Syntheses of Soluble GaN Nanocrystals by a Solution-Phase Reaction

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Abstract

A solution phase synthetic method of colloidal GaN nanocrystals at the low temperature has been reported. The syntheses involve the reaction of gallium chloride and lithium nitride in aromatic type solvents mixed surfactants, trioctylphosphine (TOPO) at the temperature below 300 °C. The resulting nanocrystals were crystalline and generally spherical with the surfaces passivated by TOPO giving the individual nanocrystals solubility in common organic solvents. The average crystal sizes varied from 50 Å to 200 Å in different reaction conditions. We have confirmed the hexagonal wurzite structure of the GaN nanocrystals by transmission electron microscope (TEM), x-ray powder diffraction. The samples were examined the optical emission by an emission spectrometer. The results indicated that the nanocrystals emit photoluminescence at 3.31 eV.

Key Words: Nanocrystals, Gallium Nitride, GaN Nanocrystals, Zinc Blende

1. Introduction

The synthesis of GaN nanocrystals is of importance for understanding the fundamental properties of a wide band gap semiconductor and for developing optoelectronic devices operated in the ultraviolet and blue ranges [1]. In the past few years, significant progress has been made in the studies of some semiconductor nanocrystals, e.g. CdSe and CdS [2] and is mainly attributed to the successful development of synthetic techniques to obtain different sizes of colloidal nanocrystals with a good solubility in common solvents [3]. However, no effective synthesis of soluble colloidal GaN nanocrystals has been reported so far. Herein, we present a simple solution-phase method to synthesize the different sizes of colloidal GaN nanocrystals. The resulting nanocrystals are crystalline, which individually have a good solubility and can be redissolved in toluene and hexane.

Several methods such as laser ablation [4], solution phase reactions at high pressure [5] and thermal decomposition [5c] have been reported to synthesize GaN nanocrystals. However, the resulting nanocrystals are insoluble in common solvents and easy to form the aggregate. To synthesize isolated and soluble semiconductor nanocrystals such as those of CdSe and CdS surface-capping agents have been included in the reaction during the synthesis process for two main reasons [6]. First, capping molecules on the surface of resulting nanocrystals prevent individual nanocrystals from aggregation and hence increasing nanocrystal solubility. Secondly, the concentration of the capping molecules may serve as an adjustable factor to control the sizes of the resulting nanocrystals. Since the bonding between gallium and nitrogen is not...
easily formed at an ambient condition, the previous attempts to synthesize GaN nanocrystal were operated at very high temperature or pressure. Under such vigorous conditions, capping molecules are expected to become reactive and easy to decompose; consequently, the passivation of capping molecules onto the nanocrystal surface is very difficult to achieve. To circumvent this obstacle, we added capping agents in the reaction and used an appropriate solvent (or catalyst) to accelerate the formation of GaN crystals in solution under a mild condition.

2. Experimental

To synthesize colloidal GaN nanocrystals, we added gallium chloride (GaCl\(_3\)), lithium nitride (Li\(_3\)N) and the capping agent trioctylphosphine oxide (TOPO) to the polar aromatic solvent dibenzofuran.

\[
\text{GaCl}_3 + \text{Li}_3\text{N} \xrightarrow{\text{TOPO}} \text{GaN-TOPO capped} + 3\text{LiCl}
\]

Small-sized GaN crystals have been synthesized previously at 280 °C under pressure using the same starting materials and benzene as a solvent [5a]. We have found that when dibenzofuran was substituted for benzene without adding TOPO, insoluble bulk GaN crystals were produced at ambient pressure and 290 °C [7]. In comparison to benzene, we expected that dibenzofuran can enhance the formation of GaN crystals more efficiently because dibenzofuran has more aromatic rings and should exhibit stronger solvation effect on ions. TOPO has been commonly used as a capping agent for the syntheses of CdSe and InP nanocrystals [8]. The spectroscopic measurement has proved that TOPO is a stable compound at the reaction temperatures below 380 °C and can be passivated on the surface of CdSe and InP nanocrystals. The high boiling points for both TOPO and dibenzofuran allow our reaction to take place at 290 °C in a solution phase without applying extra pressure, and therefore help preventing dibenzofuran and TOPO from decomposition.

To control the sizes of GaN nanocrystals we adjusted the relative amount of dibenzofuran and TOPO in the reaction of GaCl\(_3\) and Li\(_3\)N. Upon adding a fixed amount of TOPO and increasing the ratio of dibenzofuran to GaCl\(_3\) (or Li\(_3\)N), the average sizes of nanocrystals increased. On the other hand, the average sizes of nanocrystals did not change much as the amount of TOPO increased under a fixed ratio of dibenzofuran to GaCl\(_3\) was fixed. These results suggest that the amount of dibenzofuran, not TOPO play a key role on the formation of the GaN crystal, which in turn controls the crystal size. Although the detail mechanism of crystal nucleation and growth in this particular reaction is unclear, these results imply that dibenzofuran could participate in the reaction and be treated as a catalyst.

Two types of TEM instruments (Zeiss, 10C and Hitachi, Fe-200), operating at 80 kV and 400 kV were used for low and high resolution measurements, respectively. A TEM sample was prepared by depositing an aliquot of nanocrystal solution in toluene onto either an amorphous carbon film or a porous carbon film in a Cu grid. A powder x-ray diffractometer (Toshiba, A-40-Cu) with a wavelength of 1.54 Å was employed to characterize the crystal structure. The powder sample was obtained from drying the nanocrystal solution. A He-Cd laser (325 nm) was selected as an excitation source for the emission spectra. The emission signal was collected by a triple monochromator and detected by a lock-in amplifier coupled with a photomultiplier tube.

3. Results and Discussion

We used transmission electron microscopy (TEM) to study the size distribution, photomicrographs and electron diffraction patterns of the resulting GaN nanocrystals. A typical bright field image of GaN nanocrystals with average sizes of 45 Å ± 31% and 113 Å ± 20% in diameter were shown in Figure 1a and 1b, respectively. The sizes of the nanocrystals were calculated by averaging more than 200 particles from the images taken from different locations on the Cu grid. The particles were well-dispersed without any aggregation on the carbon film, and each individual discrete particle appeared in an nearly spherical shape with a crystalline core. The bright field image of an individual GaN nanocrystal from a high resolution transmission electron microscopy in Figure 2a shows clear lattice fringes. The nanocrystal appears slightly along with an average major axis of 64 Å and minor axis of 52 Å. The distance of 3.18 Å between two (001) planes in the cross lattice fringes is consistent with the value calculated based on the hexagonal (wurzite) structure of a bulk GaN crystal. The electron diffraction pattern on a selected area depicted in the inset of the Figure 2a also confirms the same structure. Figure 2b is shown a zinc blende-like GaN nanocrystal. The HRTEM image is composed of two atomic planes: (100) and (010). This gives rise to a pseudo-zinc blende symmetry appearance. Most of individual nanocrystals from the high-resolution images show a prolate shape with an aspect ratio of <1.3. Similar aspect ratios have
been observed in CdSe and InP nanocrystals \[3,8\].

![Figure 1](image1.png)

Figure 1. Transmission electron micrograph in the bright field shows a collection of GaN nanocrystals. The bar on right below corner denotes a distance of 50 nm.

![Figure 1](image2.png)

Figure 2. (a) High-resolution transmission electron micrograph of the GaN nanocrystal in a bright field shows cross lattice planes. Diffraction patterns on the left upper corner exhibit the hexagonal structure. (b) High-magnification TEM of the zinc blend-like GaN nanocrystal

We used powder x-ray diffractometer to further confirm the structure of GaN nanocrystals (Figure 3). We have found that the structure derived from the x-ray diffraction pattern was in agreement with that obtained from the electron diffraction measurement. The average sizes of nanocrystals were calculated from the Scherrer formula. We have found that in some samples, the average sizes estimated from the x-ray diffraction pattern are smaller than that from TEM. This result indicated that some samples may not be perfect crystalline.

![Figure 3](image3.png)

Figure 3. X-ray powder diffraction of GaN nanocrystals

Finally, we characterized the optical properties of the GaN nanocrystals by their emission spectra (Figure 4). The emission spectra of different sizes of the nanocrystals exhibit maximum peaks at 3.31 eV. The shift of the emission relative to the band edge transition may result from surface states associated with none-perfect surface termination or from defect states caused by nitrogen deficiencies and/or structural defects. Another possibility is that this is a result of the zinc blende domains or isolated stacking faults in the wurzite structure. Such inhomogeneous structure give rise to potential fluctuations in the conduction band of about 0.2 eV, which is the difference in the band gap between wurzite and zinc blende GaN \[9-11\]. The direct correlation between the PL spectra and the existence of a small fraction of zinc blende-like GaN
nanocrystals observed in the TEM studies support the second hypothesis.

Figure 4. Room temperature PL spectrum of the GaN nanocrystals using a He-Cd laser 325 nm as the excitation source

A further study of this problem is desirable, which may bring out the necessary information for growing zinc blend and hexagonal GaN nanocrystals. There exists a broad structure centered at 2.55 eV that is attributed to defect or impurity states observed in bulk GaN. The distribution of the size and shape of the nanoparticle can appreciably broaden this peak. The defect-related signal implies that our GaN nanocrystals contain few defects and high quality. We also expect surface states to play an important role in the PL of these materials. PL in the visible range in GaN has been observed from epitaxial GaN as well and has been attributed to impurity and defect states [12].

A possible mechanism for emission spectrum has been proposed by Well et al. They suggested that both hexagonal and zinc blend phases of gallium nitride crystals may coexist in the same reaction. Although several HRTEM images in our specific samples have shown both the hexagonal and zinc blend phases, the experimental data are still insufficient to confirm that both phases exist under the same reaction condition. Chen et al. has suggested that kinetic barrier between two metastable phases depends on the sizes and surfaces of the particles. It will be a very interesting topic to investigate whether we can alter the reaction conditions to control the growth of wurtzite, zinc blend and rocksalt phases of the resulting nanocrystals.

In conclusion, we have developed a method to synthesize different sizes of GaN nanocrystals. We are currently exploring the large range of reaction parameters to improve the size distribution of the samples.

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References

[7] Several other aromatic solvents such as phenanthrene and 1,2-diphenyl benzene have been used as solvents for the reaction. Only dibenzofuran can enhance efficiently the GaN crystal formation at ambient condition.