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Growth of Core-Shell Ga-GaN Nanostructures via a Conventional Reflux Method and the Formation of Hollow GaN Spheres

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We report the growth of core-shell Ga–GaN nanostructures by simple refluxing of a mixture of GaCl₃ and lithium bis(trimethylsily)amide (LiHMDS) in trioctylamine at 380 °C for 24 h under nitrogen flow. The resulting spherical Ga–GaN nanostructures had diameters of ~550 nm. By immersing the nanostructures in aqua regia, the gallium cores could be removed, and hollow GaN spheres with thicknesses of 15–25 nm were produced. The shells consisted of connected GaN nanocrystals of both cubic and hexagonal phases. Infrared spectroscopy confirmed the presence of silica or silicate in the GaN shells. The silicon source likely comes from the pyrolysis of LiHMDS. The growth process was studied by examining the intermediate products formed. Gallium metal cores appeared below 380 °C, followed by the slow formation of GaN nanocrystals on the core surfaces. The slow growth of the GaN shells is related to the gradual supply of the nitrogen source from the thermal decomposition of LiHMDS. Thinner shells with a thickness of ~10 nm were prepared at a reaction temperature of 340 °C, but the spheres were more prone to breakage. The hollow GaN spheres exhibited a broad emission band centered at ~550 nm.

Introduction

Gallium nitride (GaN) is an important III-V semiconductor with a wide direct band gap of \sim 3.4 eV. Demonstrations of optoelectronic applications of GaN have largely been focused on its wirelike morphology when prepared by vapor phase deposition at high temperatures (frequently at 900 °C or above).^{1,2} To find alternative preparation routes at lower reaction temperatures and obtain GaN in nanoparticle form, solutionphase syntheses of different GaN nanostructures have also been examined in recent years. Unlike the growth of many oxide and sulfide nanocrystals, successful preparation of metal nitride nanoparticles relies critically on the effective supply of the nitrogen source. Three general strategies have been adopted to provide the nitrogen source for the generation of GaN nanostructures. The first method involves metathesis such as in the reaction between GaCl₃ and NaN₃.^{3,4} Because of the explosive nature of metal azides, the product morphology and size are more difficult to control. The second method is through the design and use of single-source precursors.^{5–8} Pyrolysis of the precursors was found to yield GaN nanocrystals and even quantum dots. A related solvothermal approach with the gallium and nitrogen source coming from two separate reagents represents another distinct method for the preparation of GaN nanocrystals. For example, gallium cupferron, Ga(C₆H₅N₂O₂)₃, or GaCl₃ can react with hexamethyldisilazane (HMDS) in toluene with or without the addition of cetyltrimethylammonium bromide (CTAB) surfactant to generate ultrasmall GaN nanocrystals.^{9,10} Here, HMDS serves as the nitriding agent.¹¹ Although GaN nanostructures can also be obtained by employing an ammonolysis process on preformed Ga2O3 nanostructures, this is not a solution-phase reaction, and high temperatures of 700-900 °C are frequently required.12-14

In this study, we have synthesized unusual core–shell Ga–GaN nanostructures by the reaction of GaCl₃ and lithium

bis(trimethylsilyl)amide (LiHMDS) in trioctylamine (TOA) at 380 °C for 24 h under nitrogen flow using a conventional reflux method. Removal of the Ga cores by acid treatment resulted in the formation of hollow GaN spheres. Hollow GaN spheres have also been prepared by the conversion of hollow Ga₂O₃ spheres, formed using carbon spheres as templates, in an ammonia atmosphere at 700-900 °C¹⁴ and by the evaporation of GaCl₃ at 1000-1200 °C under ammonia flow in a tube furnace to deposit the products on silicon substrates.¹⁵ In contrast, the current reaction system for the production of hollow GaN spheres is simple, and the required reaction temperature is relatively low. This reflux procedure also offers an advantage over the solvothermal approach because intermediate products can be easily collected and analyzed to provide insight into the possible growth mechanism. Fourier transform infrared (FT-IR) spectroscopy was also used to characterize the products, and the optical properties of the hollow GaN spheres were studied.

Experimental Section

Gallium chloride anhydrous beads (GaCl₃, 99.99%, Aldrich) and ~1 M lithium bis(trimethylsilyl)amide (or hexamethyldisilazane lithium salt) solution in hexane ([(CH₃)₃Si]₂NLi, LiHMDS, Fluka) were used as the gallium and nitrogen sources, respectively, without further purification. Trioctylamine (TOA, 98%, Aldrich) served as the solvent and was dried at 120 °C under reduced pressure before use. The entire synthetic procedure described below was carried out in a nitrogen environment or under a nitrogen stream. To synthesize core-shell Ga-GaN nanostructures, 0.2 g (or 1.14×10^{-3} mol) of GaCl₃ was added to a 100-mL double-necked round bottle in a glovebox. After removal of the round bottle from the glovebox, 20 mL of dried TOA solution was introduced into the bottle by cannula transfer. After GaCl₃ had been completely dissolved in the TOA solution using a glass-covered magnetic stir bar, 4 mL of LiHMDS (4 $\times 10^{-3}$ mol) in hexane was injected into the bottle by syringe.

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Figure 1. (a) SEM image of the core-shell Ga-GaN nanostructures. The inset shows a magnified image. (b) XRD pattern of the core-shell Ga-GaN nanostructures. The inset shows a photograph of the core-shell Ga-GaN nanostructure solution. (c) SEM image of the hollow GaN spheres after removal of the gallium cores. The inset shows a magnified image. (d) XRD pattern of the hollow GaN spheres. The inset shows a photograph of the solution of hollow GaN spheres.

The solution was yellow but transparent. LiHMDS exhibits good solubility in TOA. Hexane was removed under vacuum. The round bottle was placed in a heating mantle equipped with a thermocouple and a temperature controller, and a condenser was connected to the bottle. The solution was vigorously stirred, and its temperature was raised to 380 °C at a rate of 3 °C/min. After 24 h, the solution was cooled to room temperature. The products were collected by centrifugation twice at 7000 rpm for 2 min in hexane, isopropanol, ethanol, and then deionized water. Finally, they were preserved in 4 mL of acetone. Water and alcohol can also be used to store the products. To remove the gallium cores, the core—shell Ga—GaN nanostructures were immersed in aqua regia, which was prepared with a volumetric ratio of 1:3 of concentrated HNO₃ to concentrated HCl.

The morphology of the products was characterized using field-emission scanning electron microscopes (FE-SEM, Hitachi S4700 and 7000F). Transmission electron microscopy (TEM) images were recorded on JEOL JEM-2010 and JEM-2100 electron microscopes. X-ray diffraction (XRD) patterns were obtained using a Shimadzu XRD-6000 diffractometer with Cu K α radiation. The samples were loaded on 15 mm × 15 mm Si(111) substrates. FT-IR spectra of the samples were recorded on a Perkin-Elmer Spectrum RX I spectrometer. Photoluminescence spectra were obtained using an excitation wavelength of 325 nm from a He–Cd laser and a liquid-nitrogen-cooled charge-coupled-device (CCD) detector.

Results and Discussion

Figure 1 shows SEM images and XRD patterns of the core-shell Ga-GaN nanostructures before and after the removal of gallium cores. The spherical Ga-GaN particles are reasonably uniform with an average diameter of about 550 nm. The composite nanostructures do not have a smooth appearance; tiny particles appear to evenly deposit on the surfaces of the spheres. The XRD pattern of the core-shell Ga-GaN nanostructures

shows diffraction peaks that can be indexed to those of hexagonal and cubic GaN (JCPDF card no. 52-0791 for cubic GaN). In addition, broad peaks over the 2θ ranges of $30-50^{\circ}$ and 60-75° can be attributed to tiny crystalline Ga domains in the gallium cores present under the air-conditioned room temperature of 20-22 °C. Interestingly, after core-shell Ga-GaN nanostructures placed on a silicon substrate had been crushed by the application of a pressure, a mirrorlike liquid material formed as observed under an optical microscope. This material is most likely gallium as it exhibits metallic luster and is a liquid at room temperature. (The melting point of gallium is 29 °C.) This observation can serve as evidence for the presence of gallium and the existence of the core-shell Ga-GaN nanostructures. To obtain hollow GaN spheres, the gallium cores were removed by aqua regia. Gallium metal is oxidized upon reaction with aqua regia, and hydrogen gas and possibly NO gas are generated. The initially opaque brown solution became transparent yellow after the addition of aqua regia (see Figure 1). SEM reveals that hollow GaN spheres have been formed, but these spheres have a somewhat porous appearance (Figure 1c). Without interference from the broad bands of gallium, the XRD pattern of the hollow GaN spheres shows clearly identifiable peaks from both hexagonal wurtzite and cubic zinc blende GaN. Several peaks can be assigned to both crystal structures of GaN because their expected peak positions are so close. From the relative peak intensities of the two crystal structures and a comparison of these peak intensities to those in their standard XRD patterns, it appears that cubic GaN is the more dominant crystal phase. Pure cubic GaN and mixtures of hexagonal and cubic GaN have also been synthesized at moderate reaction temperatures.¹⁶

More detailed structural characterization of the hollow GaN spheres was performed by TEM analysis. Figure 2a shows a TEM image of the synthesized hollow GaN spheres. Removal of the gallium cores gives the spheres a transparent look. The



Figure 2. (a) TEM image of the hollow GaN spheres. (b) TEM image of hollow GaN spheres with partially dissolved gallium metal. (c) SAED pattern of the hollow GaN spheres.

shells are sufficiently rigid to largely maintain their spherical shape after removal of the core and escape of gases. Practically no separate tiny GaN particles were found outside the hollow spheres. Occasionally, GaN spheres with partially removed cores were observed (Figure 2b). The gallium cores had a smooth liquidlike appearance and adhered to the sidewalls of the shells. A selected-area electron diffraction (SAED) pattern of the hollow GaN spheres with empty cores is presented in Figure 2c. The clear ring pattern due to the polycrystalline nature of the shells can be indexed to both cubic and hexagonal phases of GaN. Notice that the brighter rings are associated with cubic GaN, a result consistent with the XRD pattern obtained. Further TEM analyses on individual hollow GaN spheres were conducted (Figure 3a). A rough shell surface composed of inhomogeneous crystal domains is evident. The shell thickness is about 15-25 nm. High-resolution TEM images collected from tens of hollow spheres confirmed the presence of both cubic and hexagonal crystal domains. Figure 3b shows an edge portion of a sphere with a cubic crystal structure. Two sets of lattice fringes with d spacings of 2.57 and 2.27 Å at an angle of \sim 55° were measured, which should correspond to the (111) and (200) planes, respectively, of zinc blende GaN. Regions with the hexagonal crystal structure were also found (Figure 3c). Some GaN nanoparticles on the shells were observed to contain many crystal defects such as stacking faults and twin boundaries (Figure 3d). These defect sites might also be transitional regions of cubic and hexagonal phases formed during crystal growth.

To further analyze the composition of the shell materials, FT-IR spectra of the hollow GaN spheres were obtained (Figure 4a). The expected characteristic bands of GaN at around 500-750 cm⁻¹ resulting from the crystal vibration modes of GaN were observed.¹⁷ Interestingly, additional bands corresponding to the vibration modes of silica or silicate were also recorded. Two bands near 950 and 1100 cm⁻¹ can be assigned as the asymmetric Si-O stretching mode of the Si-OH group and the Si-O-Si stretching mode, respectively.^{18,19} The silicon source for the formation of silica/silicate is believed to come from the thermal decomposition of LiHMDS. The decomposed trimethylsilyl groups can react with a trace amount of oxygen in the container at such a high temperature to form silica/ silicate.²⁰ Because the silica/silicate is found in the shell layer, it can bind to adjacent GaN crystals and improves the structural integrity of the hollow GaN spheres. To validate this assumption, we also collected FT-IR spectra of the gel-like product formed after refluxing LiHMDS in TOA at 300 °C for 24 h (Figure 4b). The spectrum shown, which includes the strong Si-O-Si stretching band near 1100 cm⁻¹, is consistent with that of silica. The band at 1260 cm⁻¹ is assigned to the unreacted trimethylsilyl group. Thus, the silicon source of the silica formed should originate from LiHMDS. Because hydrofluoric acid can dissolve silica, treatment of the hollow GaN spheres with HF should break the spheres apart. Figure 4c,d shows SEM images of the hollow GaN spheres dispersed on a silicon substrate before and after being rinsed with HF solution. Indeed, the hollow spheres collapsed into broken pieces as the binding silica dissolved away.

The formation process of the core-shell Ga-GaN nanostructures was studied by examining the intermediate products



Figure 3. (a) High-magnification TEM image of a single hollow GaN sphere. (b) High-resolution TEM image of a portion of a hollow GaN sphere showing a cubic GaN structure. (c) High-resolution TEM image of a portion of a hollow GaN sphere with a hexagonal GaN structure. (d) TEM image of an edge portion of a hollow GaN sphere. A distinct twin structure and line defects can be observed.



Figure 4. (a) FT-IR spectrum of the hollow GaN spheres. (b) FT-IR spectrum of the product formed after refluxing LiHMDS in TOA at 300 $^{\circ}$ C for 24 h. (c,d) SEM images of the hollow GaN spheres (c) before and (d) after rinsing with hydrofluoric acid.

formed (Figure 5). Immediately when the reaction temperature had reached 380 $^{\circ}$ C, spherical particles with sizes of \sim 320 nm

and smooth surfaces formed. The particles reached diameters of about 550 nm after 2 h of reaction and maintained this size



Figure 5. SEM images of the products withdrawn from the reaction solution (a) immediately when the solution temperature reached 380 °C and after reacting for (b) 10, (c) 16, and (d) 24 h.

after 10 h of reaction. These particles are amorphous, as they do not show XRD peaks, and are presumably gallium metal droplets. Few and scattered small particles depositing on these Ga spheres began to appear in samples obtained after 12 h of reaction. The number of these small particles increased more appreciably only after 20 h of reaction. Based on an examination of the final products, the small particles depositing on the surfaces of the spheres are GaN crystals. This formation sequence is similar to that proposed for the growth of hollow GaN spheres by direct evaporation of GaCl₃ at 1000-1200 °C under ammonia flow in a tube furnace.¹⁵ From these observations, we propose that the Ga metal particles are formed first at temperatures below 380 °C. (Spheres have been observed at reaction temperatures of 280-300 °C.) LiHMDS could serve as the reducing agent here to yield Ga metal from GaCl₃. Without the presence of LiHMDS, Ga cores would not form. The supply of the nitrogen source is continuous but limited in the first few hours of reaction, and it becomes more significant only after 10 h of reaction to produce the GaN nanocrystals via interfacial reaction and eventually form a shell.

The reaction temperatures were varied to determine whether hollow GaN spheres could be produced at lower temperatures. Figure 6 shows SEM images of the core-shell Ga-GaN nanostructure products obtained at reaction temperatures of 300, 340, and 380 °C. TEM images of the hollow GaN spheres after treatment with aqua regia are also provided. Particles with smoother surfaces and smaller diameters were formed at lower reaction temperatures. After treatment with aqua regia, the hollow GaN spheres can be maintained at a reaction temperature of 380 °C, as discussed above, but hollow GaN spheres formed at 340 °C with thinner shells (~10 nm) are more likely to disintegrate into small pieces (see the upper left portion of the TEM image in Figure 6b). At 300 °C, the shells completely collapsed after treatment with aqua regia because of their even thinner shells and the incomplete coverage of GaN nanocrystals over the Ga metal particles in the first place. These results



Figure 6. SEM images of the core-shell Ga-GaN nanostructures synthesized at reaction temperatures of (a) 380, (b) 340, and (c) 300 °C and the corresponding TEM images of single hollow GaN spheres after treatment with aqua regia.

suggest that a reaction temperature of 380 °C is optimal for forming structurally more robust hollow GaN spheres.

Optical properties of the hollow GaN spheres were investigated by recording their photoluminescence spectra. Possibly



Figure 7. Photoluminescence spectrum of the hollow GaN spheres. The excitation wavelength is 325 nm from a He–Cd laser. The tiny peaks above the broad emission band are believed to come from the excitation laser.

because of the presence of a significant amount of crystal defects in the shells, the near-band-edge emission peak was not measured. The hollow GaN spheres do exhibit a broad emission band centered at \sim 550 nm (see Figure 7), which is attributed to the presence of various point and perhaps line defects within the GaN crystals, as revealed in Figure 3d.¹⁵

Conclusion

In conclusion, we have demonstrated the formation of unusual core—shell Ga–GaN nanostructures with sizes of ~550 nm by a conventional reflux method at 380 °C for 24 h. Gallium metal particles were produced first, followed by the slow formation of thin GaN shells through pyrolysis of LiHMDS. The GaN shells were composed of connected nanocrystals of GaN with both cubic and hexagonal phases. Treatment of the Ga–GaN nanostructures with aqua regia removed the gallium cores, and hollow GaN spheres, and it might serve the purpose of enhancing the overall structural integrity of the hollow GaN spheres. Thinner GaN shells can be made at a reaction temperature of 340 °C, but the spheres are more prone to breakage. The hollow GaN spheres show a broad emission band centered at ~550 nm. The synthetic procedure described here represents a new

approach to make relatively large and uniform hollow GaN spheres at substantially lower reaction temperatures than previously used in other reports.

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