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Shape-controlled synthesis of monodispersed beta-gallium oxide crystals by a simple precipitation technique

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ABSTRACT

Uniformly sized and monodispersed β-Ga_2O_3 crystalline micro-rods and ellipsoids have been successfully synthesized through a facile direct precipitation technique, respectively, using $Ga(NO_3)_3$ and NH_4OH solution as starting materials. The as-prepared particles were characterized by XRD, FESEM equipped with EDS, TEM equipped with SAED, TG-DSC and Laser diffraction particle size analyzer, respectively. The results showed that the obtained β-Ga_2O_3 particles with a narrow particle size distribution were assembled with single crystalline β-Ga_2O_3 nano-sheets with the thickness of 100 nm. Furthermore, the reaction parameters including aging temperature, the molar concentration of Ga^{3+} and pH value had an essential effect on the morphology and size of the particles. Ostwald ripening and oriented attachment growth mechanism of the uniformly hierarchical β-Ga_2O_3 crystals were proposed. Finally, the target fabricated by using the as-prepared β-Ga_2O_3 particles as the raw materials exhibited a density as high as 6.01 g/cm^3, showing potential applications in the high-quality thin film formed by magnetron sputtering for optoelectronic devices.

1. Introduction

Recently, transparent oxide semiconductors (TOSs), namely metal oxide semiconductors with band gap above 3.1 eV, such as ZnO, In_2O_3, Ga_2O_3, Sn-doped In_2O_3 (ITO) and Ga-doped ZnO(GZO), etc., have been extensively investigated as important functional materials due to their excellent optical/electronic/gas-sensitive/photocatalytic properties which are useful for many potential applications [1–7]. As one of the most important members of TOSs, Ga_2O_3, especially β-Ga_2O_3 with widest bandgap energy (Eg=4.80–4.90 eV at room temperature) and tunable electrical conductivity, and which possesses chemical and thermal stability at high temperature, is widely used as optoelectronic devices such as flat panel display, catalysts, white-LED phosphors, solar-blind photo-detectors and gas sensors [8–14]. In addition, β-Ga_2O_3 of monoclinic crystal is the most stable structure of the five well-known polymorphs of gallium oxide (α, β, γ, δ and ε form), and all of these polymorphs can be converted to β-Ga_2O_3 at a specific thermodynamic condition [15].

It is well known that, in addition to the composition and structure of materials, its morphology and size have an important effect on properties of the final particles. In recent years, due to providing high-quality properties for various applications, the preparation of β-Ga_2O_3 particles with uniformly shape and size has been attracting more attention. Zhang et al. [11] successfully prepared sphere-like β-Ga_2O_3 particles with uniform diameters of about 200 nm by using thermal evaporation method at 1350 °C for 5 h in ambient atmosphere, exhibiting a broad blue-green light emission as well as red light emission at room temperature. Kang et al., [16] also have synthesized the monodispersed β-Ga_2O_3 nano-spheres by the forced hydrolysis method using $Ga(NO_3)_3$, sulfate and urea as the reactants. Girija et al. [7] have reported the parallely arranged β-Ga_2O_3 nanorods with the length of about 200 nm synthesized by reflux condensation process using cetyltrimethylammoniumbromide (CTAB) as surfactant, achieving a good photodegradation efficiency. Qian et al. [17] developed a wet–chemical route using gallium chloride ($GaCl_3$) and ammonia as the starting materials at 60 °C for an aging of 18 h to synthesize a hierarchical organization β-Ga_2O_3 spindles with uniform size. Rod-shaped β-Ga_2O_3 crystals with uniform size had been studied by Zhang et al. [18] and Reddy et al. [13] using hydrothermal process. For the large-scale fabrication of crystalline β-Ga_2O_3, the direct precipitation process is the most convenient, time-saving and cost-effective method without using sophisticated equipment. However, little effort has been

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contributed to the fabrication of β-Ga_2O_3 crystals with uniform shape and size by the direct precipitation method using $Ga(NO_3)_3$ solution and ammonia as the starting materials.

In the present study, the uniformly sized β-Ga_2O_3 micro-rods and ellipsoids with smaller aspect ratio were synthesized by a facile direct precipitation technique, respectively, using $Ga(NO_3)_3$ and ammonia hydroxide (NH_4OH) solution as starting materials. The effects of the aging temperature, the molar concentration of Ga^{3+} and pH value in the reactant on the phase structure, morphology and size of the as-prepared samples were systematically investigated. Moreover, the possible growth mechanism of β-Ga_2O_3 hierarchical architectures was discussed. Finally, the high-density target was obtained by the as-prepared β-Ga_2O_3 particles as the raw materials, providing a potential breakthrough for further high-quality film applied to optoelectronic devices.

2. Experimental section

2.1. Material synthesis

All the chemical reagents were of analytical grade and were used without further purification. In a typical procedure: at first, metal gallium (99.99% purity) was dissolved with nitric acid (HNO_3, 65%) in the hot water bath to prepare the $Ga(NO_3)_3$ solution. Then, the resulting $Ga(NO_3)_3$ solution of 0.2 mol/L(M) was loaded into a beaker of 2000 mL in the water bath of 35 °C. Ammonia hydroxide (NH_4OH, 25%, diluted 10 times) solution was added drop by drop until the pH reached up to 8 under continuous mechanical stirring. After holding 10 min at 35 °C, the mixture was heated in the water bath from 35 °C to 70 °C and aged for 3 h with maintaining a constant pH of 8 under continuous adding NH_4OH solution. The whole reaction process was under continuous stirring to form the uniform precipitation. After the reaction setup was cooled down to room temperature naturally, the white precipitate obtained was washed repeatedly with distilled water followed by drying under 105 °C for 24 h and calcination at 900 °C for 3 h to obtain monodispersed particles of β-Ga_2O_3.

Other samples were synthesized under similar synthesis conditions except for changing the reaction parameters. The detailed synthesis conditions and corresponding results are recorded in Table 1.

2.2. Characterization

The crystalline phase of the as-prepared particles was characterized on a power XRD (Shimadzu, Japan) equipped with a Cu Kα radiation source (λ=1.5418 Å) at a scan rate of 10 °C/min (2θ from 10° to 70°); X-ray tube voltage and current were set at 40 kV and 30 mA, respectively. The size and morphology of the samples were determined using a field-emission scanning electron microscopy(FESEM, JEOL-7600F) equipped with an energy dispersive spectrometer (EDS) and transmission electron microscope (TEM, Tecnai G2 20) equipped with selected-area electron diffraction (SAED), respectively. The size distribution of the powder was analyzed by a laser diffraction particle size analyzer (Mastersizer 3000, Worcestershire, United Kingdom). Thermogravimetry and differential scanning calorimetry (TG-DSC, STA449F3) were carried out in air with a heating rate of 10 °C/min from room temperature to 1000 °C, to confirm the thermal behavior of the gallium compounds. Cold Isostatic Pressing device (CIP100/320-300, Sichuan) was used to form the β-Ga_2O_3 target. The density of sintered β-Ga_2O_3 target was measured using the Archimedes' method by Mechanical Balance (Accuracy of 1 mg, Shanghai).

Table 1
The detailed synthesis conditions and corresponding results.

Sample	[Ga^{3+}] (M)	Aging temp. (°C)	pH	Aspect ratio[a]	D_{50} (μm)	Morphology
1	0.2	70	8	1.90: 1	2.06	Monodispersed rods
2	0.2	50	8	1.72: 1	1.54	Monodispersed shaped-prisms
3	0.2	30	8	1.77: 1	1.12	Monodispersed ellipsoids
4	0.1	70	8	1.73: 1	1.35	Micro-rods
5	0.3	70	8	1.93: 1	1.50	Micro-rods
6	0.5	70	8	2.04: 1	1.38	Micro-rods
7	0.2	70	4.5	–	–	Irregular morphology
8	0.2	70	10	2.47: 1	1.78	Micro-rods

[a] Aspect ratio: the length size: the wide size (randomly selected 100 β-Ga_2O_3 particles).

3. Results and discussion

3.1. Structural and thermal analysis

Typically monodispersed β-Ga_2O_3 particles were synthesized in mixing solution with $Ga(NO_3)_3$ and NH_4OH as the starting materials through a direct precipitation process aging at 70 °C for 3 h(sample 1). Fig. 1a shows the XRD pattern of the as-prepared GaO_2H precursors and β-Ga_2O_3 annealed at 900 °C. The XRD analysis of other samples is not presented since they all have similar results. All reflection peaks of the obtained gallium compound precursors well agree with the crystalline GaO_2H orthorhombic structure (JCPDS no. 06-0180) with lattice constants a=4.58 Å, b=9.80 Å, c=2.97 Å. Furthermore, the strongest peak of the crystal planes(110) is observed at 2θ=21.48° , indicating that the preferential growth direction of the as-prepared GaO_2H particles is along the [001] direction (c axis), which is in consistent with the previous results by Qian [17]. When the anneal temperature is up to 900 °C, the as-prepared GaO_2H samples are completely converted into the monoclinic β-Ga_2O_3 crystals (JCPDS no. 87-1901) with cell constants a=12.21 Å, b=3.03 Å, c=5.80 Å and β=103.83°, respectively [space group: C2/m]. No other impurity peaks are indexed, revealing that the obtained monoclinic β-Ga_2O_3 crystals are high purity. The (111) main peak of the highest intensity exhibits the preferential planes, which is associated with the characteristics of the anionic close packing nature of β-Ga_2O_3 crystals. Fig. 1b shows the TG-DSC curves of the sample obtained before calcination by heating from room temperature to 1000 °C in air atmosphere with a heating rate of 10 °C/min. A major weight loss is 12.45 wt% from 200 °C to 429 °C in TG curve and the corresponding endothermic peak around 395 °C is detected in DSC curve, probably attributed to the evaporation of absorption water on the surface of the as-prepared precursors and the decomposition of GaO_2H. In this temperature range, the decomposition reaction occurs:

$$2GaO_2H \xrightarrow{395\ ^\circ C} \alpha - Ga_2O_3 + H_2O \quad (1)$$

According to the Eq. (1), the theoretical weight loss is calculated as 8.7 wt%, which is less than the actual value of 12.45 wt%, confirming the above deduction. After the heating temperature up to 429 °C, there is almost no weight loss and the exothermic peak about 758 °C is observed in TG-DSC curves, suggesting the conversion from α- Ga_2O_3 to β-Ga_2O_3 phase (Eq. (2)), which is in good agreement with the XRD analysis and also with the literature [19].

$$\alpha - Ga_2O_3 \xrightarrow{758\ ^\circ C} \beta - Ga_2O_3 \quad (2)$$

3.2. Morphological analysis

Fig. 2a and b show the SEM images of the monodispersed GaO_2H micro-rods and the corresponding β-Ga_2O_3 hierarchical particles obtained after calcination at 900 °C on a large scale, respectively