

# Study of Ga<sub>2</sub>O<sub>3</sub> Nanobelts Synthesized by the Thermal Annealing of GaN Powders

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We synthesized the uniform monoclinic gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) nanobelts by a simple thermal annealing of GaN powders. The as-synthesized nanobelts were rectangular in cross-sectional shape with width ranging from 100 to 700 nm. The length direction of the nanobelt was along [010]. Photoluminescence measurement under excitation at 325 nm showed that the Ga<sub>2</sub>O<sub>3</sub> nanobelts had a blue emission at around 454 nm.

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## 1. Introduction

$\beta$ -Ga<sub>2</sub>O<sub>3</sub>, a wide band gap transparent conducting oxide material ( $E_g = 4.9$  eV) [1] has been known for both conduction and luminescence properties [2]. The Ga<sub>2</sub>O<sub>3</sub> not only has potential applications for optoelectronics devices, but also is one of the most promising materials for high-temperature gas sensors [3, 4].

The nanoscale one-dimensional (1D) materials, such as nanorods, nanowire, and nanobelts, have been of great interest due to their unique properties and promising applications in the electrical, optical, and magnetic devices and among them, the belt-like nanostructure may be an ideal system for fully understanding dimensionally confined transport phenomena and fabricating functional nanodevices, due to their special morphology. Although some researchers have prepared the Ga<sub>2</sub>O<sub>3</sub> nanobelts by thermally heating or evaporating the mixtured materials [5–8], there are rare reports on the synthesis route using the GaN powders only. Furthermore, most researchers have produced the nanobelts at a distance from the source material. In this paper, we report an approach, in which we have simply annealed the GaN powders and produced the nanobelts *in situ*. We have investigated the structural and photoluminescence (PL) properties of the as-prepared Ga<sub>2</sub>O<sub>3</sub> nanobelts.

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## 2. Experimental

The synthesis was carried out in a quartz tube mounted vertically inside a high-temperature tube furnace. The Si substrate covered with a layer of Au (about 150 nm in thickness), onto which the 99.99%-pure GaN powders were placed, was heated at 900°C for 2 hours at a pressure of several hundreds Torr, under a constant flow of nitrogen (N<sub>2</sub>) as an ambient gas. As suggested by the previous studies [9, 10], we have used the Au as a catalyst. Without the Au layer, no recognizable nanostructures were formed.

As-grown samples were investigated and analyzed using X-ray diffraction (XRD, X'pert MPD-Philips with Cu K<sub>α1</sub> radiation), scanning electron microscopy (SEM, Hitachi S-4200), transmission electron microscopy (TEM, Philips CM-200), and energy-dispersive X-ray spectroscopy (EDS) attached to the TEM. TEM samples were prepared by sonicating the substrate in acetone by ultrasonic treatment. The PL measurement was performed at room temperature using a He–Cd laser line of 325 nm as the excitation source.

## 3. Results and discussion

Figure 1a shows the typical XRD spectrum of the products. The reflection peaks of (004), ( $\bar{1}04$ ), ( $\bar{2}02$ ), ( $\bar{1}11$ ), (111), ( $\bar{2}13$ ), ( $\bar{3}06$ ), and ( $\bar{4}02$ ) correspond to the monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> structure (JCPDS: 11-0370). The reflection peak at  $2\theta = 69.20^\circ$  is indexed as (004) plane of the Si substrate. Also, (111), (200), and (311) diffraction peaks of Au from the substrate are detected. The plan-view SEM image indicates that the products consist of bunches of nanobelts (Fig. 1b). Statistical analysis of many SEM images shows that the typical width is in the range of 100–700 nm. Figure 1c shows the high magnification SEM image of the nanobelts, indicating the straight shapes and smooth surface of the nanobelts. For the nanobelts, the cross-sections are rectangular.

Further analysis of the individual Ga<sub>2</sub>O<sub>3</sub> nanobelt was performed using the TEM with EDS attached. EDS measurements indicated that the nanobelts consisted only of Ga and O (not shown here). Figure 2a shows the TEM image of a nanobelt, indicating a uniform width of about 140 nm along its length. The corresponding selected area electron diffraction (SAED) pattern was taken along the [101] zone axis of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The length direction of the nanobelt is along the [010] direction. Figure 2b is a high resolution TEM (HRTEM) image obtained by enlarging an area of Fig. 2a. The clear lattice fringes illustrate that the nanobelt is single crystalline. The interplanar spacings are about 0.28 nm, 0.26 nm, and 0.26 nm, respectively, corresponding to ( $\bar{2}02$ ), (11 $\bar{1}$ ), and ( $\bar{1}11$ ) planes of monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

The growth of Ga<sub>2</sub>O<sub>3</sub> nanobelts may take place in a sequence of steps that includes the reaction of Ga from the GaN powders with oxygen. Although we have used a N<sub>2</sub> atmosphere in the furnace, we believe that the oxygen in the Ga<sub>2</sub>O<sub>3</sub>

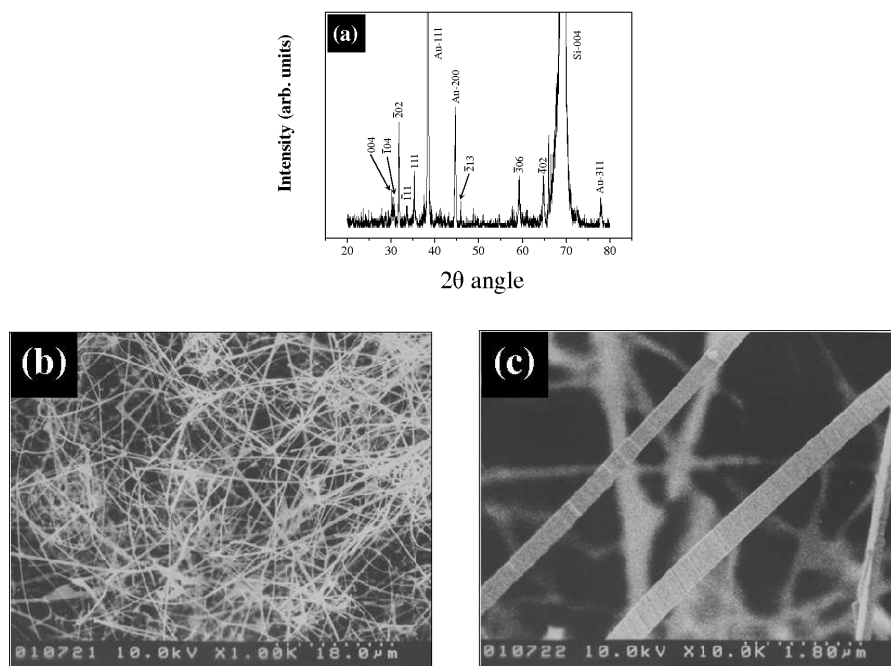


Fig. 1. (a) XRD patterns recorded from the Ga<sub>2</sub>O<sub>3</sub> nanobelts. (b) Plan-view and (c) high-magnification SEM image of the Ga<sub>2</sub>O<sub>3</sub> nanobelts.

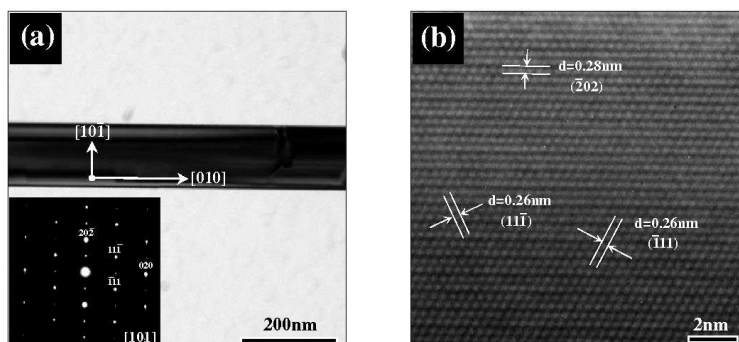


Fig. 2. (a) TEM image and (b) corresponding HRTEM image of a single Ga<sub>2</sub>O<sub>3</sub> nanobelt. The inset is the SAED pattern recorded along the [101] zone axis.

has come from the air leakage, or the residual oxygen in the furnace, consistent with the assertion made by Lee et al. [11].

Our previous experiment with the same synthesizing condition by using O<sub>2</sub> ambient gas instead of N<sub>2</sub> gas produced irregularly shaped structures (Fig. 3a). Figure 3b shows the corresponding XRD spectrum of the samples which were separated from the substrate, indicating that the irregularly shaped structures are β-Ga<sub>2</sub>O<sub>3</sub>. Guojian et al. [12] suggested that the crystal growth pattern of 1D

whiskers is associated with the supersaturation degree. According to their model, under low supersaturation, 1D structures such as whiskers are easy to grow, and under high supersaturation, the gaseous atoms nucleate evenly and powders form. In the present case, we surmise that the relatively small amount of oxygen in  $N_2$  ambient provided the condition of low oxygen supersaturation for the growth of  $Ga_2O_3$  nanobelts.

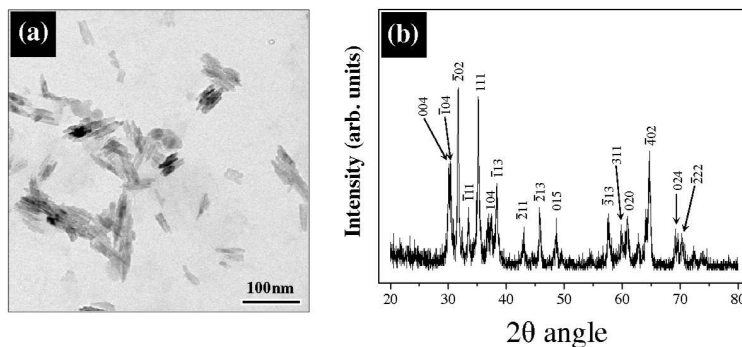


Fig. 3. (a) TEM image and (b) XRD patterns of the products when synthesized in an  $O_2$  ambient.

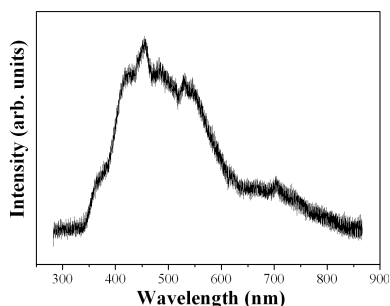


Fig. 4. Room temperature PL spectrum of the  $Ga_2O_3$  nanobelts with an excitation wavelength at 325 nm.

The PL of as-prepared  $Ga_2O_3$  nanobelts was measured at room temperature. There is an apparent broad blue emission PL peak centered at about 454 nm, as shown in Fig. 4. Binet and Gourier [2] suggested that this blue emission could be produced by a recombination of an electron on a donor formed by oxygen vacancies with a hole on an acceptor which could be either gallium vacancies [13] or a gallium–oxygen vacancy pair [14]. We surmise that the above vacancies could be easily generated in the present high temperature synthesis route, supporting the origin of blue emission. Although further systematic study is necessary in order

to reveal the detailed mechanism of the observed emissions, Ga<sub>2</sub>O<sub>3</sub> nanobelts may have potential application in optoelectronic nanodevices.

#### 4. Conclusion

In summary, we first reported the *in situ* preparation of the uniform monoclinic Ga<sub>2</sub>O<sub>3</sub> nanobelts on Au-coated Si substrate. We heated GaN powders at 900°C under N<sub>2</sub> flow. The resulting Ga<sub>2</sub>O<sub>3</sub> nanobelts have widths ranging from 100 to 700 nm and have a preferred [010] growth direction along the long axis. The ambient gas plays a crucial role in determining the morphologies of the nanomaterials. The broad PL emission band centered around 454 nm is observed at room temperature.

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