



Gallium oxide nanomaterials produced on SiO₂ substrates via thermal evaporation

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Abstract

We have prepared the novel gallium oxide (Ga₂O₃) nanomaterials on SiO₂ substrates by a thermal evaporation of GaN powders. We found that the products consisted of the nanobelts with additional nanostructures formed on the sides of nanobelts. The nanobelts had a single-crystalline monoclinic structure with a width in the range of 100–300 nm. We have discussed the possible mechanism leading to the formation of the Ga₂O₃ nanomaterials. Photoluminescence spectrum under excitation at 325 nm showed a blue emission.

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1. Introduction

One-dimensional (1D) nanostructures, such as nanobelts, -rods, and -wires, have the potential to show enhanced physical properties due to their decreased size, increased surface-to-volume ratio, and the novel morphologies, making them attractive materials with many possible applications [1–3]. Gallium oxide (Ga₂O₃) is a wide gap ($E_g = 4.9$ eV) compound and it has long been known to exhibit both

conduction and luminescence properties [4]. Therefore, 1D Ga₂O₃ nanostructures should have potential applications in 1D optoelectronic nanodevices. The 1D Ga₂O₃ nanostructures have been synthesized by various methods, including a dc arc discharge [5] and an evaporation or heating [6–17].

In this paper, we report the formation of Ga₂O₃ nanomaterials on SiO₂ substrates using GaN powders without employing a catalyst, at a temperature of 900 °C and we have examined the structural and optical properties of the products. Although the 1D β-Ga₂O₃ nanostructures have been synthesized from GaN powders on alumina [13,15] or on indium (In)-coated Al₂O₃ substrates [14] and also from Ga

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powders on quartz [6], the investigation on the production of β -Ga₂O₃ nanomaterials on SiO₂ substrate from GaN powders, which we believe, has never been reported.

2. Experimental

The SiO₂ substrates used in our experiments were prepared by thermally depositing 60 nm-thick SiO₂ layers on p-type (1 0 0) Si wafers. A dry oxidation technique has been used with the hotwall horizontal diffusion furnace, in which O₂ gas was an oxygen source. They were ultrasonically cleaned for 10 min in acetone solution. The experimental apparatus is described in Fig. 1. The 99.99%-pure GaN powders and the SiO₂ substrates, respectively, were placed on the lower and the upper holder in the furnace. The powder-to-substrate distance was 5 mm. During the experiment, a constant flow of nitrogen (N₂) was maintained at flow rate of 500 sccm. The temperature near the substrate was about 900 °C for 2 h. After evaporation, the substrate was cooled down and subsequently taken out from the furnace for structural and optical characterization.

The structural properties of the as-grown products were investigated using X-ray diffraction (XRD) with Cu K α 1 radiation ($\lambda = 0.154056$ nm), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) installed, and transmission electron microscopy (TEM) with an accelerating voltage of 200 kV. For SEM observation, we have

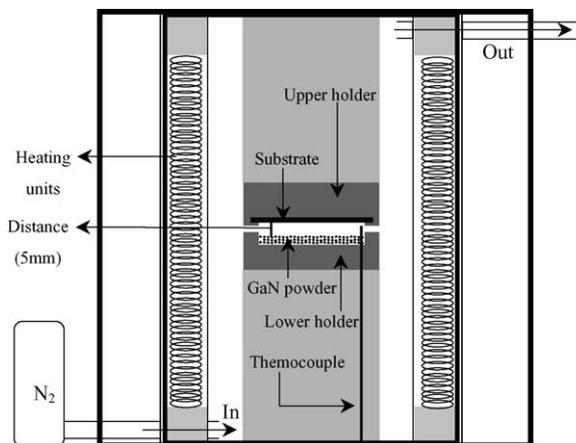


Fig. 1. Schematic illustration of the apparatus used in this work.

coated platinum (Pt) using ion sputtering system onto specimens after they have been mounted on stubs. For TEM observation, the products were ultrasonically dispersed in acetone and drops were placed on a carbon-coated copper grid. The photoluminescence (PL) measurement was carried out at room temperature using a He-Cd (325 nm, 55 mW) laser as the excitation light source.

3. Results and discussion

Fig. 2 displays the XRD patterns taken from the products on SiO₂ substrates. Miller indices are indicated on each diffraction peak. Within experimental error, all the relatively sharp diffraction peaks in the XRD pattern can be indexed to a monoclinic β -Ga₂O₃ with lattice parameters of $a = 5.80$ Å, $b = 3.04$ Å, and $c = 12.23$ Å (JCPDS-International Center for Diffraction Date No. 11-370), revealing the production of β -Ga₂O₃ deposits. No crystalline phases other than Si were found within the detection limit. The Si diffraction peaks come from the substrate.

Fig. 3a and b are typical cross-sectional and plan-view SEM images of deposits on SiO₂ substrate, respectively, revealing that the products consist of a large quantity of 1D nanomaterials with typical lengths mostly <180 μ m. Fig. 3c is the high-magnification SEM image of the deposits. The products comprise nanobelts with high aspect ratio. Certain other irregularly shaped structures, with a

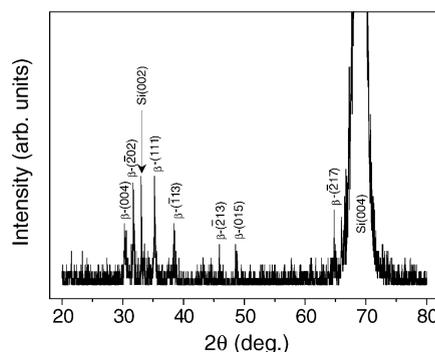


Fig. 2. XRD pattern of the as-deposited products. The Si diffraction peaks come from the substrate.

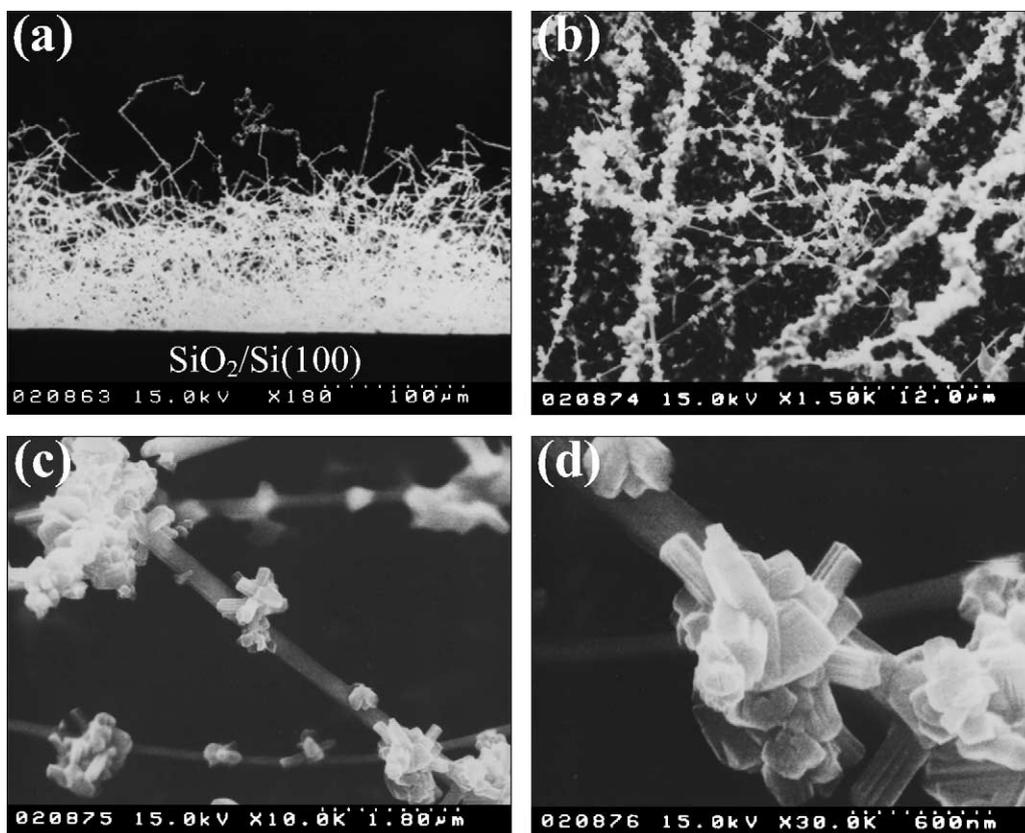


Fig. 3. SEM images showing the general morphology of as-deposited products. (a) side view image, (b) plan-view image, (c) and (d) high-magnification image.

local outgrowth originating from the nanobelts, are also seen. To our knowledge, such combined nanostructures have never been reported in synthesizing the Ga₂O₃ nanomaterials. Statistical analysis of many SEM images shows that the width of nanobelts ranges from 100 to 300 nm, and the thickness is less than 1/10 of the widths. Fig. 3d indicates that the irregularly shaped nanostructures consist of small nanorods with diameters in the range of 100–200 nm. Close examination reveals that many of the nanorod have polygonal cross-sections with no nanoparticle at their tips. Fig. 4 shows the typical EDS spectrum collected from the deposits. The spectrum clearly identifies the peaks of Ga, O, Si, and Pt. Since the Si- and Pt-related peak, respectively, are from the substrate and from the SEM sample preparation process, the spectrum indicates that the components of the deposits are Ga and O.

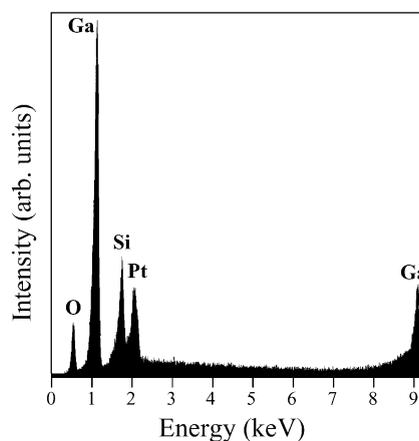


Fig. 4. The EDS spectrum showing the chemical compositions of the products.

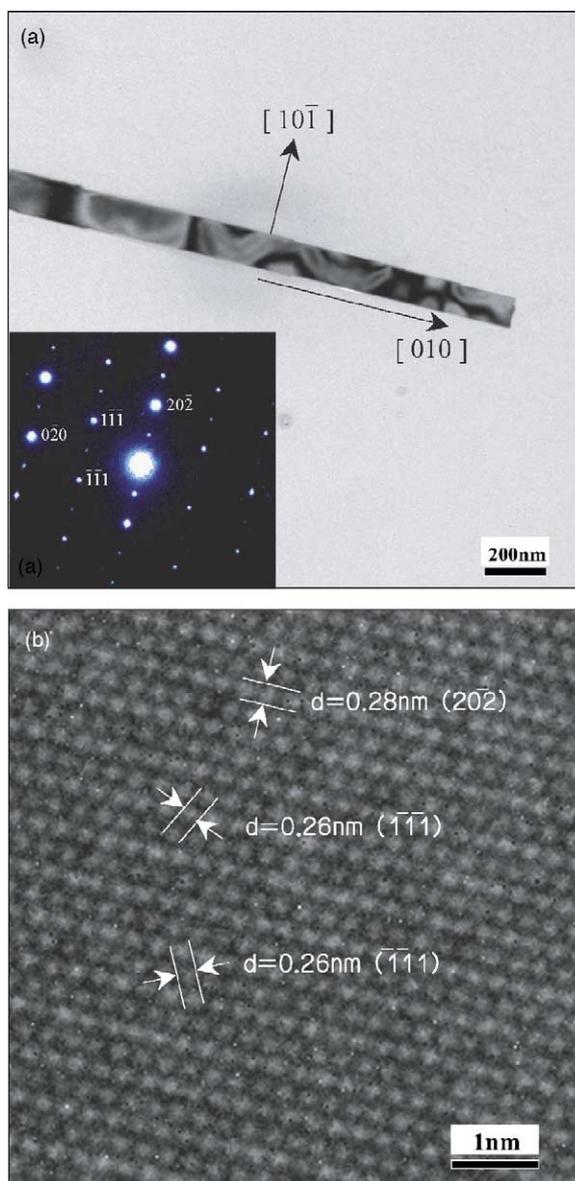


Fig. 5. (a) TEM image of a single β - Ga_2O_3 nanobelt and the inset shows corresponding SAED pattern recorded along the $[1\ 0\ 1]$ zone axis, showing $[0\ 1\ 0]$ growth direction. (b) HRTEM image of a single β - Ga_2O_3 nanobelt indicating the good crystallinity.

For obtaining more detail about the structure of the individual nanobelt, we have carried out the TEM analysis. Fig. 5a shows the low magnification TEM image of a nanobelt, indicating that the individual nanobelt has a straight and almost uniform width along its entire length. No spherical droplets or nanoparticles can be seen at a tip of this nanobelt. We surmise that the contrast observed over the nanobelt is

bending contour due to a bending of the nanobelt. The corresponding selected area electron diffraction (SAED) pattern, recorded perpendicular to the nanobelt long axis, can be indexed for $[1\ 0\ 1]$ zone axis of crystalline β - Ga_2O_3 . The length direction of the nanobelts is along the $[0\ 1\ 0]$ direction, as shown in Fig. 5a. Fig. 5b is a high resolution TEM (HRTEM) image enlarging a part of Fig. 5a, revealing a perfect

crystallinity of the nanobelt. The interplanar spacings are about 0.28 and 0.26 nm, respectively, corresponding to the $(2\ 0\ \bar{2})$ and $(1\ \bar{1}\ \bar{1})$ planes of monoclinic β - Ga_2O_3 . After sonification in TEM sample preparation, the nanorod-like structures was not found and only nanobelts could be investigated. More study is necessary in order to reveal the exact crystalline nature of the nanorod.

In the present work, no metal catalyst was used and no particle was observed at the ends of the nanobelts or -rods. Therefore, the growth mechanism of the nanomaterials can be understood on the basis of a self-catalytic process with the characteristics of vapor–solid (VS) growth mechanism. Herein, during heating, the Ga vapor generated from the GaN powders combines with oxygen, resulting in the formation of Ga_2O_3 nanomaterials.

We believe that the oxygen in the Ga_2O_3 has been originally come from the air leakage or the residual oxygen in the furnace and also from the SiO_2 substrate. In the first place, although we have used a N_2 atmosphere during the evaporation process in the furnace, there should exist the air leakage or the residual oxygen in the N_2 flow, consistent with the assertion made by Lee et al. [18] and the report of Kim et al. on the preparation of Ga_2O_3 nanomaterials (nanowires) from GaN powders in a N_2 atmosphere [13]. Secondly, there is a possibility that the additional oxygen comes from the SiO_2 substrate. This suggestion is consistent with the report by Geng et al. on the production of Ga_2O_3 nanomaterials (nanobelts) from a mixture of gallium (Ga) and SiO_2 nanopowder [7].

Guojian et al. suggested that the crystal growth pattern in the VS mechanism is associated with the supersaturation degree in the gaseous phase [19]. Under low supersaturation, 1D structures such as whiskers are easy to grow, and under high supersaturation, the gaseous atoms nucleate evenly and powders form. Under the medium supersaturation, it activates the secondary growth sites on the side of the 1D structures, tending to produce the tree-shaped structures. We surmise that the amount of oxygen in our case is sufficient to provide the condition of medium oxygen supersaturation for the growth of Ga_2O_3 nanomaterials, in which additional nanostructures are formed on the side of nanobelts. Further systematic study is necessary in order to reveal the detailed mechanism

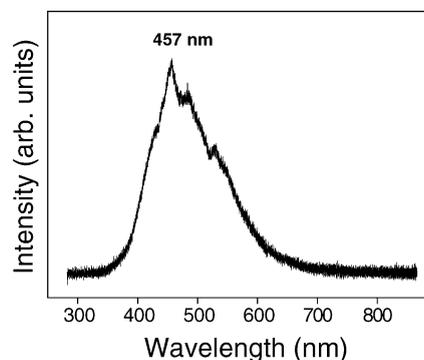


Fig. 6. Room temperature PL spectrum of the products with an excitation wavelength at 325 nm.

The PL spectrum of the deposits at room temperature is shown in Fig. 6. There is an apparent broad, strong blue emission PL peak centered at about 457 nm. The blue emission is known to be associated with the vacancies in Ga_2O_3 , such as Ga vacancies, O vacancies, [20] and Ga–O vacancy pairs [21]. According to Binet and Gourier [22], an electron in a donor is captured by a hole on an acceptor to form a trapped exciton, which recombines radiatively and emits a blue emission. Since Ga_2O_3 nanomaterials are produced at high temperature in the present work, we surmise that vacancies can be easily generated. Although further systematic study is necessary in order to reveal the mechanism of the observed emissions, Ga_2O_3 nanomaterials may have potential application in optoelectronic nanodevices due to their possibilities of strong emission.

4. Conclusion

In summary, we have demonstrated the formation of β - Ga_2O_3 nanomaterials on SiO_2 substrate via a thermal evaporation method of heating GaN powders at 900 °C under N_2 flow. The deposits are composed of single-crystal β - Ga_2O_3 nanobelts with an agglomeration of nanorods attached. The single nanobelt, with a diameter in the range of 100–300 nm is found to be monoclinic β - Ga_2O_3 structure. The attached nanorods have polygonal cross-sections with the diameter of about 100–200 nm. We suggest that the growth of Ga_2O_3 nanomaterials is controlled by VS growth mechanism. The PL

spectrum shows a broad and strong emission band around 457 nm.

Acknowledgement

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