sensor and electrons are released from the β-Bi$_2$O$_3$ shell layers, and attracted to the adsorbed NO$_2$ molecules because an oxidizing gas, such as NO$_2$ acts as an electron acceptor in the reaction. This reaction will result in an increase in the depletion layer width, and an increase in the resistance of the nanorod sensor. On the other hand, trapped electrons are released to the In$_2$O$_3$ shell layer by NO$_2$ gas after stopping the supply of NO$_2$ gas, leading to a decrease in the depletion layer width and resistance. The electron exchange between the surface states and the β-Bi$_2$O$_3$ shell layer occurs within the surface layer excluding the depletion layer. The width of the surface layer is the order of the Debye length $\lambda_D$ which can be expressed as follows:

$$\lambda_D = (\varepsilon k T/ q^2 n_c)^{1/2} \quad (3)$$

where $\varepsilon$ is the static dielectric constant ($= 9.11 \times 8.85 \times 10^{-12} \text{ F/m in In}_2\text{O}_3$), $k$ is the Boltzmann constant ($= 1.38 \times 10^{-23} \text{ joule/K}$), $T$ is the absolute temperature ($= 573 \text{ K}$), $q$ is the electrical charge of the carrier ($= 1.6 \times 10^{-19} \text{ coulomb}$), and $n_c$ is the carrier concentration ($= 1.0 \times 10^{17} \text{/cm}^3$; the value obtained by Hall measurement for the In$_2$O$_3$ thin film prepared on the Si (100) substrate by sputtering). For the In$_2$O$_3$ layer in the core-shell nanorods fabricated in this study, the $\lambda_D$ value for 300 °C was calculated to be approximately 15.8 nm. This means that NO$_2$ molecules not only deplete the electrons in the In$_2$O$_3$ shell layer, the width of which is as small as approximately 8 nm, but also further take electrons from the β-Bi$_2$O$_3$ core. Therefore, in the β-Bi$_2$O$_3$-core/In$_2$O$_3$-shell nanorods, the heterojunction barrier existing at the interface of the core and shell should also be considered because electron transport is modulated by the heterojunction. The conductivity $\sigma$ can be expressed as follows:

$$\sigma = \sigma_0 \exp(-\Phi_{e\text{ff}}/kT), \quad (4)$$

where $\sigma_0$ is a constant, $\Phi_{e\text{ff}}$ the effective energy barrier at

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**Table 1.** Relative responses measured at different NO$_2$ concentrations, for the bare β-Bi$_2$O$_3$ nanorod sensor and the β-Bi$_2$O$_3$-core/In$_2$O$_3$-shell nanorod sensor

<table>
<thead>
<tr>
<th>NO$_2$ Conc.</th>
<th>Response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppm</td>
<td>4.39</td>
</tr>
<tr>
<td>2 ppm</td>
<td>22.57</td>
</tr>
<tr>
<td>3 ppm</td>
<td>36.91</td>
</tr>
<tr>
<td>4 ppm</td>
<td>68.97</td>
</tr>
<tr>
<td>5 ppm</td>
<td>98.91</td>
</tr>
</tbody>
</table>
the heterojunction, \( k \) a Boltzmann constant, \( T \) the absolute temperature. Upon exposure to NO\(_2\) gas, \( \Phi_{\text{eff}} \) will increase because NO\(_2\) gas is adsorbed by the core-shell nanorod and electrons will be attracted to the adsorbed NO\(_2\) molecules. Consequently, the conductivity of the core-shell nanorod will decrease or the resistivity will increase. On the other hand, after stopping the NO\(_2\) gas supply, the electrons trapped by the adsorbed NO\(_2\) molecules will be released and then trapped not only by the In\(_2\)O\(_3\) shell layer but also by the \( \beta\)-Bi\(_2\)O\(_3\) core via the heterojunction. \( \Phi_{\text{eff}} \) will decrease because the trapped electrons will return to the conduction bands of \( \beta\)-Bi\(_2\)O\(_3\) and In\(_2\)O\(_3\). Consequently, the resistivity of the core-shell nanorod will will decrease. Therefore, electron transport is modulated by the heterojunction with an adjustable energy barrier height. In other words, the heterojunction acts as a lever in electron transfer by which the electron transfer is facilitated or restrained, resulting in enhanced sensing properties of the core-shell nanorod sensor.

**Conclusions**

\( \beta\)-Bi\(_2\)O\(_3\)-core/In\(_2\)O\(_3\)-shell nanorods were fabricated using a two-step process comprising thermal evaporation of Bi powders and sputter-deposition of In\(_2\)O\(_3\). The nanorods were 100-300 nm in diameter and a few tens to a few hundreds of micrometers in length. The Bi\(_2\)O\(_3\) core was found to be a tetragonal-structured single crystal and the In\(_2\)O\(_3\) shell was mainly amorphous but locally crystalline. Multiple networked \( \beta\)-Bi\(_2\)O\(_3\)-core/In\(_2\)O\(_3\)-shell nanorod sensors showed responses in a range of 12-156% at 1-5 ppm NO\(_2\) at 300 °C. These response values were 1.3-2.7 times larger than those of bare \( \beta\)-Bi\(_2\)O\(_3\) nanorod sensors at 1-5 ppm NO\(_2\). The enhancement in the response of the Bi\(_2\)O\(_3\) nanorods to NO\(_2\) gas by the encapsulation of them with In\(_2\)O\(_3\) can be accounted for based on the space-charge model. The \( \beta\)-Bi\(_2\)O\(_3\)-In\(_2\)O\(_3\) heterojunction acts as a lever in electron transfer by which electron transfer is facilitated or restrained, resulting in enhanced sensing properties of the core-shell nanorod sensor.

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**References**


