Synthesis and Characterization of Monodispersed $\beta$-Ga$_2$O$_3$ Nanospheres via Morphology Controlled Ga$_4$(OH)$_{10}$SO$_4$ Precursors

Bong Kyun Kang,† Hyeong Dae Lim,‡ Sung Ryul Mang,‡ Keun Man Song,† Mong Kwon Jung‡ and Dae Ho Yoon§†§

†School of Advanced Materials Science and Engineering and‡SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea
§R&D Business Laboratories, Hyosung Corporation, Anyang 431-080, Republic of Korea

ABSTRACT: To our best knowledge, monodispersed $\beta$-Ga$_2$O$_3$ nanospheres were successfully synthesized for first time via morphology-controlled gallium precursors using the forced hydrolysis method, followed by thermal calcination processes. The morphology and particle sizes of the gallium precursors were strongly dependent on the varying ($R = \text{SO}_4^{2-}/\text{NO}_3^-$) concentration ratios. As $R$ decreased, the size of the prepared gallium precursors decreased and morphology was altered from sphere to rod. The synthesized S2 ($R = 0.33$) consists of uniform and monodispersed amorphous nanospheres with diameters of about 200 nm. The monodispersed $\beta$-Ga$_2$O$_3$ nanospheres were synthesized using thermal calcination processes at various temperatures ranging from 500 to 1000 °C. Monodispersed $\beta$-Ga$_2$O$_3$ nanospheres (200 nm) consist of small particles of approximately 10−20 nm with rough surface at 1000 °C for 1 h. The UV (375 nm) and broad blue (400−450 nm) emission indicate recombination via a self-trapped exciton and the defect band emission. Our approach described here is to show the exploration of $\beta$-Ga$_2$O$_3$ nanospheres as an automatic dispersion, three-dimensional support for fabrication of hierarchical materials, which is potentially important for a broad range of optoelectronic applications.

INTRODUCTION

In recent years, increasing interest has been given to the synthesis of metal-oxide semiconductor nanomaterials such as nanotubes, nanowires, nanoparticles, and hollow nanostructures.1−4 Especially, metal-oxide semiconductor nanomaterials are attractive candidates as active elements for advanced nanoscale devices due to their unique electronic and optical properties, low effective density, high specific surface area, and shell permeability that are important in many technology applications such as catalysis, photonics, sensors, solar energy conversion, and electrochemical energy storage.5−9

To date, many chemical methods such as template-free, surfactant-assisted, and salt-mediated processes have been developed for the synthesis of various metal-oxide semiconductor nanostructures through controlling the reaction rates and selectively altering the growth kinetics of different crystal facets using different molecular precursors, capping agents, and organic surfactants at reaction temperatures for certain growth times.10−12 However, simple and effective synthesis routes for the preparation of metal-oxide nanomaterials need to be intensively re-examined to improve their unique properties with controllable morphology, size, desired chemical composition, and structural features.

Among the various semiconductor nanostructures, gallium oxide (Ga$_2$O$_3$) with $\alpha$, $\beta$, $\gamma$, $\delta$, and $\varepsilon$-crystal structures, and which has a wide band gap of 4.9 eV at room temperature, is a promising candidate material for transparent conducting oxide, electroluminescent devices, photocatalysis, and gas sensors.13−15 Among these phases, the thermodynamically stable phase of the $\beta$-Ga$_2$O$_3$ monoclinic structure has received attention because it also has excellent chemical and thermal stability, electric conductivity, and luminescence properties that depend on the native oxygen, gallium vacancies, and gallium oxide complex vacancies.16

The forced hydrolysis method provides an especially promising homogeneous chemical precipitation route for large-scale production of nanosized and well dispersed metal hydrous particles.17,18 However, to our knowledge, no attempt was made in the reports to synthesize monodispersed gallium hydrate nanospheres (NSs) by changing the ratio of sulfate and nitrate ions using both the forced hydrolysis method at low temperature and the phase transition of gallium hydrate precursor to $\beta$-Ga$_2$O$_3$ nanostructures by heat treatment.

In this study, we synthesized the monodispersed Ga$_4$(OH)$_{10}$SO$_4$ precursors by controlling the various experiment conditions. The effect of sulfate ions was intensively studied throughout the forced hydrolysis method. The sulfate ions play an important role as a regulator that can mediate the nucleation and growth of the precursors. Also, the characterization of the monodispersed $\beta$-Ga$_2$O$_3$ NSs was confirmed at various firing temperatures. This study therefore suggests a...
synthesis strategy of monodispersed metal oxide NSs or hierarchical materials to extend their applications.

■ EXPERIMENTAL SECTION

Synthesis of GaOOH, Ga₄(OH)₁₀SO₄ Precursors, and Monodispersed β-Ga₂O₃ NSs. The mixed solution was prepared by dissolving reagent grade of Ga₂(SO₄)₃·xH₂O (Sigma-Aldrich, 99.99%), Ga(NO₃)₃·xH₂O (Sigma-Aldrich, 99.9%), and urea powder (Sigma-Aldrich) in 100 mL of deionized water. Briefly, gallium nitrate, sulfate (Ga³⁺ concentration of 0.01 M), and urea (0.1 M) were dissolved in deionized water. Rodlike structures of GaOOH and spherical Ga₄(OH₁₀)SO₄ precursors were obtained after aging the mixture in a 98 ±1 °C oil bath for 2 h, at varying (SO₄²⁻/NO₃⁻) 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 Ga₄(OH)₁₀SO₄ precursors were calcined in an air atmosphere as a function of firing temperatures from 500 to 1000 °C for 1 h.

Characterization. The surface morphology of the precursors and the monodispersed β-Ga₂O₃ NSs as a function of firing temperatures were observed using field-emission scanning electron microscopy (FESEM, JEOI 7500F). Scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM) were carried out using a JEM2100F with an accelerating voltage of 200 kV. The crystallinity and structure of the precursors and β-Ga₂O₃ NSs were examined by powder X-ray diffraction (PXRD, Bruker D8 FOCUS) using Cu Kα radiation. Fourier transform infrared (FTIR, Bruker IFS-66/S) spectroscopy was employed to analyze the chemical bonding within the materials. The thermogravimetry–differential thermal analysis (TG-DTA, Seiko Exstar) was measured in air at a heating rate of 5 °C/min from 30 to 1000 °C to confirm the reaction of Ga₄(OH)₁₀SO₄ precursors and crystallization of β-Ga₂O₃ NSs. The optical properties of the monodispersed β-Ga₂O₃ NSs were analyzed using a room temperature cathodoluminescence (MONO CL3+, GATAN) equipped with an excitation energy of 10 keV.

■ RESULTS AND DISCUSSION

The monodispersed spherical Ga₄(OH)₁₀SO₄ precursors were conveniently obtained at 98 ±1 °C for 2 h before calcination. Uniform spherical precursors with average diameters around 200 nm were fabricated with gallium salts containing sulfate and nitrate ions in the presence of urea. The total concentrations of Ga³⁺ ions and urea were fixed at 0.01 and 0.1 M, respectively, and the concentration ratio R = SO₄²⁻/NO₃⁻ was fixed at 0.33. The types of starting materials and various concentration ratios effect not only the morphologies but also the crystalline phase of the gallium precursors. The changed ratios of the gallium salts are listed in Table S1.

The controlled morphology of the gallium precursors as a function of concentration ratios was investigated using FESEM. When only using the gallium nitrate starting materials, the precursors (sample S1) have prismatic rod structures and smooth faceted surfaces with diameters in the range of 200–400 nm and lengths of about 1.5–2 μm (Figure 1a). Figures 1b and 1c show that complete precursors (sample S2) and aggregated precursors (sample S3) were formed with increasing gallium sulfate. Moreover, the size of these precursors gradually increased as the concentration ratio (SO₄²⁻/NO₃⁻) of the reactant solution increased (Figure S1). Also, these experimental results suggest that gallium sulfate played an important role in imparting the spherical morphology.
role in the controlled morphology, size, and dispensability of the gallium precursors.

Figures 1d–1h show TEM, scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS) mapping images as well as the EDS spectrum of the monodispersed gallium precursors (sample S2). The TEM image (Figure 1d) indicates that the synthesized S2 consists of uniform and monodispersed amorphous precursors with diameters of about 200 nm. It can be clearly seen from the element mapping in the EDS mapping images that the elements of Ga, O, and S clearly existed in the S2. The EDS mapping result shows the relative locations of Ga, O, and S within the precursors. The Ga and S atoms appear in the same positions with similar diameters, demonstrating that the Ga and S atoms were combined as $\text{Ga}_4(\text{OH})_{10}\text{SO}_4$ precursors. The element mapping of C is not shown because a large amount of C existed in the support film of the TEM grid.

Based on the above experiments, it can be seen that the $\text{SO}_4^{2-}$-mediated precipitation process involves the formation of $\text{Ga}_4(\text{OH})_{10}\text{SO}_4$ precursors followed by several growth steps, as illustrated in Figure 2. Sequential hydrolysis and homogeneous nucleation occurred and formed spheres similar to the precursors which are amorphous $\text{Ga}(\text{OH})_3$. In the case of the $\text{Ga}(\text{OH})_3$ precursors without $\text{SO}_4^{2-}$ ions, the amorphous $\text{Ga}(\text{OH})_3$ precursors such as negatively charged complexes of $\text{Ga}(\text{OH})_4$ were dissolved as temperatures increased up to 98 °C because the urea decomposed at around 80 °C and released uniform $\text{H}_2\text{O}$ ions into the solution. Furthermore, the increase in the pH caused enhanced gelation and increased the polymeric sizes. By prolonging the refluxing at high pH and aging time, the $\text{Ga}(\text{OH})_4$ aqueous solution spontaneously formed aggregated crystalline GaOOH rod structures.19,26 However, in the case of the $\text{Ga}(\text{OH})_3$ precursors with $\text{SO}_4^{2-}$ ions, the amorphous $\text{Ga}(\text{OH})_3$ precursors were precipitated and polymerized with a spherical shape. The better coordination bond strength and higher affinity of $\text{SO}_4^{2-}$ than $\text{NO}_3^-$ ions can cause a spherical composition of $\text{Ga}_4(\text{OH})_{10}\text{SO}_4$ and result in a favorable formation of spherical amorphous precursors. In addition, the amorphous $\text{Ga}_4(\text{OH})_{10}\text{SO}_4$ precursors are neutral, and the compact primary particles resulted in the morphological transformation of the amorphous $\text{Ga}_4(\text{OH})_{10}\text{SO}_4$ and aggregated individual fine precursors (Figure S2).21,22 The crystallinity, chemical bonds, and thermal analysis of gallium precursors were further conformed by PXRD, FTIR, and TG-DTA analysis (Figures S3, S4, and S5).

Figure 3a shows the PXRD patterns of the $\beta$-$\text{Ga}_2\text{O}_3$ NSs after firing from 600 to 1000 °C for 1 h. The PXRD pattern of the $\beta$-$\text{Ga}_2\text{O}_3$ NSs indicates no obvious diffraction peaks occurred because the prepared $\text{Ga}_4(\text{OH})_{10}\text{SO}_4$ precursors are amorphous and cannot be deformed by the crystalline $\beta$-$\text{Ga}_2\text{O}_3$ at insufficient temperatures at 600 °C. The PXRD patterns at 1000 °C were easily indexed to the monoclinic crystalline $\beta$-$\text{Ga}_2\text{O}_3$ (JCPDS Card 41-1103). The PXRD patterns for the $\beta$-$\text{Ga}_2\text{O}_3$ NSs at firing temperatures of 800 °C could barely be indexed because of the residual $\text{SO}_4$ ions in the $\beta$-$\text{Ga}_2\text{O}_3$ NSs and the low-intensity peaks of $\beta$-$\text{Ga}_2\text{O}_3$ with a large full width at half-maximum (fwhm). The fwhm of the PXRD peaks for the $\beta$-$\text{Ga}_2\text{O}_3$ NSs decreased with increasing firing temperatures.
ranging from 600 to 1000 °C. This result was attributed to the fact that the amorphous Ga$_2$(OH)$_{10}$SO$_4$ precursors were perfectly crystallized after the firing temperatures were controlled (Figure S6). The intensities of the diffraction peaks sharply increased due to the enhanced crystallization and crystallite growth.23 In addition, the grain sizes of β-Ga$_2$O$_3$ nanospheres were calculated using the Scherrer equation (1) based on the XRD patterns.24

\[ t = 0.9\lambda /B \cos \theta \]  
(1)

A calculated grain size is \( t \), and \( \lambda = 1.54056 \) Å is the X-ray wavelength. 0.9 is a constant for spherical particles, and \( B \) is the fwhm for the diffraction angle. The grain sizes of the β-Ga$_2$O$_3$ nanospheres hollow NSs were 20.19 nm at a firing temperature 1000 °C. Figure 3b shows the FTIR spectra in the 4000–400 cm$^{-1}$ region of the β-Ga$_2$O$_3$ NSs after firing from 600 to 1000 °C. The vibration modes of the β-Ga$_2$O$_3$ NSs are attributed to the symmetric stretching of the S=O (1106 cm$^{-1}$) vibrations by the strong bond with Ga(OH)$_3$ during the forced hydrolysis treatment.25 The results suggest that the component of the prepared S2 consists of Ga$_4$(OH)$_{10}$SO$_4$. With increasing firing temperatures, the absorption peak at 1106 cm$^{-1}$ was drastically decreased. Strong absorption peaks positioned at 466 and 681 cm$^{-1}$ (Ga–O stretching vibration) are identified in the β-Ga$_2$O$_3$ NSs obtained above 600 °C for 1 h.26 These results are in good agreement with the PXRD results and revealed the formation of crystalline β-Ga$_2$O$_3$ NSs using firing conditions. Furthermore, the FTIR spectra show a broad absorption band of the –OH group (1631, 3443 cm$^{-1}$), which results from the remaining –OH ions or the H$_2$O absorbed by the β-Ga$_2$O$_3$ NSs when the samples were analyzed at room temperature in air.27

The amorphous spherical precursor S2 can crystallize into β-Ga$_2$O$_3$ NSs after the calcination process at 1000 °C for 1 h in air. The prepared monodispersed β-Ga$_2$O$_3$ NSs consist of small particles of approximately 20–50 nm with rough surface, as shown in Figure 4a. The average particle size of the β-Ga$_2$O$_3$ NSs is around 200 nm. However, no necking phenomenon was observed between particles. According to the FESEM images, the porous and granular particles without necking were attributed to the decomposition of sulfate ions on the S2 at around 1000 °C.28 The HRTEM image in Figure 4b reveals the monodispersed β-Ga$_2$O$_3$ NSs are constructed by the good crystallinity of small particles. The interplanar spacing of about 0.2967 nm corresponds to the (400) crystal plane of monoclinic β-Ga$_2$O$_3$, which agreed well with the PXRD patterns shown in Figure 3a.

A broad blue emission band from 300 to 600 nm was observed over the 700 °C. A strong blue emission peak was centered at around 400–450 nm up to 900 °C. In addition, a UV emission at around 375 nm suddenly increased at 1000 °C, which resulted from the enhanced recombination via a self-trapped exciton.29 Furthermore, the blue emission of β-Ga$_2$O$_3$ indicates the defect band emission due to the vacancies in the β-Ga$_2$O$_3$ structure, such as oxygen vacancies (donor band), gallium vacancies, and gallium–oxygen vacancy pairs (acceptor band). It was suggested that the emission peak originated from the recombination of an electron on a donor with a hole on an acceptor formed by an oxygen and gallium or gallium–oxygen vacancy pair in the β-Ga$_2$O$_3$ crystal structures.30–32

CONCLUSION

The monodispersed β-Ga$_2$O$_3$ NSs were successfully synthesized by facile and reproducible by urea based forced hydrolysis method using gallium sulfate and nitrate as starting materials. The morphology of gallium precursors was controlled by the molar ratio of sulfate and nitrate. We obtained uniform and monodispersed spherical Ga$_4$(OH)$_{10}$SO$_4$ precursors at \( R = 0.33 \). As \( R \) decreased, the size of the prepared gallium precursors decreased and morphology was altered from sphere to rod. The formation of uniform polycrystalline β-Ga$_2$O$_3$ NSs with diameters of about 200 nm at 1000 °C for 1 h were

Figure 4. FESEM image (a) inset STEM image and HRTEM images (b) inset corresponding fast Fourier transform patterns of sample S2 calcined at 1000 °C for 1 h in air.

Figure 5. Cathodoluminescence (CL) spectra of the β-Ga$_2$O$_3$ NSs as a function of the firing temperatures ranging from 500 to 1000 °C for 1 h in air.
confirmed by FESEM, STEM, and HRTEM analysis. The UV and broad blue emission indicate recombination via a self-trapped exciton and the defect band emission due to the vacancies in the β-Ga2O3 structure, such as oxygen vacancies (donor band), gallium vacancies, and gallium–oxygen vacancy pairs (acceptor band). Further works are being carried out to explore the potential application of these monodispersed nanoparticles as photocatalysts and optical device.

**ASSOCIATED CONTENT**

1. **Supporting Information**

Tables summarizing experimental details for sample preparation, FESEM images, illustration of the demonstration and morphology evolution, PXRD, FTIR, and TG-DTA data of the gallium precursors, PXRD, FTIR, CL data and representative band-structure scheme for the UV and blue luminescence in β-Ga2O3 nanocrystals. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*Corresponding Author*

*Tel +82-31-290-7361; Fax +82-31-290-7410; e-mail dhyoon@skku.edu (D.H.Y.).

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF- 2013R1A2A2A01010027).

**REFERENCES**


