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Introduction

Gallium oxide (Ga_2O_3) and nitride (GaN) are wide band-gap semiconductors with energy gaps of \sim 4.6 and \sim 3.4 eV, respectively.^{1,2} Both have attracted considerable interest for potential applications in spintronic, electronic and optoelectronic devices due to their intrinsic properties.3-7 The morphologies of these materials show significant impacts on their properties, and, therefore, they have received extensive attention in past decades.8-10 Various morphologies of GaN nanocrystals, e.g. nanowires, nanorods, nanotubes, nanobelts and nanohollows, have been successfully constructed and applied as electronic or optoelectronic devices.11-16 For example, Fan et al. prepared GaN nanorods through a confined reaction by using Ga₂O vapour and NH₃ gas in the presence of carbon nanotubes as templates.¹¹ Yang et al. developed a chemical vapour deposition route to synthesize single GaN nanowire on sapphire substrate and further explored its promising applications in lasers.14 Subsequently, they reported the epitaxial growth of single-crystal GaN nanotubes by adopting hexagonal ZnO nanowires as templates also through chemical vapour deposition.¹⁷ Chou et al. prepared GaN nanobelts through Au-assisted nucleation and non-Au-assisted anisotropy vaporsolid growth on LiAlO₂ substrate.¹⁸ In addition, other strategies, e.g. metalorganic vapor phase epitaxy19 and rapid thermal ammonolysis of complex gallium fluoride,^{20,21} have been reported for the synthesis of GaN and doped GaN nanostructures.

through nitridation at elevated temperatures, which provides a top-down strategy to gallium oxide and nitride nanocrystals. The synthesis results are investigated by means of X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical properties, *i.e.* ultra-violet visible absorption (UV-vis) and photoluminescence, of as-obtained α -Ga₂O₃ nanocrystals with different morphologies are examined and the morphology–property relationship is discussed. According to these reports, it can be seen that the synthesis of GaN nanostructures always involves expensive and/or poisonous reagents, templates or substrates, and complicated processes.¹⁸⁻²³ It is known that the nitridation of Ga₂O₃ represents a most simple strategy to free-standing GaN material. Theoretically, the morphology of parent Ga₂O₃ material can be preserved under controlled nitridation conditions, which provides a top-down morphology control strategy to GaN. It has been already reported that Ga₂O₃ nanorods can be synthesized *via* a thermal decomposition method using GaOOH nanorods.²⁴ Moreover,

A simple synthesis of Ga_2O_3 and GaN nanocrystals⁺

The synthesis of gallium oxide and nitride nanocrystals is challenging. Herein, a forced hydrolysis route is developed to synthesize α -GaOOH and the morphology control of nanocrystals is realized by adjusting the ratios of ionic strength in the synthesis system. The as-prepared α -GaOOH nanorods can be transformed into α -Ga₂O₃ nanorods upon calcination and can be further transformed into GaN nanocrystal assemblies

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Inspired by these achievements, we herein report a so-called forced hydrolysis route to GaOOH nanorods, which can be transformed to Ga_2O_3 nanorods through calcination and be further transformed to GaN nanocrystal assembles through nitridation. During the forced hydrolysis process, the hydroxyls are produced from urea decomposition²⁶ and morphology control of GaOOH is realized by adjusting the ratio of ionic strength in the synthesis system.

GaN nanoparticles can be produced from Ga₂O₃ nanoparticles

under a flow of ammonia gas at elevated temperatures.25

Experimental

Synthesis of Ga_2O_3 and GaN samples

All the chemical reagents were of analytical reagent grade and directly used without further purification. GaOOH was prepared *via* a forced hydrolysis route starting from solution containing $Ga(NO_3)_3$ and $NaNO_3$ with different ionic strength ratios (see below for details).

Ionic strength (*I*) is calculated by the formula of $I \underline{\det} \frac{1}{2} \sum_{B} m_{B} z_{B}^{2}$, where m_{B} is the molality of an ion *B* in the solution and Z_{B} is its charge number (positive for cations and

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negative for anions). The ratio of ionic strength (R) is defined as $R = \frac{I_1}{I_2}$, where I_1 represents the ionic strength of Ga(NO₃)₃ in the solution and I₂ represents the ionic strength of NaNO₃ in the solution.

In a typical synthesis, an appropriate amount of $Ga(NO_3)_3 \cdot nH_2O$ and urea were dissolved into a small amount of deionized water (the molar ratio of $Ga(NO_3)_3 \cdot nH_2O$ and urea being kept at 1:6) and heated to 90 °C. More deionized water was then added to reach a final molarity of urea is $0.18 \text{ mol } \text{L}^{-1}$ $(Ga^{3+} of 0.03 mol L^{-1})$ and the temperature was kept at 90 °C for 9 h to initiate forced hydrolysis. The solid product was centrifuged, thoroughly washed, dried and defined as GaOOH ($R = \infty$). The as-obtained GaOOH was calcined in the vacuum at 450 °C to derive Ga₂O₃, which was further nitridized in NH₃ flow $(100 \text{ mL min}^{-1})$ at 950 °C for 6 h to derive GaN. With the addition of NaNO₃ into $Ga(NO_3)_3 \cdot nH_2O$ solution at different ionic strength ratios, GaOOH products (R = 3, 2, 1, 0.5, 0.3 or 0.2), were obtained, which could also be transformed to Ga2O3 and GaN samples (R = 3, 2, 1, 0.5, 0.3 or 0.2) via identical procedures.

For reference, commercial Ga₂O₃ (defined as Raw) was nitridized at 950 °C for 6 h to derive GaN.

Characterization of Ga₂O₃ and GaN samples

The X-ray diffraction (XRD) patterns of samples were acquired on a Rigaku Smart Lab 3 kW powder diffractometer with Cu Ka radiation ($\lambda = 0.1542$ nm) at a scanning rate of 6° min⁻¹.

The specific surface areas of samples were determined through N₂ physisorption at 77 K on a Quantachrome iQ-MP gas adsorption analyzer.

Scanning electron microscopy (SEM) images of Ga2O3 and GaN samples were obtained on a JSM-7500F electron microscope.

Transmission electron microscopy (TEM) and highresolution transmission electron microscopy (HRTEM) images of Ga₂O₃ and GaN samples were obtained on a FEI Tecnai G² F20 electron microscope at 200 kV. Alcohol suspensions containing the Ga₂O₃ or GaN were dropped onto a carbon-coated copper grid, followed by evaporation at ambient temperature.

The Raman spectra of Ga2O3 and GaN were recorded on a Renishaw InVia Raman spectrometer with the green line of an Ar-ion laser (514.53 nm) in micro-Raman configuration.

Diffuse reflectance ultra-violet visible absorption (UV-vis) spectra of Ga2O3 and GaN samples were performed on a Varian Cary 300 UV/vis spectrophotometer.

Photoluminescence spectra of Ga₂O₃ and GaN samples were acquired on a Spex FL201 fluorescence spectrophotometer. Selfsupporting wafers of samples (ca. 100 mg) were excited by 270 nm laser and the spectra were recorded in vacuum at ambient temperature.

Results and discussion

The XRD patterns of GaOOH, Ga2O3 and GaN samples prepared at R = 1 are shown in Fig. 1. It can be seen that pure orthorhombic phase α-GaOOH is obtained from forced hydrolysis (JCPDS no. 06-0180; a = 4.58 Å, b = 9.80 Å, c = 2.97 Å). GaOOH can be



Fig. 1 XRD patterns of GaOOH, Ga₂O₃ and GaN prepared at R = 1.

transformed to pure hexagonal phase α -Ga₂O₃ (JCPDS no. 06-0503; a = b = 4.98 Å, c = 13.43 Å) upon calcination at 450 °C and Ga₂O₃ can be transformed to pure hexagonal phase GaN (JCPDS no. 50-0792; a = b = 3.19 Å, c = 5.19 Å) upon nitridation at 950 °C. These results clearly demonstrate the feasibility of Ga2O3 and GaN synthesis through a so-called top-down strategy.

Fig. 2 shows the XRD patterns of Ga₂O₃ samples synthesized via forced hydrolysis at different R values and followed by calcination. All the samples exhibit similar diffraction peaks of α -Ga₂O₃ (JCPDS no. 06-0503), a monoclinic system and C2/m space group with a = b = 4.98 Å and c = 13.43 Å as its cell parameters.27 No diffraction peaks corresponding to impurity phases can be observed in all cases. We notice that, however, the intensities of diffraction peaks of Ga₂O₃ samples synthesized at different R values are different, indicating that different morphologies and/or crystallinities were obtained for these Ga_2O_3 samples. With increasing R value from 0.2 to 1, the



Fig. 2 XRD patterns of Ga₂O₃ synthesized at different *R* values and Raw Ga₂O₃.



Fig. 3 XRD patterns of GaN from the nitridation of Ga₂O₃ synthesized at different R values and Raw Ga₂O₃.

relative crystallinity increases distinctly, while the relative crystallinity decreases with further increase in R value. That is, Ga₂O₃ with highest crystallinity can be obtained with optimized ionic strength ratio of 1 during forced hydrolysis.

Raman spectroscopy is further employed to determine the structure of as-prepared Ga₂O₃ samples. As shown in Fig. S1,† Raman bands at 410, 560 and 700–710 cm^{-1} are observed in the 300–1000 cm⁻¹ region, corresponding to the E_g, A_{1g} and E_g modes of α-Ga₂O₃, respectively.^{1,28} The Raman bands broadening and the noticeable shifts of bands at 700-710 cm⁻¹ are due to the presence of surface defects on the samples.

The XRD patterns of GaN samples from the nitridation of different Ga₂O₃ samples are shown in Fig. 3. Pure GaN phase of wurtzite structure and $P6_3mc$ space group with a = b = 3.189 Å and c = 5.185 Å as its cell parameters is obtained in all cases.²⁷ We also notice the different intensities of diffraction peaks, similar to the trend observed for Ga2O3 samples. It can be proposed that the morphologies and crystallinities of Ga₂O₃ samples are preserved, at least partially preserved, through nitridation at elevated temperature of 950 °C. Raman spectra of GaN samples are presented in Fig. S2[†] and a series of Raman bands can be observed in the 300–1000 cm⁻¹ region. The band at 420 cm⁻¹ is related to the N-rich structure of GaN,²⁹ while the shifts of other Raman bands, e.g. at 515, 595 and 695 cm⁻¹, compared with standard hexagonal GaN, should be related to the formation of abundant defects on the surface.²⁰

The SEM images of Ga₂O₃ samples synthesized by forced hydrolysis at different R values are shown in Fig. 4. It is very clear that different morphologies are obtained at different ratios of ionic strength during forced hydrolysis, i.e. R values. At $R = \infty$, Ga₂O₃ crystals appear as spindle-like nanorods with two narrow sides and a wide center (Fig. 4a). At R = 3 and 2, Ga₂O₃ crystals appear as nanorods with the same broad sides and center (Fig. 4b and c). With decreasing R value to 1, Ga_2O_3 crystals transform to dumbbell-shaped nanorods with two wide sides and narrow center (Fig. 4d). Further decrease in the ratio

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Fig. 4 SEM images of Ga₂O₃ synthesized at different R values: $R = \infty$ (a); R = 3 (b); R = 2 (c); R = 1 (d); R = 0.5 (e); R = 0.3 (f); R = 0.2 (g) and Raw Ga₂O₃ (h).

of ionic strength during forced hydrolysis (R = 0.5 and 0.3) results in the exfoliation of nanorods to nanoplates and strips and fragments (Fig. 4e and f). At R = 0.2, the Ga₂O₃ crystals are totally broken up to fragments. According to the SEM images of Ga_2O_3 samples synthesized at different R values, we can infer that the crystallinities of Ga₂O₃ samples vary with *R* values. The highest crystallinity of Ga₂O₃ sample is obtained at the R value of 1, in accordance with the results from XRD patterns (Fig. 2). The surface areas of Ga_2O_3 samples synthesized at different R values are measured to be in the range of $30-50 \text{ m}^2 \text{ g}^{-1}$, distinctly higher than commercial Ga_2O_3 (15 m² g⁻¹).

Fig. 5 shows the SEM images of GaN samples obtained from the nitridation of Ga₂O₃ samples. It is seen that the overall shape of GaN sample follows its Ga₂O₃ precursor. However, after careful observation, we find that some tiny nanoparticles do exist on the external surface of GaN crystals. These observations indicate that nitridation starts from a local point of Ga₂O₃ crystal. The surface areas of as-obtained GaN samples are measured to be 40–60 m² g⁻¹, even higher than parent Ga_2O_3 $(30-50 \text{ m}^2 \text{ g}^{-1})$ due to the formation of tiny nanoparticles on the surface. To confirm the phase purity of as-obtained GaN samples, the energy-dispersive X-ray mapping analysis was



Fig. 5 SEM images of GaN from the nitridation of Ga₂O₃ synthesized at different *R* values: $R = \infty$ (a); R = 3 (b); R = 2 (c); R = 1 (d); R = 0.5 (e); R = 0.3 (f); R = 0.2 (g) and Raw Ga₂O₃ (h).

performed on representative GaN sample (R = 1). As shown in Fig. S3,† the homogeneous distribution of Ga and N species in selected GaN crystal grain is clearly observed (Ga/N = 0.86; Ga/N < 1 due to the presence of N-containing impurities), ruling out the formation of metallic Ga islands from nitridation at high temperature of 950 °C.

For a more clear view of the morphology changes during nitridation, TEM images of Ga_2O_3 and GaN samples synthesized at R = 1 are shown in Fig. 6. A typical Ga_2O_3 crystal assembly appears as a nanorod with length of 2 µm and diameter of 0.4 µm (Fig. 6a). In the HRTEM images (Fig. 6b and c), clear lattice fringes with interplanar spacing of 0.249 nm are observed, corresponding to the (110) planes of Ga_2O_3 crystal. After nitridation, the overall shape of Ga_2O_3 is well preserved (Fig. 6d), in accordance with SEM observations. It is also found that the GaN crystal assembly is composed of tiny nanoparticles with sizes of a few to a dozen nanometers. Accordingly, some nanoscale mesopores can be observed in GaN crystal assembly. HRTEM images (Fig. 6e and f) reveal the lattice fringes with interplanar spacing of 0.276 nm, corresponding to the (100) planes of GaN crystal.

On the basis of SEM (Fig. 4) and TEM observations (Fig. 6), we demonstrate that Ga_2O_3 samples with different morphologies



Fig. 6 TEM images (a, d), HRTEM images (b, e) and enlarged view of HRTEM images (c, f) of Ga_2O_3 and GaN samples synthesized at R = 1.

can be prepared *via* controlling the ratio of ironic strength during forced hydrolysis. With decreasing *R* value, the morphology of Ga_2O_3 crystals gradually transforms from spindle-like to dumbbell-shaped nanorods and then to exfoliated fragments, which gives us a hint on the formation process of Ga_2O_3 sample.

A schematic diagram of morphology-controlled synthesis of Ga_2O_3 *via* forced hydrolysis route is summarized in Fig. 7. In the first step, different ratios of $Ga(NO_3)_3 \cdot nH_2O$, NaNO₃ and urea are mixed in deionized water and heated at 90 °C to form unstable $Ga(OH)_3$ transition state. Then, the unstable $Ga(OH)_3$ transition state crystallizes to different morphologies of α -GaOOH at 90 °C with the presence of different concentrations of sodium ions as structure-directing and mineralizing agents. In the final step, GaOOH is transformed to α -Ga₂O₃ through calcination in vacuum, with its morphology well preserved. Besides, the as-obtained α -Ga₂O₃ can be transformed to GaN with overall morphology well preserved (Fig. 6).

The optical properties of as-obtained α -Ga₂O₃ samples with different morphologies are examined to explore the possible morphology-dependent effects. The UV-vis spectra of α -Ga₂O₃ synthesized at different *R* values are shown in Fig. 8. Commercial α -Ga₂O₃ sample (Raw) shows significant absorption in the ultraviolet region with edge up to ~290 nm, corresponding to the



Fig. 7 Schematic diagram of morphology-controlled synthesis of Ga_2O_3 via forced hydrolysis route.



Fig. 8 UV-vis spectra of Ga₂O₃ synthesized at different *R* values.

band gap of ~4.3 eV. While for α -Ga₂O₃ samples prepared *via* forced hydrolysis, two absorption peaks can be distinguished, *i.e.* intrinsic absorption with edge up to ~260 nm (4.8 eV) and subband absorption with edge up to ~360 nm (3.5 eV). The subband absorption should be related with the existence of abundant defect sites in α -Ga₂O₃, *e.g.* oxygen vacancies as proposed in other oxide semiconductors.^{30,31} It is seen that the highest absorption with edge up to ~360 nm is obtained with α -Ga₂O₃ sample at *R* = 1, indicating its highest defect site concentration.

For GaN samples from the nitridation of α -Ga₂O₃ samples, significant absorption in the ultraviolet and visible region is observed (Fig. S4[†]). The band-edge energy cannot be distinguished due to the overlap by sub-band absorption as well as the serious light scattering effects caused by the formation of mesoporous structure (Fig. 5 and 6).

The photoluminescence properties of α-Ga₂O₃ samples synthesized at different R values are examined. It is known that the photoluminescence emissions are originated from the radiative recombination of photo-generated electrons and holes on semiconductors. Two major photo-physical processes, i.e. direct band-band transition and indirect transition from trapping states, can give rise to photoluminescence signals. Under 270 nm ultraviolet light excitation, a broad photoluminescence signal from 350 to 700 nm (centered at 500 nm) is observed for commercial α -Ga₂O₃ sample (Fig. 9). While for α -Ga₂O₃ samples prepared via forced hydrolysis followed by calcination, two significant photoluminescence signals at 460 (blue photoluminescence) and 600 nm (orange photoluminescence) are observed. The blue photoluminescence signal should be originated from the recombination of photogenerated electrons on donors and holes on acceptors while the orange photoluminescence from the recombination on deep trapping states.32,33 Undoubtedly, all these two photoluminescence signals are associated with the defect sites in as-prepared α -Ga₂O₃ samples, which distinguish them from commercial sample. In this context, the intensity of photoluminescence signals is determined by both the defect sites and the crystallinity of the sample.



Fig. 9 Photoluminescence spectra of Ga_2O_3 synthesized at different R values.

We find that the sequence of photoluminescence intensity (Fig. 9) correlates well with the optical absorption (Fig. 8), both of which indicate the morphology-dependent optical properties of α -Ga₂O₃ samples. At R = 1, the highest photoluminescence intensity is obtained, several times higher than commercial α -Ga₂O₃ sample.

We also investigate the optical properties of GaN samples prepared from the nitridation of α -Ga₂O₃ samples and the results are shown in Fig. S5.† Significant photoluminescence signals at 380 and 450 nm are observed for all samples in the 350–480 nm region, and the highest photoluminescence intensity is obtained with GaN (R = 1). Besides, we cannot draw other convincing conclusions on the morphology-dependent effects due to the serious light scattering effects caused by the formation of mesoporous structure. Further researches on these issues are still in progress.

Conclusions

In summary, we have successfully developed a forced hydrolysis route to α-GaOOH starting from inorganic gallium salt and urea as raw materials, and we have realized the morphology control by adjusting the ratios of ionic strength in the synthesis system, i.e. Ga^{3+}/Na^{+} . The as-prepared α -GaOOH nanorods can be transformed to α-Ga₂O₃ nanorods upon simple calcination with the morphology well preserved, and be further transformed to GaN nanocrystal assembles through nitridation. This process provides a top-down strategy to Ga_2O_3 and GaN nanocrystals. Typically, the morphology of as-obtained α-Ga₂O₃ crystals gradually transform from spindle-like to dumbbell-shaped nanorods and then to exfoliated fragments with decreasing ratios of ionic strength in the synthesis system. While for the GaN samples prepared from nitridation at elevated temperature, the overall shape of α -Ga₂O₃ precursor can be preserved and nanoscale mesopores originated from nanoparticles assembling are clearly observed.

The UV-vis absorption and photoluminescence properties of Ga₂O₃ crystals with different morphologies are examined, and the

results clearly demonstrate the morphology-dependent effects. The methodology presented here may be extended to the synthesis and applications of other oxide and nitride semiconductors.

Conflicts of interest

There are no conflicts to declare.

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