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Morphology controllable synthesis and characterization of gallium compound hierarchical structures via forced-hydrolysis method

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ABSTRACT

To our best knowledge, β-Ga_2O_3 via hierarchical gallium precursors from nanoparticles to microrods was successfully synthesized for first time using the forced-hydrolysis method and the calcination process. We report the growth mechanism and formation of various morphological gallium precursors such as $Ga_4(OH)_{10}SO_4$ nanospheres and α-GaOOH microrods. The influence of the growth time on the crystal structure and its morphology was studied. The results indicate that the growth time played an important role in the transformation from amorphous to single-crystal structures. After calcination at 1000 °C for 1 h, well-crystallized and porous β-Ga_2O_3 microrods are formed. The enhanced broad blue emission of porous β-Ga_2O_3 microrods were related to defect band emission, such as oxygen vacancies and gallium-oxygen vacancy pairs. We propose that this oriented growth and transformation model may also be applicable to crystal growth and phase transformations and support the fabrication of other three-dimensional hierarchical materials, which is potentially important for a broad range of optoelectronic applications.

1. Introduction

In recent years, designing and controlling the fabrication of metal-oxide semiconductor micro/nanomaterials such as tubes, wires, rods and particles has attracted tremendous attention because of their unique and intriguing size- and shape-dependent electronic and optical properties and geometrical characteristics, and potential technological applications [1–4]. As is well-known, some synthetic methodologies such as template-free, surfactant-assisted, and sol–gel processes have been employed to synthesize various metal-oxide semiconductor hierarchical structures [5–8]. Generally, metal-oxide semiconductor hierarchical structures can be formed by using templates and catalysts to control their orientation and anisotropic growth [9]. But this way of synthesizing the hierarchical structures introduced heterogeneous impurities and increased production costs. The template-free and self-assembled architectures provide an alternative and efficient “bottom up” route to the design and fabrication of hierarchical structures with ideal functional materials and controllable shapes and sizes, by a simple and spontaneous process [10,11].

Gallium oxide (Ga_2O_3) with wide band-gap of ~4.9 eV at room temperature, and which has α-, β-, γ-, δ-, and ε-crystal structures, is widely used as optoelectronic devices, photocatalysis, and solar energy conversion devices [12–14]. Among these phases, the β-Ga_2O_3 monoclinic structure which has a chemically and thermodynamically stable phase and n-type semiconductor received extensive attention because it also has excellent chemical and thermal stability, electric conductivity, and luminescence properties that depend on intrinsic point defects such as oxygen, gallium vacancies, and gallium oxide complex vacancies [15,16]. Moreover, the properties of β-Ga_2O_3 micro/nanomaterials are strongly affected by size, shape and morphology [17]. Among the numerous synthesis procedures for the preparation of Ga_2O_3 crystals, thermal decomposition of Ga_2O_3 precursors such as α-GaOOH crystals is a most convenient and forgiving route. Up to now, extensive research has been carried out to synthesize Ga_2O_3 micro/nanomaterials from morphology-controlled α-GaOOH crystals (rod-like, spindle-like and hollow structures) via wet-chemical processes such as hydrothermal treatments, sonochemical reactions, forced hydrolysis, and the sol–gel method [18–20]. To our knowledge, although the fabrication of Ga_2O_3 micro/nanomaterials with different morphologies have been reported by several groups [21–23], the growth

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and phase-change mechanism of Gallium precursors via the forced-hydrolysis method are rarely reported.

Herein, we successfully fabricated monodispersed nanospheres (NSs) and microrods of β-Ga_2O_3 under different experimental procedures via forced-hydrolysis method. We report first the synthesis and in-situ growth mechanism, from amorphous NSs to crystalline α-GaOOH microrods, under controlled experimental conditions. In addition, detailed characterization of the samples' morphology, structural and optical properties were investigated.

2. Experimental

2.1. Synthesis of hierarchical gallium precursors and Ga_2O_3

The mixed solution was prepared by dissolving reagent-grade $Ga_2(SO_4)_3 \bullet xH_2O$ (Sigma–Aldrich, 99.99%), $Ga(NO_3)_3 \bullet xH_2O$ (Sigma–Aldrich, 99.9%), and urea powder (Sigma–Aldrich) in 100 mL of deionized water. Briefly, gallium nitrate, sulfate (Ga^{3+} concentration of 0.01 M), and urea (0.1 M) were dissolved in deionized water. Rod-like structures of *α*-GaOOH and spherical $Ga_4(OH)_{10}SO_4$ precursors were obtained after aging (2–10 hour) the mixture in a 98 ± 1 °C oil bath, with R = 0.33 ($R = SO_4^{2-}/NO_3^-$) concentration ratios. The precipitate was separated by centrifugation, then washed three times with deionized water and ethanol to remove excess surfactants, and then freeze dried at −110 °C. Using the forced-hydrolysis method, the prepared monodispersed $Ga_4(OH)_{10}SO_4$ precursors and α-GaOOH microrods were calcined in air at 1000 °C for 1 hour to transform them in to β-Ga_2O_3.

2.2. Materials characterization

The surface morphology of the hierarchical gallium precursors as a function of growth time was observed by using a field-emission scanning electron microscopy (FESEM, JEOL 7500F). High-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) mapping was carried out using a JEM2100F with an accelerating voltage of 200 kV. The crystallinity and structure of the hierarchical gallium precursors and *β*-Ga_2O_3 were examined by powder X-ray diffraction (PDR-XRD, Bruker D8 FOCUS) using CuKα radiation. Fourier transform infrared (FTIR, Bruker IFS-66/S) spectroscopy was employed to analyze the chemical bonding within the materials. Thermogravimetry and differential thermal analysis (TG-DTA, Seiko Exstar) was performed in air at a heating rate of 5 °C/min from 30 to 1000 °C, to confirm the reaction of gallium precursors and the crystallization of β-Ga_2O_3. The optical property of β-Ga_2O_3 microrods and nanospheres were analyzed using a room temperature cathodoluminescence (MONO CL3+, GATAN) equipped with excitation energy 10 keV, respectively.

3. Results and discussion

Fig. 1 shows TEM, HAADF-STEM, HRTEM images (inset SAED patterns) and PXRD patterns obtained from the crystalline β-Ga_2O_3 via thermally-treated $Ga_4(OH)_{10}SO_4$ NSs and α-GaOOH microrods. The β-Ga_2O_3 NSs and microrods preserved their initial shapes at the calcination temperature of 1000 °C. The prepared monodispersed β-Ga_2O_3 NSs (200 nm) consist of small particles of approximately 50 nm with rough surfaces, as shown in Fig. 1a and b. The HRTEM image (inset SAED pattern) in Fig. 1c indicate the monodispersed β-Ga_2O_3 NSs are constructed, with good crystallinity, of small particles with an interplanar spacing of about 0.287 nm that corresponds to the (002) crystal plane of monoclinic β-Ga_2O_3. The formation of these nanopores inside rods and β-Ga_2O_3 nanoparticles as shown on Fig. 1d and e were attributed to the large volume loss (ca. 20%) due to the dihydroxylation of α-GaOOH and recrystallization [24]. The clearly-resolved interplanar distances are measured to be 0.253 and 0.281 nm, corresponding to the (111) and (002) crystal planes of monoclinic β-Ga_2O_3.

All the diffraction peaks at 1000 °C are in good accordance with the monoclinic crystalline β-Ga_2O_3 structure (JCPDS 41-1103), and the intensity of the peaks indicates the high crystallinity of the β-Ga_2O_3 NSs and microrods, as shown Fig. 1g. This result suggests that the amorphous $Ga_4(OH)_{10}SO_4$ and crystalline α-GaOOH precursors were perfectly crystallized and deformed to β-Ga_2O_3 after the calcination process. To evaluate the thermal stability, Fig. 1h shows the thermal degradation patterns of the gallium precursors in air. Total weight losses of 33.8 and 16.1% were noticed for $Ga_4(OH)_{10}SO_4$ NSs and α-GaOOH microrods, respectively. A slow loss of weight at ~270 °C could be accounted for by the dehydration of the surface-bound hydroxyl group, and a sharp loss of weight at ~398 °C is attributable to the constitutional hydroxyl group at α-GaOOH microrods [25]. A gradual weight loss of 2% in the range 500–800 °C indicates the phase change to β-Ga_2O_3. However, for $Ga_4(OH)_{10}SO_4$ NSs, a sharp loss of weight occurs at 700–800 °C due to the decomposition of sulphate ions with the evolution of SO_3 from the surface and from inside the bonded sulfate and Ga ions [26].

We have reported that the growth mechanism of monodispersed $Ga_4(OH)_{10}SO_4$ NSs with different ratio $R = SO_4^{2-}/NO_3^-$ [27]. Furthermore, the controlled morphology of the gallium precursors as a function of growth time, from 2 to 10 hour, was investigated using FESEM at Fig. 2a–e when the concentration ratio $R = SO_4^{2-}/NO_3^-$ was kept at 0.33. To investigate the growth mechanism of the single-crystal α-GaOOH microrods, the growth processes were systematically studied by analyzing the as-prepared samples at different times from the start. Uniform spherical precursors with average diameters of around 200 nm in Fig. 2a were fabricated with gallium salts containing sulfate and nitrate ions in the presence of urea, after 2 hours of reaction. The α-GaOOH rod structures are constructed of lots of small nanoparticles and the nanoparticles were coherently assembled into microrods. After the reaction time was increased to 6 hours, the microrod structures dominated. Furthermore, the size of the α-GaOOH microrods was increased as the sizes of the NSs were decreased. That suggests that uniform spherical nanoparticles as Ga precursors were dissolved in the solution and aggregated with each other or on the surfaces of the micorods. At a reaction time of 10 h, well-defined α-GaOOH microrods were formed that had prismatic shapes with specific facets. The crystal structure and phase purity of the as-prepared samples of Fig. 2d were examined by PXRD as a function of growth time. The PXRD pattern of $Ga_4(OH)_{10}SO_4$ NSs indicates that at 2 hours there are no obvious diffraction peaks because the synthesized gallium NS precursors are amorphous and cannot be deformed into well-crystallized α-GaOOH microrods via crystallization and transformation of the amorphous gallium NS precursors. With increasing growth time, the strong and sharp diffraction peaks can be easily assigned to a pure α-GaOOH (space group Pbnm) phase corresponding to an orthorhombic structure (JCPDS Card 06-0180) with the cell parameters a = 4.58 Å, b = 9.80 Å, and c = 2.97 Å. In addition, no additional peaks from contamination or other impurity phases such as $Ga(OH)_3$ were noted, indicating that with further growth time the synthesized samples are not only entirely composed of high purity α-GaOOH phase but also the transformation of the amorphous gallium NS precursors is complete. Meanwhile, we observed that the ratios of the intensities of the (110) and (111) peaks have different values 1.5–3.47 as a function of growth time, which indicates the possibility of different preferential orientation growth along the [001] direction at different growth times [28,29].