Morphology Controllable Synthesis of α-Fe₂O₃ 1D Nanostructures: Growth Mechanism and Nanodevice Based on Single Nanowire


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Single crystalline α-Fe₂O₃ nanoflakes and nanowires are controllably synthesized simply by heating iron foil at different temperatures. The growth mechanisms are proposed based on the electron microscopy results. Electrical transport studies reveal n-type semiconducting behavior of α-Fe₂O₃ nanowire. A new type of α-Fe₂O₃ gas sensor based on single α-Fe₂O₃ nanowire as sensing unit is developed. The gas sensing on electron transport through the nanowire is investigated. Moreover, the CO detection sensitivity can be modulated by the gate voltage. Our results indicate that α-Fe₂O₃ nanowire holds good potential for nanoscale sensing applications.

1. Introduction

Sensing of poisonous gas is very important for saving human lives and preserving industrial safety. In order to improve the integration, sensitivity, selectivity, and chemical and thermal stability of the poisonous gas detectors, intensive efforts have been afforded in developing gas sensors based on nanostructured materials, such as carbon nanotubes, metal oxide nanoparticles, and nanowires.

Several semiconducting oxides such as SnO₂, ZnO, α-Fe₂O₃, and In₂O₃ have been employed as gas sensors, by utilizing the change of the electrical conductivity of these materials upon exposing to target gases. α-Fe₂O₃, which is the most stable iron oxide under ambient conditions, exhibits a rhombohedral structure with indirect band gap of 2.1 eV. In recent years, various α-Fe₂O₃ nanostructures have been studied, including their shape-specific properties, synthesis methods, and potential applications on lithium ion battery electrodes, gas sensors, field effect transistor, catalysts, and field emission. α-Fe₂O₃ has long been used in gas sensing applications, for example detecting gases like H₂, ethanol, NO₂, CO, H₂S, and CH₃OH. Nanowires are considered as ideal building blocks for constructing nanosized devices due to their high surface to volume ratio and their special physical and chemical properties resulting from the reduced sizes. However, few studies focus on gas sensors based on a single α-Fe₂O₃ nanostructure.

In this paper, α-Fe₂O₃ nanostructures were prepared by heating Fe foil in a box oven. The morphologies of the products could be effectively controlled either as nanoflakes or nanowires by altering the growth temperature. The nanostructures obtained are n-type semiconductor. Nanodevices based on a single α-Fe₂O₃ nanowire such as field effect transistor and gas sensor were developed. The α-Fe₂O₃ nanowire based gas sensor has fast response and high sensitive to reductive gases in air at room temperature. This work is a continuation of our ongoing efforts toward the nanodevice of transition metal oxide nanostructures.

2. Experimental Section

2.1. Synthesis and Characterization. Fresh iron foils (10 × 10 × 0.1 mm) with a purity of 99.9% (Aldrich) were used as both reagents and substrates for the growth of α-Fe₂O₃ nanostructures. The cleaned Fe foil was heated in a box oven under ambient conditions. The growth temperature was varied between 300–800 °C, while the heating duration was fixed at 10 h.

The microstructures and morphology of α-Fe₂O₃ nanostructures were characterized by X-ray diffraction (XRD, D8 Advanced) and scanning electron microscopy (SEM, JEOL JSM-6700F). Transmission electron microscopy (TEM) was performed using a 200 kV JEOL 2010F field-emission-gun. A Raith electron-beam lithography system was used to fabricate the Au electrodes.

2.2. Fabrication and Measurement of Nanodevice. The as-grown α-Fe₂O₃ nanowires were dispersed on SiO₂/Si substrate. The thickness of the thermally grown SiO₂ layer was 200 nm. A photore sist layer of SU-8 was subsequently spun over the SiO₂/Si substrate. Two electrical contact fingers together with their bonding pads were exposed by electron-beam lithography. After the development, a 200-nm thick Au film was deposited over the structure and followed by a lift-off process.

Gas sensing properties of the samples were examined at room temperature. The testing gases were pure air and 50–400 ppm CO gas in air. The gas sensing response of the nanodevice was defined as the ratio of the electrical resistance in air (Rₐ) to that in testing gas (Rₐ). The sample resistance as a function of time was measured by using a Keithley 4200 SCS semiconductor characterization system.

3. Results and Discussion

A low-magnification SEM image (Figure 1) shows the α-Fe₂O₃ nanostructures on the Fe foil substrate. The α-Fe₂O₃
nanoflakes were obtained by annealing the Fe foil at 300–400 °C, whereas the R-Fe₂O₃ nanowires could be obtained when the heating temperature was raised to 750–800 °C. Clearly, the nanoflakes become broader with increasing reaction temperature, indicating the obvious heating temperature’s effect on the morphologies of the nanostructures. In general, the random aligned nanoflakes synthesized at the low temperature are about 5–20 nm in thickness, 5–10 nm at the tips, and 1–2 µm in length. The vertical aligned R-Fe₂O₃ nanowires fabricated at higher temperatures were about 10 µm in length, and about 100 nm in diameter. It is noted that neither nanoflakes nor nanowires are able to be synthesized when the heating temperature is within the range of 400–750 °C or above 800 °C (as shown in Figure 1, panels e and f). The proposed explanation could be found in the growth mechanism discussion below.

Figure 2 displays the XRD patterns of the samples. As can be seen, two phases of iron oxide, R-Fe₂O₃ and Fe₃O₄, are present in the low-temperature synthesized samples. However, when the growth temperature is raised to 750–800 °C, the samples show pure R-Fe₂O₃ phase (rhombohedral structure). Furthermore, the (110) peak at 35.2° is dominant, indicating that the α-Fe₂O₃ nanowires grow along the [110] direction; that is, the growth axis is along the c direction.¹⁰

Figure 3a shows the typical TEM image of α-Fe₂O₃ nanoflakes. As can be seen in the high resolution TEM (HRTEM) image (Figure 3b) of the region taken from Figure 3a, the fringe spacing of 0.25 nm concurs well with the interplanar spacing of the plane (110). The TEM image of an individual α-Fe₂O₃ nanowire is shown in Figure 3c. The selected area electron diffraction (SAED) pattern of the nanowire is shown as inset of panel c shows the SAED pattern.

Figure 4. SEM (a) and TEM (b) images of the catalyst of a single α-Fe₂O₃ nanowire. (c) A schematic diagram of the formation and growth of α-Fe₂O₃ nanowires.
minimize the surface energy. A schematic view of the formation of the α-Fe$_2$O$_3$ nanowire is shown in Figure 4c. First, the top layer of Fe foil was oxidized directly by the oxygen molecules in air and formed a very thin layer of α-Fe$_2$O$_3$ nanocrystals as catalysts. Then, α-Fe$_2$O$_3$ vapor was generated by oxidizing the Fe vapor molecular or directly vaporizing the thin top oxide layer. The relatively low pressure of Fe vapor molecular or directly vaporizing the thin top oxide layer of Fe foil was oxidized directly by the oxygen molecules in air and formed a very thin layer of Fe vapor in the reaction chamber ensure the growth of low dimensional, in this work wire-like nanostructures. Within the temperature range of 400–750 °C, instead of nanoflakes or nanowires, a relatively dense α-Fe$_2$O$_3$ film was formed on the top of the substrate Fe foil. This gap could be explained by the fact that the energy is high enough to facilitate surface diffusion in all directions and results in the formation of nanoparticles. However, the heating temperature is lower than the vapor point of Fe, and consequently, there are not enough sources for triggering the growth of nanowires. Likewise, when the temperature is above 800 °C, the worm-like structures are formed on the surface shown in Figure 1f, because the vapor pressure might be too high and causes the three-dimensional growth.

For future applications, we fabricated the nanodevices based on a single α-Fe$_2$O$_3$ nanowire. The schematic diagram of configuration and SEM image of a single α-Fe$_2$O$_3$ nanowire field effect transistor is shown in Figure 5, panels a and b. Figure 5c displays the $I_{ds}$–$V_{ds}$ curves of the nanodevice. From the $I_{ds}$–$V_{ds}$ curves obtained under gate voltages ($V_{gt}$) of −20, −10, 0, 20, and 40 V, it can be clearly seen that the conductance of the nanowire increases monotonically as the gate potential increases. The $nA$ current level reveals low conductivity of the nanowires. Figure 5d shows the $I_{ds}$–$V_{gt}$ curve of the nanowire field effect transistor. As known, the electron carrier concentration ($n$) and field effect mobility ($\mu$) in a typical cylindrical nanowire system with radius $r$ can be expressed as:

\begin{align}
  n &= \frac{V_{gt}^2}{e} \frac{2\pi\epsilon_0\epsilon_r}{\ln(2h/r)} \\
  \mu &= \frac{dI}{dV_{gt}} \frac{\ln(2h/r)}{2\pi\epsilon_0\epsilon_r} \frac{L}{V_{ds}}
\end{align}

where $V_{gt}$ is the threshold gate voltage, $e$ is the electron charge, $\epsilon_r$ ($\epsilon_r = 3.9$ for SiO$_2$) is the relative dielectric constant, $h$ is the thickness of gate oxide layer, and $L$ is the channel length.

Figure 6a is the corresponding $Slt$ (sensitivity vs time) curve of a single α-Fe$_2$O$_3$ nanowire gas sensor subjected to CO gas with various concentrations at room temperature, where $S$ is defined as the ratio of $R_A$ to $R_B$ as described in the experimental section. High CO sensitivity and short response time (less than 10 s) were obviously seen in this work. The α-Fe$_2$O$_3$ nanowire sensor has a good sensing performance as compared to other α-Fe$_2$O$_3$ nanostructures and film devices as well as metal-oxide bulk material CO sensors at room temperature shown in Table 1. The curve of sensitivities versus CO concentration is shown in Figure 6b where the sensitivity of the sample exhibits nonlinear behavior with CO concentration. The sensitivity increases with increase in the CO gas concentration. In fact, the sensitivity of the semiconducting metal oxide can usually be empirically represented as $S = S_0 + aP_g^\beta$, where $a$ is a constant, and $P_g$ is the target gas partial pressure that is directly proportional to its concentration. The sensitivity is characterized by the prefactor, $P_g$, and exponent, $\beta$. $\beta$ may have some rational fraction value (usually 1 or 2), depending on the charge of the surface species and the stoichiometry of.

Figure 5. (a) SEM image of a single α-Fe$_2$O$_3$ nanowire field effect transistor, (b) the schematic diagram of configuration of a single α-Fe$_2$O$_3$ nanowire field effect transistor, (c) $I_{ds}$–$V_{ds}$ curves of a single α-Fe$_2$O$_3$ nanowire field effect transistor, (d) $I_{ds}$–$V_{gt}$ curves of a single α-Fe$_2$O$_3$ nanowire field effect transistor.
the elementary reactions on the surface. In the case of single α-Fe₂O₃ nanowires device, β was found to be 1/2 with the CO concentration in the range 50–800 ppm. For comparison, a theoretical curve of the empirical model of the gas sensitivity is also shown in Figure 6b. It is found that our measured data show good agreement with the empirical model. Similar results, which are not shown here, have been reproduced for another ten gas nanosensors.

Figure 6c shows the dependence of the sensitivity on the gate voltage for 50 ppm CO. The maximum sensitivity of 3.8 appears at -10 V, which is just above the gate threshold voltages -20 V in 50 ppm CO. The gate dependence of CO detection sensitivity can be attributed to the gate modulation of the electron concentration in the nanowire channel.23 When the gate voltage is far above the threshold voltage, electron concentration in the nanowire channel is quite high and the CO molecules absorbed on the nanowire surface capture only a small portion of the available electrons. Therefore, the relative conductance change is very small. However, when the nanowire field effect transistor is gated just above the threshold, channel electrons are substantially depleted and the conductance change was caused by CO adsorption becomes much more significant. The above results are reproducible. This effectively demonstrates the advantage of α-Fe₂O₃ nanowire FET as a CO sensor, for example not only offering the large surface-to-volume ratio, but also the increased detection sensitivity at appropriate gate voltages.

We also measured the response of the sensor to other gases at concentration of 200 ppm, such as CO, H₂, ethanol, gasoline, NO₂, O₂, and H₂S under a bias voltage of 5 V. The sensitivity of α-Fe₂O₃ sensor to different gases is shown in Figure 6d. The sensor response to oxidation gas was low with respect to that obtained for reductive gas. The result also proves that the gas sensitivity mechanism is based on the modulation model of the depletion layer.21,31 The surface of the nanowire absorbs O₂ from air by trapping conductive electrons in α-Fe₂O₃, resulting in a decrease of electron concentration in nanowire and consequently an increase of resistance $R_a$. The more the absorbed O₂, the higher $R_a$. After exposing it to CO or other reductive gases, the trapped electron is released to α-Fe₂O₃, which causes the electron concentration of nanowire to increases and $R_g$ decreases.

4. Conclusion

In conclusion, α-Fe₂O₃ nanostructures with various morphologies were prepared by heating metal foil in a box oven at different temperatures. The growth mechanism of nanowires was proposed. The α-Fe₂O₃ nanowire is a typical n-type semiconductor. Single α-Fe₂O₃ nanowire-based field effect transistor and gas sensor have been fabricated. Furthermore, the gas sensor based on a single α-Fe₂O₃ nanowire has fast response and high sensitive to CO in air. This new type of gas nanosensor is expected to find wide applications in various complicated gas for quick detection of poisonous and inflammable gases.

References and Notes