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O_2 and CO sensing of Ga_2O_3 multiple nanowire gas sensors

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Abstract

Gallium oxide nanowires were synthesized by a chemical thermal evaporation method using gallium metal as a source material. X-ray diffraction, scanning electron microscopy, and transmission electron microscopy characterizations indicate that the obtained nanowires are well-crystallized single phase monoclinic Ga_2O_3. Multiple nanowire gas sensors were fabricated by dispensing the Ga_2O_3 nanowires on an interdigitated Pt-electrode. The Ga_2O_3 nanowire gas sensors show reversible response to O_2 and CO gases in a working temperature range of 100–500 °C. A peak response is found at 300 °C for O_2 gas and the peak response appears at 200 °C for CO gas. For both kinds of gases, the sensor response increases empirically with an increase of gas concentration. The results demonstrate the possibility of using the Ga_2O_3-based gas sensor at low working temperature field.

Keywords: Gallium oxide; Nanowires; Gas sensor; O_2; CO

1. Introduction

Monoclinic gallium oxide (Ga_2O_3) is a versatile wide band gap semiconductor material. Pure or doped Ga_2O_3 has wide applications in transparent conducting electrodes [1], phosphors [2], gas sensors [3–6], dielectric gates [7], etc. Ga_2O_3 thin film-based gas sensors are very promising to detect oxygen at high temperature of 600–1000 °C [8,9]. It can also be used to detect reducing gases such as H_2, CO, CH_4, etc. [10,11] at high temperature. These characters are benefited from its high structure stability and thermally activated electronic conductivity. At elevated temperature, the conductivity of Ga_2O_3 can be influenced by an ambient atmosphere. But at low temperature, the oxygen-vacancies diffusion is frozen and the bulk electrical conductivity no longer responds to the change of circumstance gas composition [10,12]. The high working temperature limits the application of Ga_2O_3-based gas sensors.

One-dimensional (1D) nanomaterials are considered as ideal candidates for gas sensing applications due to their large surface area-to-volume ratio and the size effect [13]. The 1D nanostructures of well-established gas sensing materials such as SnO_2 [14,15], ZnO [16], WO_3 [17,18], and In_2O_3 [19] have shown higher sensitivity, faster response, and/or enhanced capability to detect low concentration gases compared with the corresponding thin film materials. Furthermore, gas sensors made from 1D nanomaterials showed lower optimal operating temperature, which is favorable for power saving and device integration. Ga_2O_3 1D nanomaterials have been studied widely in recent years [20–22]. However, few works focus on their gas sensing properties.

Herein, we report the synthesis, microstructure, and the gas sensing of Ga_2O_3 nanowires. The gas sensing measurements show that the Ga_2O_3 multiple nanowire gas sensor has reversible response to O_2 and CO gases in a low temperature range of 100–500 °C. The results demonstrate the possibility to develop Ga_2O_3-based low power consumption gas sensors and to extend their application.

2. Experimental

The Ga_2O_3 nanowires were synthesized by a reactive thermal evaporation method. In detail, 0.5 g gallium metal (99.999%)

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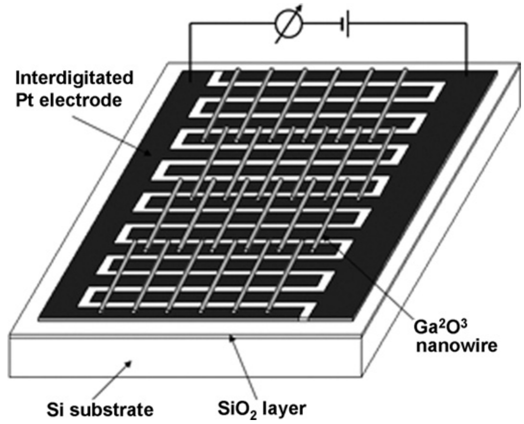

Fig. 1. A schematic diagram of the Ga_2O_3 multiple nanowire gas sensor.

was put on an alumina substrate in an alumina boat. Then the alumina boat was heated in a tube furnace at 900 °C for 1 h in an Ar flow of 100 ml/min at ambient pressure. A layer of white product was obtained on the alumina substrate around the gallium metal after cooling down the system to room temperature naturally. The structural characterizations were performed using an X-ray diffractometer (XRD) (Shimadzu XRD-6100), a field emission scanning electron microscope (FESEM) (JEOL JSM-6700F), and a transmission electron microscope (TEM) (Shimadzu SPM-9500J). The photoluminescence spectrum was measured on a Perkin-Elmer LS-55 luminescence spectrometer with a Xenon discharge lamp light source.

In order to make gas sensors, the nanowires were collected and dispersed in methanol with the assistance of ultrasonic. Gas sensors were fabricated by dispensing the Ga_2O_3 nanowire suspension onto oxidized Si substrates with interdigitated Pt electrodes as described in Ref. [23]. The diagram of the Ga_2O_3 nanowire gas sensor is shown in Fig. 1. The gas sensing properties were measured in a tube furnace with a resistance heater. A carrier gas mixed with a desired concentration of a target gas was flowed at 200 ml/min through the quartz tube kept at the setting temperature. Highly pure dry nitrogen (99.99%) was used as the carrier gas for detecting O_2 and dry synthetic air was used for detecting CO and other reductive gases. The electrical measurement was done by a voltamperometric method at a constant bias of 10 V, and a multimeter (Agilent 34970A) was used to monitor the change of electrical resistance upon turning the target gases on and off.

3. Results and discussion

Fig. 2(a) shows a typical FESEM image of the obtained nanowires. The nanowires are about 50–150 nm in diameter and tens of micrometers in length. The XRD pattern represented in Fig. 2(b) matches well with the standard pattern of monoclinic Ga_2O_3 (β-Ga_2O_3) from JCPDS card No. 43-1012. A TEM image of the nanowires is illustrated in Fig. 2(c). The selected area electron pattern (SAED) inset in Fig. 2(c) also confirms that the nanowires have the well-crystallized monoclinic structure of Ga_2O_3.

In our investigation, the Ga_2O_3 nanowires were synthesized in an Ar flow, which provided a lean oxygen environment. The Ga_2O_3 nanowires obtained under such a condition contain a high concentration of oxygen vacancies. This is confirmed by using photoluminescence (PL) measurement. As shown in Fig. 2(d), the PL spectrum of the obtained Ga_2O_3 nanowires shows a

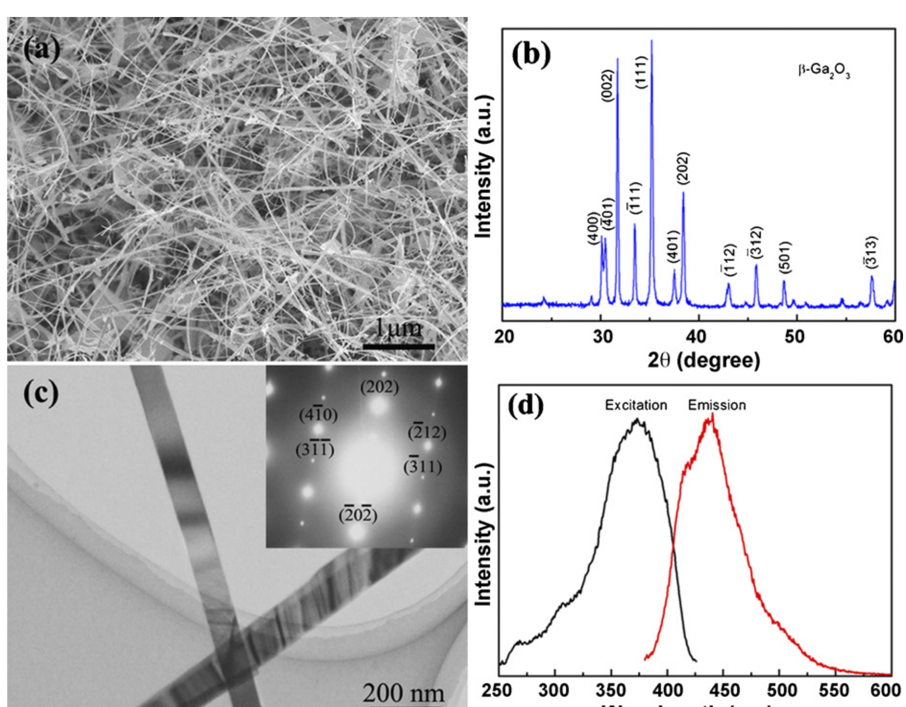

Fig. 2. (a) SEM image, (b) XRD pattern, (c) TEM image, and (d) photoluminescence spectrum of Ga_2O_3 nanowires. Inset in (c) is the SAED pattern.

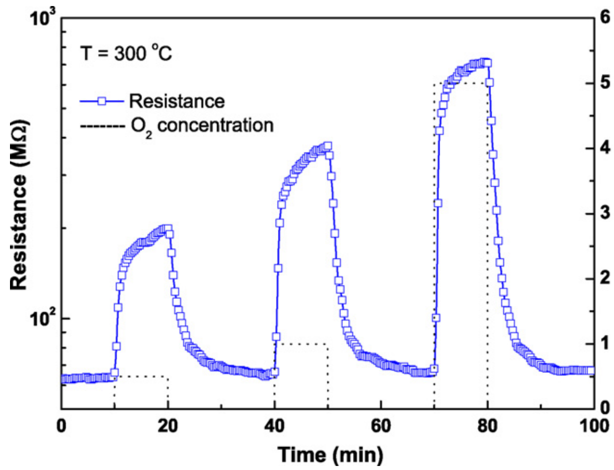

Fig. 3. Dynamic response of the Ga_2O_3 nanowire sensor to O_2 gas pulse at 300 °C.

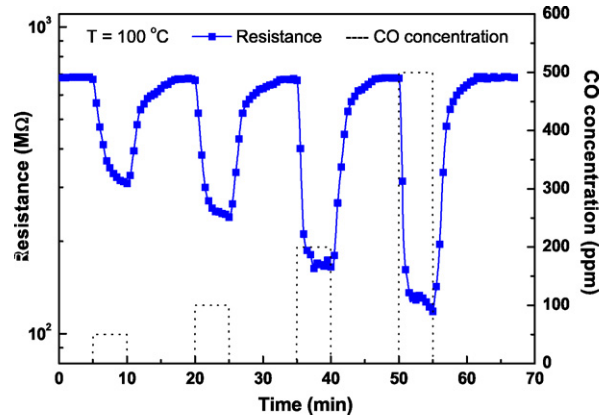

Fig. 4. Dynamic response of the Ga_2O_3 nanowire sensor to CO gas pulse at 100 °C.

broad strong PL peak centered at about 440 nm. According to previous study [24], the broad blue luminescence at about 400–500 nm is attributed to the electron transition mediated by oxygen vacancies in the band gap. These oxygen vacancies contribute to the n-type electrical conduction of the Ga_2O_3 nanowires.

The gas sensing of the Ga_2O_3 nanowire sensors was evaluated upon exposure to O_2 and CO gases. The sensors show obvious responses to the target gases at temperatures much lower than the reported working temperature of the Ga_2O_3 film sensors. Fig. 3 shows the dynamic responses of the Ga_2O_3 nanowire gas sensor towards 0.5%, 1%, and 5% O_2 gas operated at 300 °C. One can see that the resistance increases upon exposure to oxygen and the resistance changes of 2.1, 4.7, and 10.0 times with respect to the baseline are observed towards 0.5%, 1%, and 5% oxygen, respectively. Fig. 4 represents dynamic gas responses of the Ga_2O_3 nanowire gas sensor to CO pulses with concentrations of 50, 100, 200, 500 ppm at 100 °C. The resistance decreases reversibly upon each CO pulse.

We define the sensor response as $S = |\Delta R|/R_o$, where ΔR is the resistance change caused by gas exposure. R_o designates to the baseline resistance in nitrogen for O_2 and the equilibrium resistance in detected gas for CO. The response as a function of gas concentration is plotted in Fig. 5. For both kinds of gases, the response value increases with the rising of gas concentration. In fact, the response of the Ga_2O_3 nanowire gas sensor increases empirically and can be represented as $S = aC^b$, where C is the target gas concentration. a and b are constants for a given gas. The experimental data and the theoretical curves from the empirical model are shown in Fig. 5(a) and (b). For O_2 gas, the a and b values can be fitted to $a = 3.989 \pm 0.330$ and $b = 0.571 \pm 0.061$. For CO gas, the values are $a = 0.156 \pm 0.028$ and $b = 0.555 \pm 0.031$. These results are very near to the expression of Ga_2O_3 films developed in Ref. [10] based on a chemisorption model, which suggested that the surface chemisorptions dominated the elec-

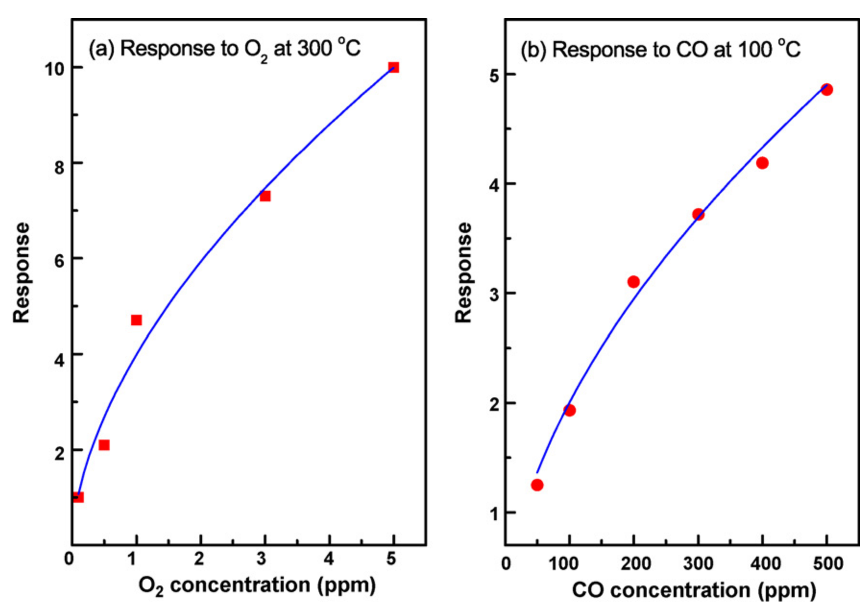

Fig. 5. Concentration dependence of the response to (a) O_2 and (b) CO. The solid lines are the theoretical curves of the empirical model.

trical properties of Ga_2O_3 material at temperatures lower than the thermal activation temperature.

In our experiments, the operating temperatures are much lower than the reported thermal activation temperature. Although the nanowires contain a large amount of oxygen vacancies, the oxygen species in gas phase cannot go into Ga_2O_3 nanowires to fill the vacancies at a temperature lower than the thermal activation temperature [10]. So it is most likely that the surface adsorption/desorption dominates the response of the Ga_2O_3 nanowires towards target gases. The adsorption of O_2 molecules, which tend to trap electrons, will lead to an increase in resistance. In contrast, the adsorption of CO molecules on the surface of Ga_2O_3 nanowires will donate electrons and lead to a reduction of resistance. The large surface area-to-volume ratio of the Ga_2O_3 nanowires contributes to the high response to target gases.

The temperature dependence of the gas sensing performance was investigated in the 100–500 °C range. Fig. 6 shows the response of the Ga_2O_3 nanowire gas sensor towards 1% O_2 and 200 ppm CO at different temperatures. For both kinds of gases, the histogram goes through a peak. The highest response value of 4.75 is obtained when the sensor is exposed to 1% O_2 at 300 °C and the peak response appears at 200 °C for CO with a value of 3.95. The decrease of response may be because that adsorption/desorption balance shifts to the desorption side at higher temperature. It is important to note that the working temperature of our Ga_2O_3 nanowire gas sensor is much lower than the reported sensitive temperature of Ga_2O_3 film sensors, which are normally operated at high temperatures of 600–1000 °C. This casts light on extending the application of Ga_2O_3-based gas sensors to the low working temperature area.

The gas sensing of the Ga_2O_3 nanowire gas sensor towards the reductive gases of H_2, NH_3, and H_2S was also investigated. Fig. 7 represents the sensor response to 200 ppm H_2, 400 ppm NH_3, and 200 ppm H_2S gases at 200 °C. For comparison, the response to 200 ppm CO is also presented. The sensor shows reversible responses to these gases. However, the sensor responses to H_2, NH_3, and H_2S are much lower than that to CO. In other words, the Ga_2O_3 nanowire gas sensor responds selectively to CO gas.

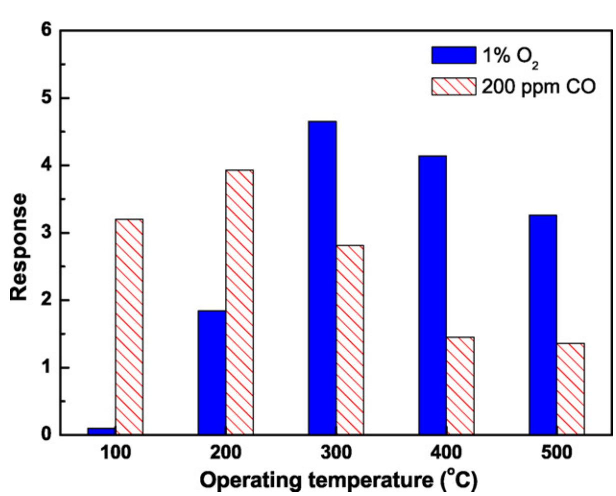

Fig. 6. Temperature dependence of the response of the Ga_2O_3 nanowire sensor to O_2 and CO gases.

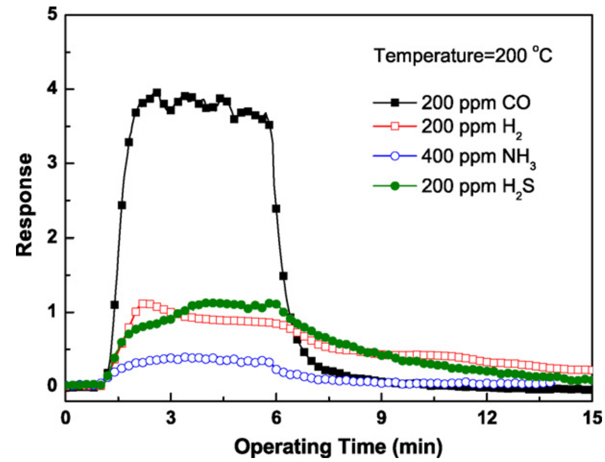

Fig. 7. Responses of the Ga_2O_3 nanowire sensor when exposed to 200 ppm CO, 200 ppm H_2, 400 ppm NH_3, and 200 ppm H_2S at 200 °C.

4. Conclusion

In summary, we fabricated a Ga_2O_3 gas sensor using the nanowires synthesized by a chemical thermal evaporation method. The Ga_2O_3 nanowire sensors show reversible responses to O_2 and CO in a low working temperature range of 100–500 °C. A peak response is found at 300 °C for O_2 gas. For CO gas, the peak response appears at 200 °C. The sensor response increases empirically with an increase of gas concentration for both kinds of gases. The adsorption/desorption on the nanowire surface dominates the gas sensing of the Ga_2O_3 nanowires. The results demonstrate the possibility of using the Ga_2O_3-based gas sensor in the low working temperature field.

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