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Short communication

Synthesis of one-dimensional Ga_2O_3 nanostructures via high-energy ball milling and annealing of GaN

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Abstract

β-Gallium oxide (β-Ga_2O_3) is a promising material for sensors that can withstand high-temperature, high-pressure, and corrosive environment in advanced fossil fuel power plants. Synthesis of one-dimensional nanostructures of β-Ga_2O_3, which are of particular interest, by ball milling of gallium nitride followed by annealing in nitrogen flow is attractive due to relatively inexpensive equipment and simple procedures, but the long milling time is an obstacle for widespread use of this method. In the present work, high-energy mechanical milling of GaN in a planetary ball mill is used for shortening the milling time in the fabrication of one-dimensional Ga_2O_3 nanostructures. Effects of milling parameters on the morphology of GaN powders as well as on the morphology and chemical composition of the obtained Ga_2O_3 structures are studied. When annealing was conducted in ultra-high purity ($O_2 < 1$ ppb) nitrogen flow, a variety of Ga_2O_3 one-dimensional nanostructures such as rods, belts, sheets, and leaf-like shapes were obtained.

Keywords: High-energy ball milling; One-dimensional nanostructures; Gallium oxide; Gallium nitride

1. Introduction

Operating conditions of advanced fossil fuel power plants require sensors and controls that can withstand high temperature, pressure, and corrosive environment [1,2]. The desired characteristics of sensors in such applications are long shelf life and stability, high sensitivity, and low threat of poisoning or contamination. One promising material is β-gallium oxide (β-Ga_2O_3). It has a high melting point (1740 °C) and a stable structure at high temperatures. It also exhibits n-type semiconductor properties (wide band gap, $E_g = 4.9$ eV) above 600 °C and is sensitive to reducing gases such as CO and H_2 below 700 °C as well as to oxygen above 900 °C [3]. All these properties make Ga_2O_3 attractive for using in sensors and controls. Currently, one-dimensional nanostructures of Ga_2O_3 are of great interest since they can be easily integrated to nano-electronics [4].

Gallium oxide nanowires, nanorods, nanobelts, nanosheets, and thin films have been prepared by various methods such as evaporation of gallium powder with [5] and without [6] catalyst, RF magnetron sputtering of gallium powder [7], plasma-enhanced atomic layer deposition (PEALD) of gallium oxide [8], electric current heating method of gallium oxide ceramic bars [9], evaporation of gallium nitride (GaN) powders [10] and pure Ga_2O_3 powder [11], annealing of compacted GaN powder [12], and ball milling of GaN powders followed by annealing in nitrogen [13,14]. Among these methods, the combination of ball milling with annealing [13,14] is especially attractive as it involves relatively inexpensive equipment and simple procedures. However, the long milling time reported (from 4 h to 40 h [13,14]) is an obstacle for widespread use of this method. In the present paper, high-energy mechanical milling of GaN in a planetary ball mill is used for shortening the milling time in the fabrication of one-dimensional Ga_2O_3 nanostructures. Effects of milling parameters on the morphology of GaN powders as well as on the morphology and chemical composition of the obtained Ga_2O_3 structures are studied.

2. Materials and methods

Gallium nitride powder (99.99% metals basis, Alfa Aesar) was used as the starting material. Milling was

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conducted in air environment in a planetary ball mill (Fritsch Pulverisette 7 Premium Line). Zirconia-coated grinding bowls (20 mL) and zirconia grinding balls were used. The milling procedure included 14 milling–cooling cycles. The rotation speed, the milling time per cycle, and the cooling time per cycle were 1100 rpm, 5 min, and 70 min, respectively, in all experiments. To determine optimal conditions for grinding GaN powder, several milling parameters such as the mass of sample, the diameter of grinding balls, and the total mass of grinding balls were varied (Table 1). To break down the agglomerates formed during milling, the samples were additionally treated for 5 min using a mortar and a pestle (both made of agate).

For the experiment, the sample (0.5 g) of ball-milled GaN powder in an alumina crucible (diameter 25.4 mm, height 25.4 mm) was placed in the center of a horizontal tube furnace (Lindberg Blue M, three zones, max. temp. 1200 °C). The nitrogen gas was fed to the furnace at the rate of 3 L/min for 15 min and then at the rate of 0.3 L/min. The furnace temperature increased linearly at a rate of 10 °C/min until it reached 1100 °C. The entire annealing process was carried out for 12 h (including 110 min at increasing temperature). Next, the heater was turned off and the sample was cooled in nitrogen flow to room temperature.

Initially, high-purity (99.995% pure, $O_2 < 5$ ppb) nitrogen was used in the experiments. Later, ultra-high purity nitrogen (99.999% pure, $O_2 < 1$ ppb) was used, which significantly improved the results as shown in the next section.

The initial and milled GaN powders as well as the obtained products were analyzed using X-ray diffraction (Bruker D8 Discover XRD). The surface morphology and elemental composition of the products were examined using scanning electron microscopy and electron dispersive X-ray spectroscopy (SEM–EDS Hitachi S-4800). The products were also characterized using Brunauer–Emmett–Teller (BET) specific surface area analysis (Microtrac SAA) and laser diffraction particle size analysis (Microtrac Bluewave).

3. Results and discussion

Comparison between XRD patterns of as-received GaN and ball-milled GaN powders is shown in Fig. 1. It is seen that ball-milled GaN powder peaks are much smaller than the original GaN powder peaks, which is associated with decreasing the particle size. This correlates well with the previous results [14]. It should be noted, however, that the total operation time in the planetary ball mill was significantly shorter (14 5 min cycles, i.e., 70 min) as compared to previous studies where conventional, low-energy milling was used (4–40 h [13,14]). Note that the cooling time could be significantly decreased in the future optimization of the milling process. Based on the analysis of milled GaN powders, operational procedure ♯3 (see Table 1) was used for the synthesis of Ga_2O_3.

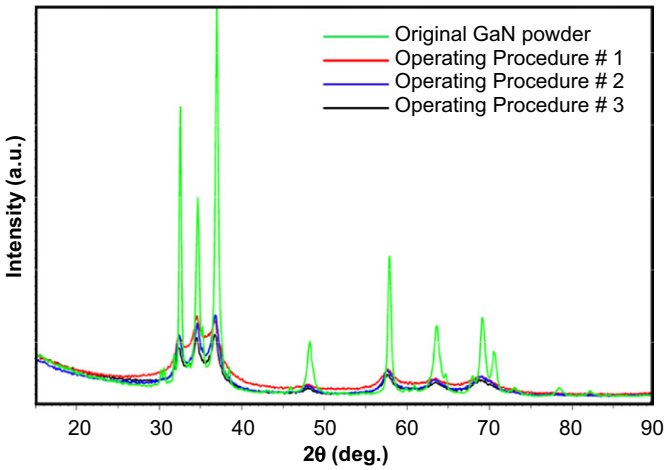

Fig. 1. XRD patterns of the GaN powders (original and milled using different operating procedures).

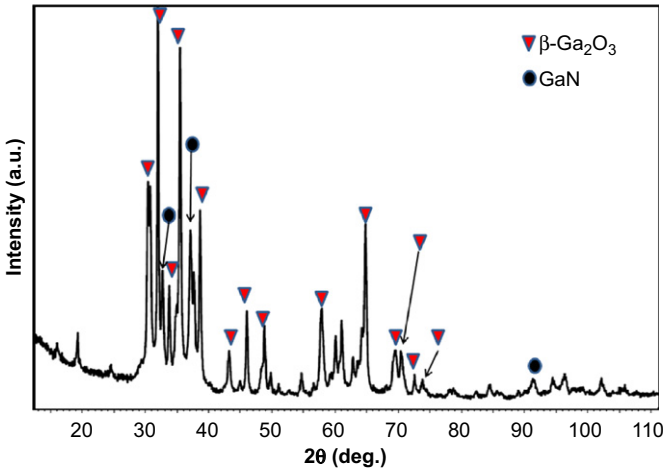

Fig. 2. XRD patterns of the products obtained by annealing ball-milled GaN powder.

Table 1
Milling parameters.

Operating procedure #	Mass of GaN (g)	Mass of grinding balls (g)	Diameter of grinding balls (mm)	Rotation speed (rpm)	Milling time per cycle (mm)	Cooling pause (min)	Number of cycles
1	1	20	1	1100	5	70	14
2	1	15	0.5	1100	5	70	14
3	2	30	0.5	1100	5	70	14

After annealing and cooling of a 0.5-g-sample of ball-milled GaN powder, about 0.2 g of product was obtained. Apparently, the rest of the GaN powder (0.3 g) was decomposed and carried away by the nitrogen flow. White wool-like structures (about 0.1 g) were seen in a yellow powder matrix. XRD pattern of the obtained products (Fig. 2) indicates the presence of β-Ga_2O_3 (monoclinic, $a=12.23$, $b=3.04$, $c=5.80$, and $\beta=103.7^{\circ}$) in a GaN matrix.

According to the particle size analysis, the median diameters of the original and ball-milled GaN powders

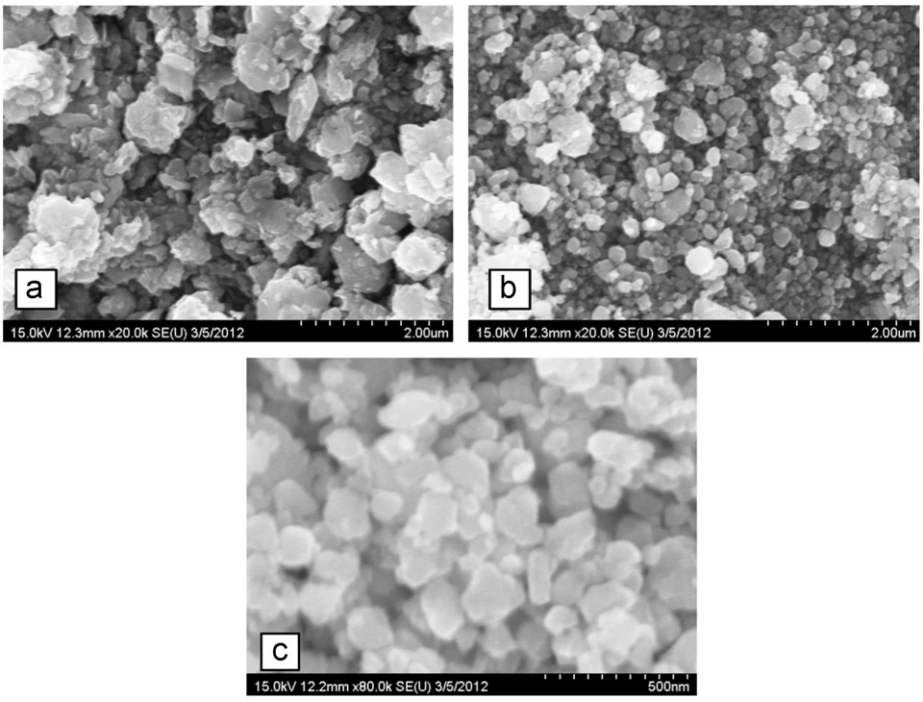

Fig. 3. SEM microphotographs of GaN powders: (a) original GaN powder, (b) ball-milled GaN powder, and (c) ball-milled GaN powder at higher magnification.

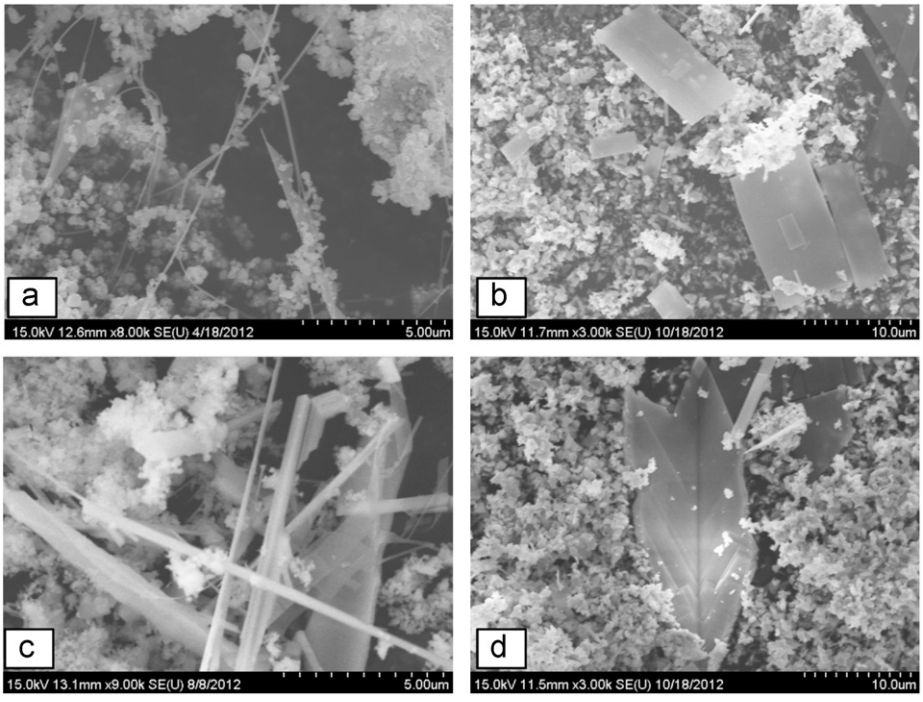

Fig. 4. SEM microphotographs of the reaction products obtained by annealing ball-milled GaN powder in a tube furnace: (a) nanobelts, (b) nanosheets, (c) nanorods, and (d) leaf-like structures.

are 2.3 μm and 1.2 μm, respectively. The measured values of BET specific surface area for original and ball-milled GaN powders are 5 m^2/g and 12.4 m^2/g, respectively. These data indicate that ball milling does reduce particle size and increases surface area, thereby creating numerous reaction sites for annealing process.

Fig. 3 shows the SEM microphotographs of the GaN powders. Comparison of the image for the original GaN powder (Fig. 3a) with that for the ball-milled powder at the same magnification (Fig. 3b) demonstrates that ball milling decreases particle size to the sub-micron range and makes the powder more uniform. Fig. 3c shows the ball-milled powder at a higher magnification. It is seen that many particles in the powder are as small as 100 nm. The larger values of particle size obtained in the particle size analysis may be attributed to agglomeration.

When high-purity nitrogen was used as the carrier gas, no nanostructures were obtained. The use of ultra-high purity nitrogen dramatically changed the results. Fig. 4 shows the SEM microphotographs of the products obtained after annealing ball-milled GaN powder in an ultra-high purity nitrogen environment. Rods, belts, sheets, and leaf-like structures can be seen in a powder matrix. The rods and belts are several microns in length and 10–300 nm in diameter/width.

Fig. 5a shows the EDS spectrum for the obtained powder (nanostructures in a powder matrix), while Fig. 5b shows the EDS spectrum for one of the obtained nanobelt. It is seen that the former indicates the presence of Ga, O, and N, while the latter shows only Ga and O atoms.

It should be noted that, as suggested in [14], the formation and growth of gallium oxide nanostructures

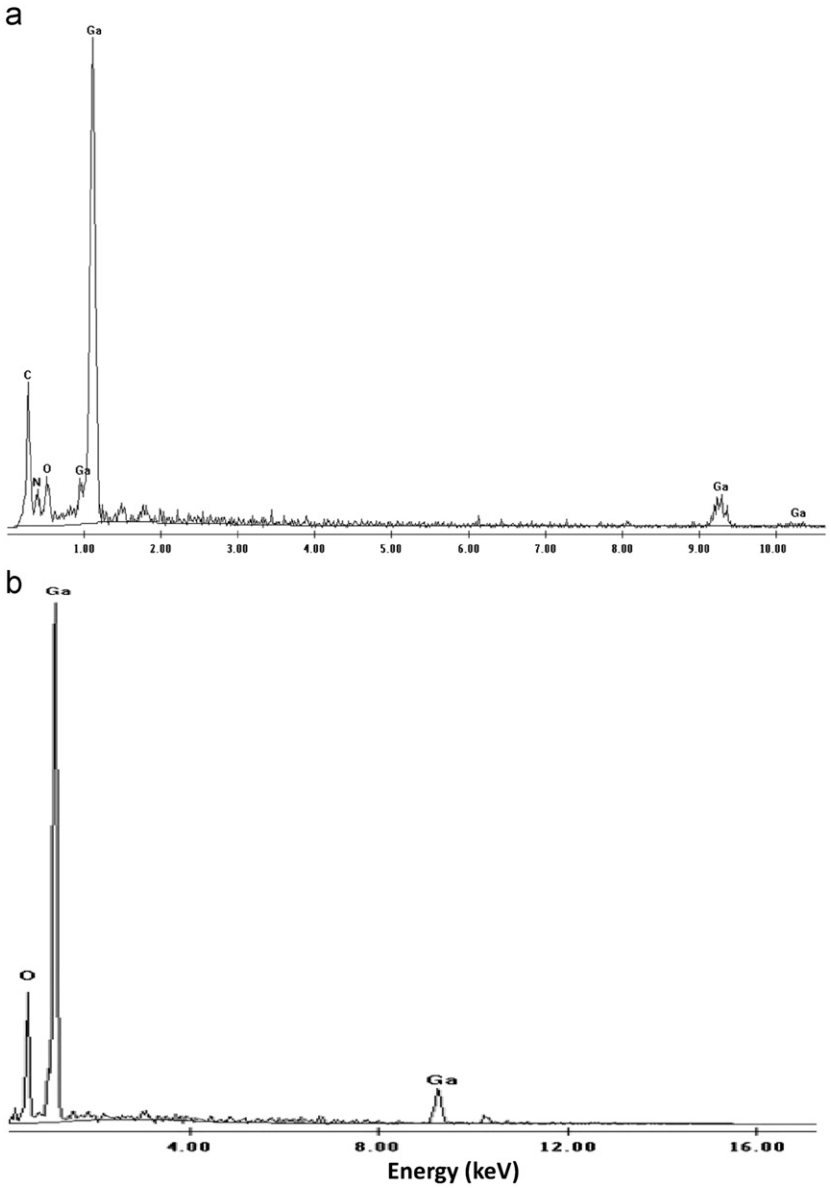

Fig. 5. EDS spectra of the reaction products: (a) nanostructures in a powder matrix and (b) a nanobelt.

during annealing of GaN in nitrogen gas is explained by thermal decomposition of GaN followed by reaction of gallium atoms with oxygen present in the gas flow. When the oxygen content in the gas exceeds some value, the competing process of heterogeneous oxidation of GaN prevails over the growth of Ga_2O_3 one-dimensional nanostructures via the described vapor–solid mechanism.

4. Conclusions

Synthesis of Ga_2O_3 nanostructures from GaN powder through high-energy mechanical milling in a planetary ball mill and annealing in nitrogen has been investigated. The employed high-energy milling of GaN powder reduced the particle size to the sub-micron range and made the powder more uniform. The use of high-energy milling dramatically shortened the milling time as compared to conventional ball milling. When annealing was conducted in ultra-high purity ($O_2 < 1$ ppb) nitrogen flow, a variety of Ga_2O_3 one-dimensional nanostructures such as rods, belts, sheets, and leaf-like shapes were obtained.

Acknowledgments

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