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A simple fabrication method of randomly oriented polycrystalline zinc oxide nanowires and their application to gas sensing

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Abstract

Randomly oriented polycrystalline ZnO nanowires with a mean diameter of 100–150 nm have been successfully synthesized on SiO₂/Si substrates through the thermal oxidation of sputtered Zn nanowires in dry air at 400 °C. Structural characterization by x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that each ZnO nanowire consisted of a chain of ZnO nanocrystallites. From gas sensing measurements for CO, H₂ and NO gases, the polycrystalline ZnO nanowires showed a highly sensitive and fast response to both reducing and oxidizing gases in dry air at relatively low concentrations and operating temperatures, indicating potential applications of polycrystalline ZnO nanowires as sensing materials for gas sensors.

Keywords: zinc oxide, nanowires, gas sensors, sputtering

Classification number: 4.08

1. Introduction

Zinc oxide (ZnO) has been extensively investigated as a gas sensing material for the detection of many kinds of gases in air. The gas sensing mechanism of ZnO-based gas sensors is based on the phenomenon that the electrical conductivity of the ZnO material is governed by the composition and concentration of the gas atmosphere surrounding them. ZnO-based gas sensors have been fabricated in various forms of ZnO, including single crystals, pellets, thick films and conventional thin films [1–4]. With rapid development in thin film technology, ZnO and other semiconducting metal oxides, such as SnO₂, TiO₂, WO₃ and In₂O₃, have become the most promising in the field of solid-state gas sensors due to their advantageous features, such as small dimensions, low cost, low power consumption and high compatibility with microelectronic processing [5]. However, there are still some limitations, especially low sensitivity and high operating

temperature, in making commercial ZnO thin-film-based gas sensors [6, 7].

For traditional thin-film devices, due to the limited surface-to-volume ratio, only a small fraction of the gas species adsorbed onto the exposed surface is active in modifying the electrical conductivity, leading to a low maximum sensitivity. Many efforts have been made to overcome the limitations of the ZnO thin-film-based gas sensors, especially in enhancing the sensitivity from the fact that the demand of highly sensitive gas sensors has increased because some toxic gases in air may affect human life and health even at very low concentrations. For that matter, the addition of noble catalytic elements, such as gold (Au) and palladium (Pd), has been found to clearly enhance this sensitivity [8, 9]. On the other hand, recent advances in the synthesis of nanostructures with controllable size, shape, etc, provide a great opportunity for improving gas sensing properties. Among them, one-dimensional (1D) ZnO



nanostructures, such as nanorods, nanobelts and nanowires, have attracted much attention due to their great potential in gas sensing applications, not least owing to their high surface-to-volume ratio and small grain size [10].

Various synthesis techniques of ZnO nanostructures, such as thermal evaporation, hydrothermal, sputtering, pulsed laser deposition and molecular beam epitaxy have been reported. Notably, there has been an attempt at large scale preparation of shape-controlled ZnO nanostructures using a simple two-step method [11, 12], providing a great opportunity for ZnO-based gas sensor development. In the present work, we report the growth of randomly oriented polycrystalline ZnO nanowires using the simple two-step method combined with sputtering and subsequent thermal oxidation at low temperatures, as well as their gas sensing behaviors for various target gases, such as H₂, CO and NO in dry air. The observed good sensing properties together with a simple fabrication process imply that the polycrystalline ZnO nanowires are very promising for low-cost and high-performance gas sensors.

2. Experimental

2.1. Fabrication of ZnO nanowires and gas sensing elements

Polycrystalline ZnO nanowires were prepared by thermal oxidation of sputtered Zn nanowires in dry air, following the reported procedure [12]. The substrate temperature was set ranging from 100 to 200 °C. Because pure ZnO nanowire thin films normally have high initial resistance values, which are not suitable for sensing oxidizing gases (e.g. NO), we also attempted to grow metallic Zn nanowires containing a small amount of Al (~2%) from two separate Zn and Al metal targets by a rf cosputtering method, with the rf power densities being maintained at 2 and 1 W cm⁻² for the Zn and Al targets, respectively, at the deposition temperature of 200 °C. Thermal oxidation of the as-deposited Zn nanowire thin films was processed in dry air at 400 °C for 5 h to obtain randomly oriented polycrystalline ZnO nanowires. The ZnO samples grown at different substrate temperatures of 100, 150 and 200 °C are named ZnO-100, ZnO-150, and ZnO-200, respectively.

To investigate the gas sensing properties of the synthesized polycrystalline ZnO nanowires, we fabricated ZnO-nanowire-based gas sensing elements, following the reported procedure [12]. For the electrical measurements, 50 μm diameter Au wires were attached to the electrode pads with silver paste. The formation of an Ohmic contact between the ZnO-based active layer and electrodes was confirmed by observing the linear current–voltage (*I*–*V*) characteristic of the sensing elements before measuring the gas sensing properties.

2.2. Characterization methods and gas sensing measurements

The crystalline structure of the fabricated films was characterized by x-ray diffraction (XRD) using CuK_α radiation, revealing the formation of the hexagonal wurtzite phase of ZnO after the thermal oxidation process. The microstructures and compositions of the films were examined by transmission electron microscopy (TEM) and scanning

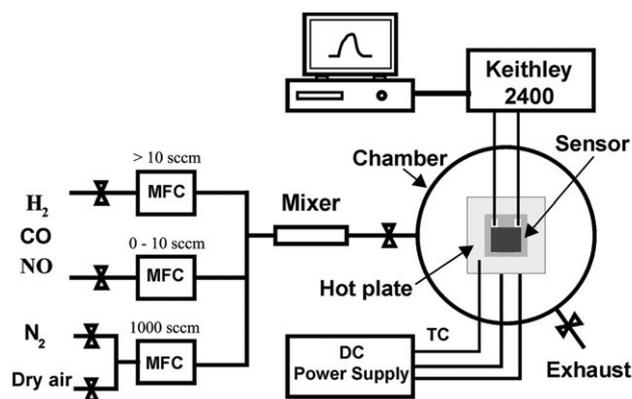


Figure 1. Schematic diagram of a computer-controlled gas sensing characterization system.

electron microscopy (SEM), equipped with an energy dispersive x-ray spectroscopy (EDX) detector. SEM analysis was also used for much closer investigation of the growth mechanism of the ZnO nanowires.

The electrical and gas sensing properties of the fabricated ZnO-nanowire-based gas sensors were measured via two conductive electrodes using a multi-meter (Keithley 2400) assembled in a computer-controlled gas sensing characterization system as schematically shown in figure 1 [13]. The gas sensing properties of the fabricated sensor elements were measured for various gases in dry air at different measurement conditions using a flow-through method. The target gases H₂, CO and NO at initial concentrations of 10 000, 1000 and 100 ppm with nitrogen balance, respectively, were further diluted in dry air (flow rate of 500 ml min⁻¹) by adjusting the flow rate of the target gases from 0 to several 10 ml min⁻¹ using separate mass flow controllers. The detailed measurement parameters can be found elsewhere [11–13]. The sensor response S_g is defined as follows: $S_g = \Delta G/G_a = (G_g - G_a)/G_a$ for a reducing gas, whereas $S_g = \Delta R/R_a = (R_g - R_a)/R_a$ for an oxidizing gas, where G_a and G_g (or R_a and R_g) are the electrical conductance (or electrical resistance) in dry air and upon exposure to the target gas in dry air, respectively.

3. Results and discussion

3.1. Structural and morphological properties

Figure 2 shows SEM images of the Zn products deposited on SiO₂/Si substrates at 200 °C for various deposition times of 1, 3, 5 and 10 min. It is noteworthy that no Zn nanowires were observed for the 1 min sample, but Zn grains with a mean diameter of about 50 nm were formed on the SiO₂/Si substrate, as seen in figure 2(a). These tiny grains are revealed to act as seeds for further nanowire growth. When the deposition time increases, the subsequent growth leads to the formation of nanowires, as observed in figures 2(b)–(d). From figure 2(d), the mean wire dimension was estimated to be about 50 nm in diameter and several microns in length.

It should be noted here that the growth of Zn nanowires occurs during the sputtering process without a catalyst. The growth of the nanowires is thus thought to be governed by a ‘self-catalytic’ vapor–solid (VS) growth mechanism, in

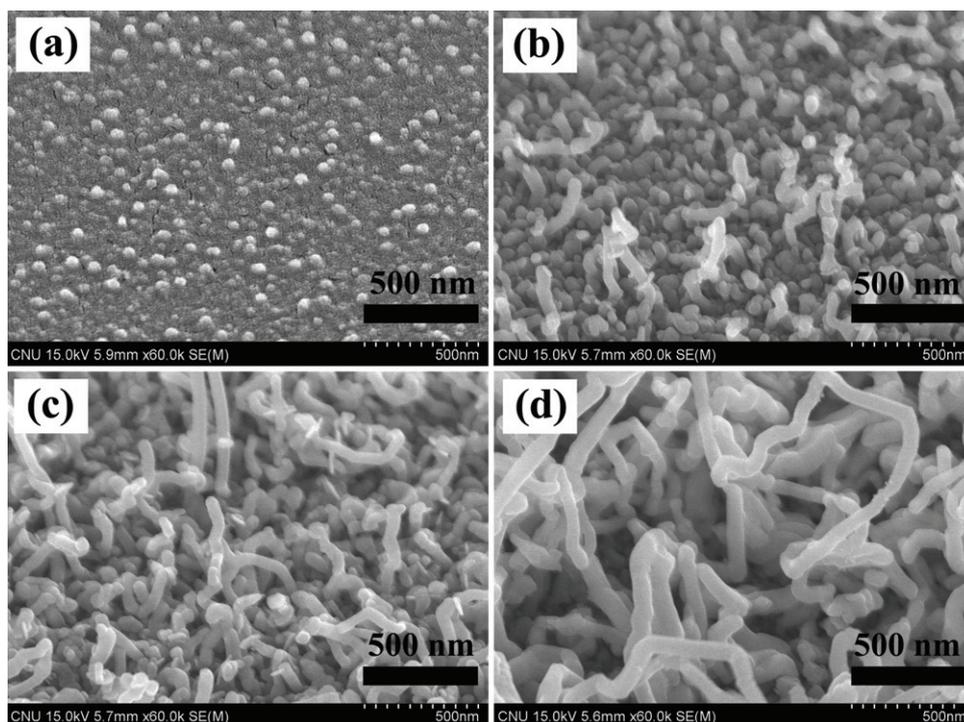


Figure 2. SEM images of Zn products obtained at a deposition temperature of 200 °C for various deposition times of (a) 1 min, (b) 3 min, (c) 5 min and (d) 10 min.

which Zn vapors generated by sputtering are transported and condensed onto a hot substrate to first form Zn grains, in turn acting as nucleation seeds for the subsequent growth of Zn nanowires. Because the substrate temperatures were kept far below the melting point of Zn (419.5 °C), a liquid state of Zn was not formed. As the Zn vapor becomes saturated, the vapor of Zn condenses onto the substrate, first forming nanosized Zn clusters or grains. These Zn nuclei individually grow further in the upper direction in the form of nanowires, as can be seen in figures 2(a)–(c). The Zn nanowires were found to be not single crystalline but polycrystalline. Normally, the predominant growth morphology of Zn nanostructures depends on the degree of supersaturation of the Zn vapor and the diameter of the Zn nanowires depends on the size of the initial Zn nuclei. We confirm from SEM observations that the Zn nanowire diameter is almost the same as the initial Zn grain diameter. Moreover, when the substrate temperature increases, the rf power applied to the Zn target should be reduced so that 2D film growth can be prevented. The change in growth morphology may originate from the change in the supersaturation of the Zn vapor with different growth temperatures, as reported in our previous work [11]. The point is that Zn nanowires can be obtained only when the deposition temperature is no less than 100 °C. When the deposition temperature increases, the length of the nanowires also increases.

Now polycrystalline ZnO wire-like thin films can be obtained simply by oxidizing the metallic films at suitable temperatures because the structural and morphological properties of an oxidized film may be inherited from the original structure of its precursor metallic film. Figures 3(a) and (b) show the low-magnification SEM image for the as-grown Zn nanowire and ZnO wire-like thin films, respectively, prepared by oxidizing the Zn nanowire film in

dry air at a temperature of 400 °C for 5 h. The crystalline structure of the films characterized by XRD revealed that the metallic Zn was completely transformed into ZnO (hexagonal wurtzite phase) even at a low annealing temperature of 400 °C [14]. As can be seen from figures 3(a) and (b), a large scale of uniform, polycrystalline Zn nanowires has been produced, as expected. The wire dimension estimated from SEM images was about 100–150 nm in diameter and several microns in length.

The change in surface morphology of the wire structure during the transformation of Zn nanowires into ZnO nanowires was studied by TEM. Figures 3(c) and (d) show the TEM images of the as-grown Zn nanowire and ZnO nanowire after oxidation at 400 °C for 5 h, respectively. Obviously, the surface of the Zn wires is quite smooth, whereas the surface of the ZnO wires is severely roughened, but the wire structure is still preserved. As can be seen from figure 3(d), a ZnO wire actually consists of a chain of many small grains, giving a relatively higher active surface area in comparison with a single-crystalline nanowire having the same average dimensions.

3.2. Response to H₂

The typical dynamic responses of the ZnO-150 nanowire gas sensors to H₂ in dry air at various H₂ gas concentrations measured at 200 °C are shown in figure 4(a). The sensor resistance decreases on exposure to H₂, revealing *n*-type semiconducting behavior of the ZnO-150 nanowire gas sensors. It is well known that for the semiconducting metal-oxide-based gas sensors, the electron trapping-releasing process from the sensing layers is responsible for the gas sensing mechanism. In the case of H₂ gas, the H₂ gas reacts with the oxygen species adsorbed on the active layer surface

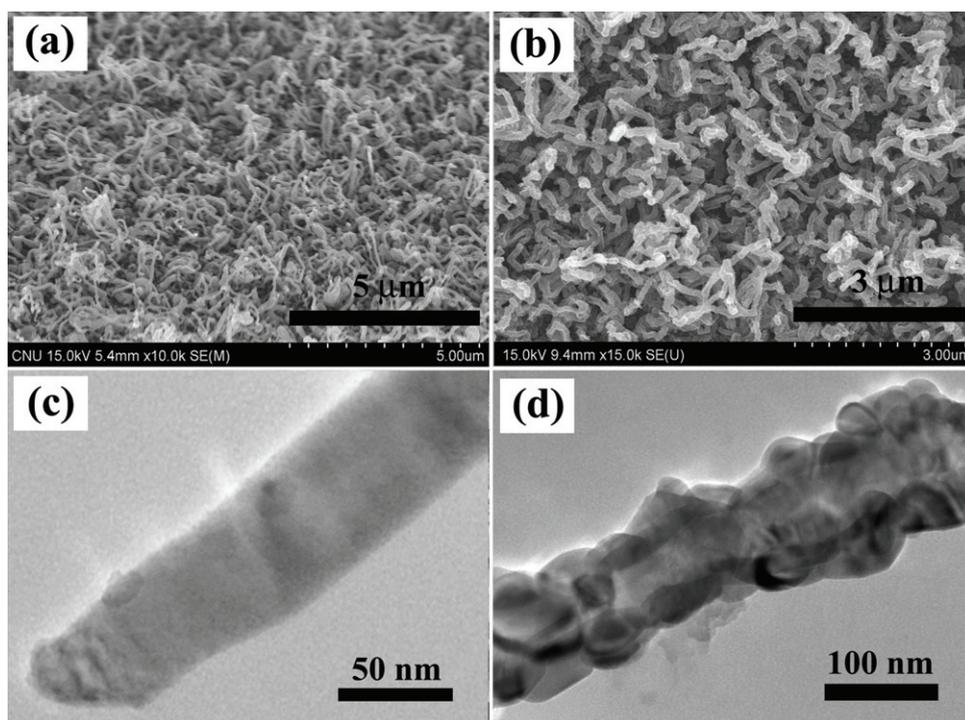


Figure 3. SEM and TEM images. SEM images of (a) Zn nanowires and (b) polycrystalline ZnO nanowires obtained by oxidizing the Zn nanowires in dry air at 400 °C for 5 h. TEM images of (c) an individual Zn nanowire and (d) an individual ZnO nanowire.

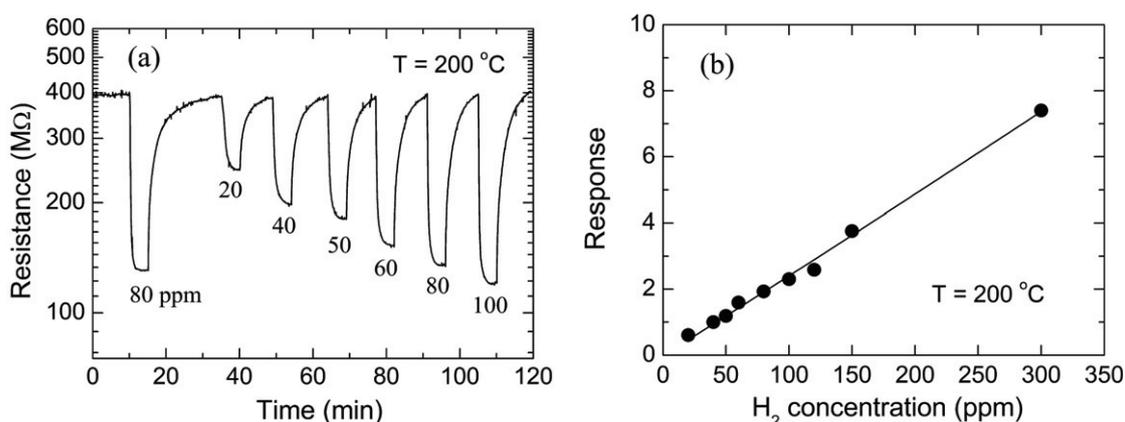


Figure 4. (a) Resistance response curves of the ZnO-150 nanowire gas sensor for various H₂ gas concentrations in dry air at an operating temperature of 200 °C. (b) Variation in the response as a function of H₂ gas concentration for the ZnO-150 nanowire gas sensor operated at 200 °C.

of the sensors and releases electrons back from the trapped states to the conduction band of ZnO, leading to an increase in electron density in the ZnO-based active layer and a decrease in sensor resistance, as observed [12]. The response time t_r , as conventionally defined [13], was found to be from 0.6 to 2.1 min, depending on the H₂ gas concentration in dry air measured at 200 °C.

In figure 4(b), we present the response of the ZnO-150 nanowire gas sensor varying as a function of the H₂ gas concentration in dry air at 200 °C. A linear increase in the sensor response with increasing gas concentration is clearly seen. The response sensitivity was found to be 7.4 at 300 ppm H₂, which is roughly two times higher than that of the ZnO-100 sample (3.55 at 300 ppm H₂) [12].

3.3. Response to CO

Figure 5(a) shows the resistance response curves of a ZnO-100 nanowire gas sensor for a CO gas concentration of 20 ppm in dry air at various operating temperatures of 250, 300, 350 and 400 °C. The CO sensing mechanism is discussed in [13]. The response calculations for the ZnO-100 nanowire gas sensor at different operating temperatures reveal that no significant difference in response in the temperature range of 200–350 °C is observed. This indicates that the optimal operating temperature of the ZnO-100 nanowire gas sensor for CO sensing is still high and unclearly identified although the response is reproducible and stable.

Figure 5(b) shows the variation in the response as a function of CO gas concentration for the ZnO-150 nanowire

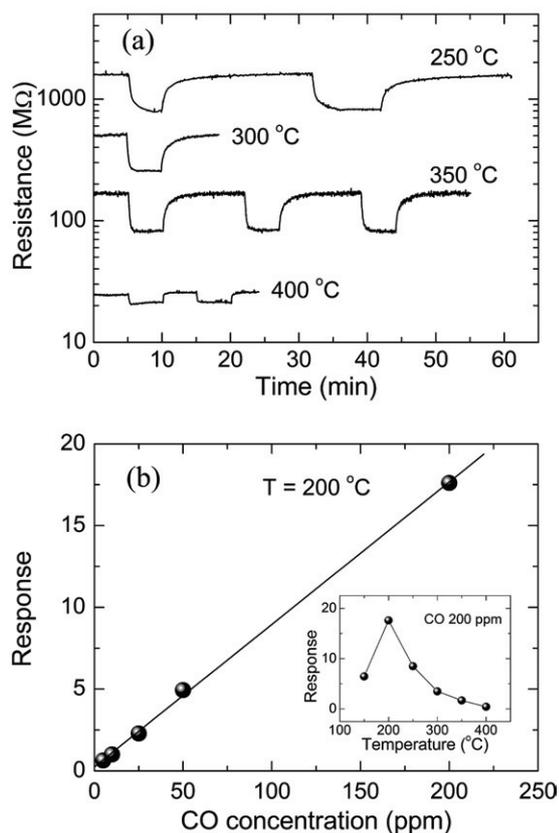


Figure 5. (a) Resistance response curves of the ZnO-100 nanowire gas sensor upon exposure to 20 ppm CO in dry air at several operating temperatures. (b) Response versus gas concentration of the ZnO-150 nanowire gas sensor measured at an operating temperature of 200 °C. The inset shows the response as a function of operating temperature, showing the maximum response at 200 °C.

gas sensor operated at 200 °C. The optimal operating temperature was found to be 200 °C as clearly seen in the inset of figure 5(b). At 200 °C, the maximum response of the ZnO-150 nanowire gas sensor is 17.6 for 200 ppm CO in dry air, which is higher than that of the ZnO-100 nanowire gas sensor. This maximum response is comparable with the nano-crystalline Cu-doped ZnO thin film gas sensor operated at 350 °C [4] and roughly several times higher than those of other forms of ZnO-based gas sensors operated at 250–300 °C [15–17]. These results indicate that the ZnO-150 nanowire gas sensor has a high sensitivity to CO gas at a relatively low temperature. Furthermore, it should be noted here that the ZnO-150 nanowire gas sensor can detect the CO gas in a wide concentration range from several ppm to several hundred ppm in dry air, and the sensor response increases linearly with CO concentration in the measurement range.

In general, the ZnO-100 and ZnO-150 nanowire gas sensors are poorly selective because they can detect many kinds of reducing gases in dry air. Indeed, beside H₂ and CO, the ZnO-150 nanowire gas sensors are also sensitive to other reducing gases, e.g. NH₃, as reported in previous work [11]. In fact, a better gas selectivity could be obtained at different operating temperature ranges, since any gas sensing effect has its own temperature dependence and the sensor sensitivity shows its maxima at different temperatures for different gases. However, by comparing the maximum response of the ZnO

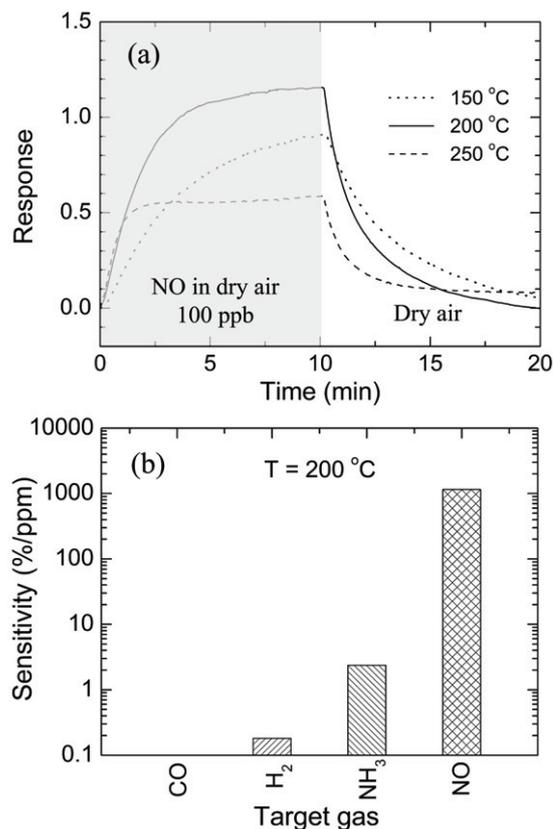


Figure 6. (a) Response of the ZnO-200 nanowire gas sensor to NO gas in dry air at various operating temperatures. (b) The sensitivity of the ZnO-200 nanowire gas sensor to different gases in dry air measured at the optimal operating temperature of 200 °C.

nanowire gas sensors to different gases, i.e. H₂, CO and NH₃, we found that they had almost the same optimal operating temperature, resulting in poor gas selectivity.

3.4. Response to NO

Figure 6(a) shows the typical response curves of the ZnO-200 nanowire gas sensor upon exposure to 100 ppb NO in dry air at various operating temperatures of 150, 200 and 250 °C. Unlike the cases of reducing gases, such as H₂ and CO, the resistance of the sensor increases when it is exposed to NO, revealing the oxidation behavior of NO. It is clear from figure 6(a) that the response characteristics of the sensor depend on the operating temperature. It is worth noting that the detection limit of the sensor for NO can be down to ppb level at the optimal operating temperature of 200 °C. The ZnO-200 nanowire gas sensor also shows both higher sensitivity and faster response to NO in dry air at 200 °C than ZnO nanorods ($t_r > 10$ min for 500 ppb NO) [18] operated at 300 °C.

In figure 6(b), we present the sensitivity, defined as response (in %) normalized to a gas concentration of 1 ppm, of the ZnO-200 nanowire gas sensor for the detection of common different gases including CO (50 ppm), H₂ (500 ppm), NH₃ (50 ppm) and NO (100 ppb). As clearly seen from figure 6(b), the ZnO-200 nanowire gas sensor exhibits excellent selectivity for NO over other test gases, even at a very low concentration in dry air.

Comparing the responses of these three ZnO-nanowire-based gas sensors to H₂, CO and NO at 200 °C, we realize that the Zn-150 nanowire gas sensor is suitable for sensing reducing gases, including H₂, CO and NH₃, but not suitable for the detection of oxidizing gases, e.g. NO, due to its high initial resistance. In contrast, the ZnO-200 nanowire gas sensor with a small amount of Al was almost not sensitive to CO in dry air at 50 ppm, and less sensitive to H₂ and NH₃ than the ZnO-150 nanowire sensors. At a working temperature of 200 °C, the resistance of the ZnO nanowire gas sensors is found to decrease with increasing deposition temperature (e.g. the resistance of the ZnO-100 and ZnO-150 were 2.5 GΩ and 400 MΩ, respectively). In addition, the initial resistance of the ZnO-200 nanowire gas sensor at 200 °C was about 2 MΩ, being far lower than the pure samples and therefore becoming suitable for the detection oxidizing gases in air, e.g. NO. The observed high sensitivity and fast response of the ZnO-200 nanowire gas sensor to NO indicates that the ZnO-200 nanowires are a highly sensitive material for sensing NO in dry air.

4. Conclusion

In summary, we have developed a simple technique for the growth of randomly oriented polycrystalline ZnO nanowires via thermal oxidation of sputtered Zn nanowires in dry air. The as-synthesized Zn nanowires were completely transformed into polycrystalline ZnO nanowires at an oxidation temperature as low as 400 °C. The surface of ZnO nanowires was profoundly roughened while the wire structure was still preserved in comparison with its precursor metal nanowires. The gas sensors fabricated from ZnO nanowires exhibited excellent gas sensing properties for H₂, CO, NH₃ and NO, such as high sensitivity and low operating temperature. The ZnO nanowires actually consisted of a chain of many small grains, giving a relatively higher active surface area in comparison with single-crystalline nanowires of the same average dimensions, thus causing enhancement in the gas sensitivity. Randomly oriented polycrystalline ZnO nanowires have promising advantages for the large-scale fabrication of low-cost and high-performance gas sensors.

Acknowledgments

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