Preparation and NO_2-gas sensing property of individual β-Ga_2O_3 nanobelt

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Monoclinic gallium oxide (β-Ga_2O_3) nanobelts are synthesized from gallium and oxygen by thermal evaporation in an argon atmosphere and their NO_2 sensing properties are studied at room temperature. Electron microscopy studies show that the nanobelts have breadths ranging from 30 to 50 nm and lengths up to tens of micrometers. Both the x-ray diffraction (XRD) and the selected are electron diffraction (SAED) examinations indicate that β-Ga_2O_3 nanobelts have grown into single crystals. Room temperature NO_2 sensing tests show that the current of individual β-Ga_2O_3 nanobelt decreases quickly, and then gently when the NO_2 concentration increases from low to high. It is caused by the NO_2 molecule chemisorption and desorption processes in the surface of β-Ga_2O_3 nanobelt.

Keywords: gallium oxide, sensors, nanobelts, NO_2
PACC: 6110M, 7360L, 8280T

1. Introduction

One-dimensional structure with a diameter on the order of nanometers, such as nanobelt and nanowire, has aroused increasing interest due to its remarkable electrical, gas sensing, optical, and mechanical properties:[1,2] especially n-type semiconductor exhibits prominent conduction and gas sensing characteristics.[3,4] Monoclinic gallium oxide (β-Ga_2O_3) is a wide-band gap semiconductor (E_g = 4.8 eV). It also exhibits conduction and luminescence properties,[5] and thus has potential applications in optoelectronic devices, and high and room temperature stable gas sensors.[6]

The gas sensors in the previous studies were based on material: bulk or thin-film. However, due to the very low surface-to-volume ratio of gas-sensitive materials, the effect is small and not evidently detectable. Nanoscale-sized gallium oxide with a large surface area/volume ratio may have a particular ability to detect toxic or bad smelling gases in the surrounding gas environment, such as NO_2, H_2S.

In fact, intrinsic monoclinic gallium oxide (β-Ga_2O_3) has been widely used as the insulating oxide layers for gallium based electric devices.[7,8] As it is prepared under a high temperature condition, gallium oxide becomes an n-type semiconductor due to oxygen vacancies, and the vacancies can act as shallow donors with ionization energy $E_d \approx 0.03-0.04$ eV.[8,9] The β-Ga_2O_3 nanowires and nanobelts can be synthesized by several methods, such as physical evaporation[9] silica-assisted catalytic growth,[10] laser ablation[11] and carbon thermal reduction and so on.[12] However, little research has been done on the gas-sensing of an individual β-Ga_2O_3 nanowire.

In this paper, we synthesize high quantity β-Ga_2O_3 nanobelts by thermal evaporation method in an argon atmosphere with the starting material Ga, and study the influence of NO_2 gas concentration on the NO_2 gas sensing sensitivity of the individual β-Ga_2O_3 nanobelt.

2. Experiment

Silicon substrates (10 mm×10 mm) were cleaned first in an ultrasonic bath with acetone for about 30 min, and then dried in air. Afterwards their surfaces were each deposited by a 20 nm layer of Au in a DC sputtering system. An appropriate amount of metal gallium (Ga, 99.999 %) (500 mg) was loaded into an alumina boat and the cleaned Si–Au substrate was placed at the downstream end of the boat with a separation of 10–15 mm from Ga source. The alumina boat was transferred to the centre of a long alumina tube located in a horizontal tube furnace. The furnace

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was heated to 1050 °C within 55 min, and maintained at the temperature for 1 h, with Ar/O_2 mixed gas ($Ar/O_2 = 60/2$ sccm) flowing. After the reaction was completed, the furnace was cooled down. A white deposition was found on the surface of the substrate and on the inner wall of alumina boat.

The morphologies and microstructures of synthesized products were analysed by field emission scanning election microscopy (FE-SEM, S-4800) transmission electron microscope (TEM) (H-800) operating at an accelerating voltage of 200 kV, and the structures of products were analysed by using x-ray diffraction (XRD) (Cu Kα1, $\lambda = 0.15406$ nm). High-Ohmmeter (ZC36A) and High-Sensitivity Flowmeter (RQ-2) were employed to examination the NO_2-gas sensing property.

To investigate the NO_2-sensing properties of an individual β-Ga_2O_3 nanobelt, the device was fabricated to have a structure of a single nanobelt connected with two Au electrodes, by a method similar to that used in Ref. [9]. The structure was fabricated by using optical lithography. First, we fabricated 200 nm-thick SiO_2 to be used as an insulator on a Si wafer and then deposited a 50 nm-thick Au Pt electrode and 200 nm-thick source and drain electrodes. In this device, the gap distance between facing electrodes was about 2 μm. As-gowned β-Ga_2O_3 nanobelts were ultrasonically dispersed in ethanol, and then the solution containing the NWs was dropped onto the electrodes.

3. Result and discussion

Figure 1 shows the XRD pattern of the white product on the substrate. All diffraction peaks in the pattern can be indexed to the monoclinic structured β-Ga_2O_3, which are in good agreement with the reported values of β-Ga_2O_3 with the lattice constants $a = 1.223$ nm, $b = 0.304$ nm, $c = 0.580$ nm, $\beta = 103.7°$ (ICDD-JCPDS PDF-2 No. 76-0573), and belong to $C2/m$ space group.

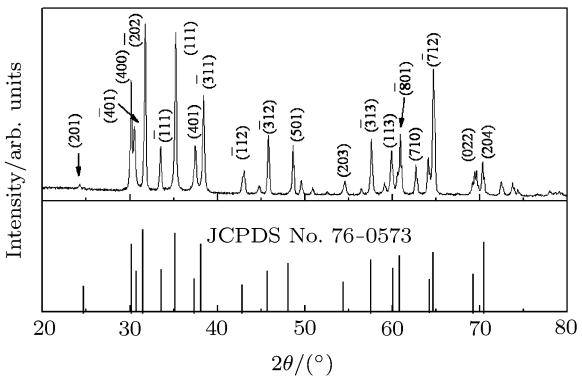


Fig. 1. XRD pattern for the white product on the substrate.

The morphology of the product was investigated by SEM and TEM equipped with an SAED. Figure 2 exhibits typical SEM and TEM images of the product. SEM images revealing a general morphology of belt-type structure of β-Ga_2O_3 are shown in Figs. 2(a) and 2(b).

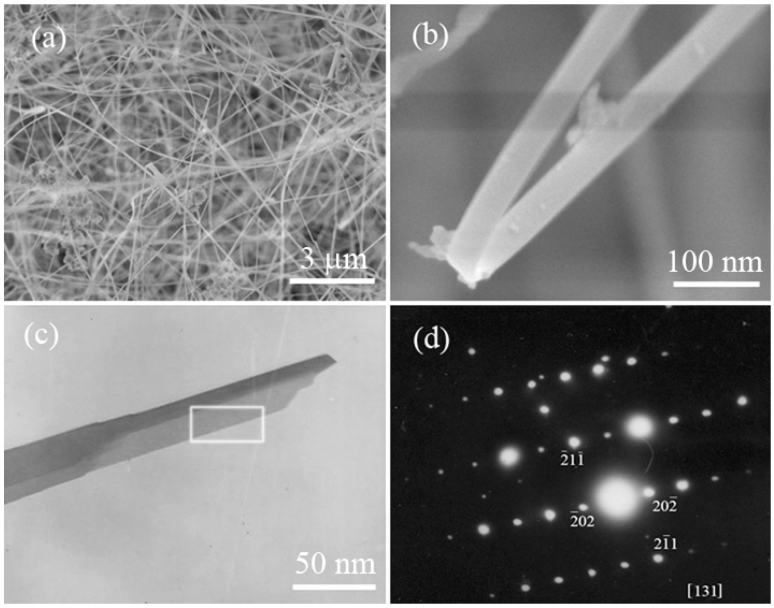


Fig. 2.(a) Typical SEM images of the synthesized β-Ga_2O_3 , (b) highly-magnified images (c) TEM image of an individual β-Ga_2O_3 nanobelt, and (d) SAED image showing the box in (c).

The widths of nanobelt are about 50 nm, and their thicknesses are about 1/10 of the widths. Most of these nanobelts are rather long and their lengths are up to a few tens of micrometers. The TEM investigation of the nanobelts is shown in Fig. 2(c); it confirms that the as-produced nanobelt is about 30nm in width and of a perfect single crystal in structure, which was further supported by the SAED pattern taken along the [131] axis as shown in Fig. 2(d).

To examine the NO_2-gas sensing property of an individual β-Ga_2O_3 nanobelt at room temperature, we employed a high ohmmeter and stopwatch to investigate the current and record the response time, and their results are given in Table 1.

Table 1. Current and response time with different NO_2 concentrations.

C/ppm	0.5	1	5	10	50	100	500	1100
I/nA	1.15	1.1	0.98	0.78	0.56	0.23	0.15	0.095
Time/s	16	22	43	58	114	146	252	301

Figure 3 shows the current of β-Ga_2O_3 nanobelt under different NO_2 concentrations at room temperature, with the bias voltage set at 12 V. When the air-diluted NO_2 was introduced into the chamber, the current decreased and finally stabilized at about 0.15 nA when the mixed gas flow increased from 10 to 1100 ppm.[1)]

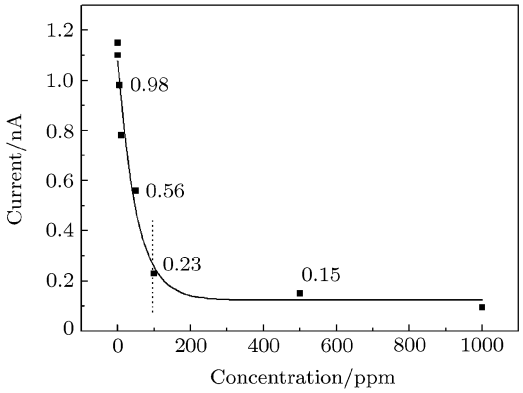


Fig. 3. Current vs NO_2 concentration curve of an individual β-Ga_2O_3 nanobelt.

The NO_2 concentration versus response time is shown in Fig. 4. Figure 3 indicates that the current decreases quickly and becomes slowly with NO_2 concentration increasing and so does the response time when the current changes. From Table 1, Figs. 3 and 4, we find that this device is suitable for low NO_2 concentration, especially below 100 ppm (response time is about 2 min). If the gas concentration is above 100 ppm, the current becomes very slow and the response time becomes longer with NO_2 concentration increasing.

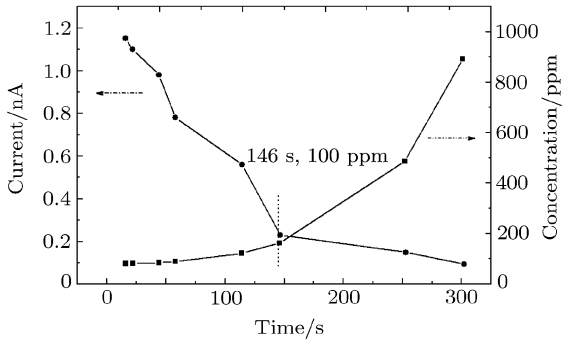


Fig. 4. NO_2 concentration and current characteristics of the sensors at room temperature versus response time.

Many researchers investigated the mechanism of onedimensional nanomaterials gas sensors.[13,14] The conductivity or current of the β-Ga_2O_3 is very sensitive to the nature and the concentration of adsorbed species on its surface. Especially the nanowire or nanobelt has an ultrahigh surface-to-volume ratio. The further adsorption of oxidizing NO_2 molecules on the surface of the β-Ga_2O_3 nanobelt is likely to trap electrons and reduce the carrier concentration in the n-type β-Ga_2O_3 nanobelt,[15,16] so we can find that the current of an individual β-Ga_2O_3 nanobelt becomes falling down (shown in Figure 3) with concentration increasing.

In general, the surface adsorbed NO_2 ions can affect the conductance of a nanobelt. The surface NO_2 ions act as scattering centres, thereby reducing the carrier mobility. So, the current across the nanobelt decreases with the increase of NO_2 concentration.

4. Conclusion

We have successfully synthesized β-Ga_2O_3 nanobelts by simple thermal evaporation. Both the XRD and the SAED examinations indicate that β-Ga_2O_3 nanobelts have grown into single crystals. The study of their gas sensing under room temperature with different NO_2 concentrations suggests that this device is suitable for the case of low NO_2 concentration, especially below 100 ppm (response time is about 2 min). The current of an individual β-Ga_2O_3 nanobelt decreases quickly and then gently when NO_2 concentration increases from low to high, it is caused by the NO_2 molecule chemisorption and desorption processes on the surface of β-Ga_2O_3 nanobelt.

[1)] Here ppm stand for NO_2-gas volume concentration, 1 ppm=0.37 mg/m^3.

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