

Nanoporous gallium nitride square microtubes

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Abstract Porous gallium nitride microtubes were self-fabricated from gallium nitride submicron irregular structures. The microtubes were of square cross-section. Electron diffractions indicated that the microtubes were composed of zincblende gallium nitride. Electron energy-loss spectrum and photoluminescence spectrum of the microtubes were collected and compared with that of single crystals.

Introduction

Gallium nitride (GaN) semiconductors have a direct band-gap of 3.2–3.4 eV and have found wide applications in blue and UV light emission devices and laser devices [1, 2]. To date, GaN nanoparticles [3], nanorods [4, 5], nanowires [6–9], nanotubes [10–13], as well as single crystals [14–16]

have been synthesized using a variety of techniques. The quantum confinement of these nanomaterials yields unique physical properties over bulk crystals, making the GaN nanomaterials wider applications, such as on photocatalytic water splitting [17, 18] besides light emission devices and laser devices. However, it is still challenging to assemble GaN nanomaterials into macroscaled bulks for industrial applications.

Up to now there are three achievements on the self-assembly of GaN nanoparticles. It was reported that GaN nanoparticles (diameter of ~ 12 nm) can be self-assembled into millimeter scale bulk nanocomposites [19] under supercritical high-pressure solution environments. GaN nanoparticles were closely compacted into bulks under the supercritical conditions. GaN nanoparticles (diameter of several nanometers) were also self-assembled into nanospheres [20] with diameters of 20–25 nm or nanotubes [20] with shell thicknesses of 2.5–4.5 nm by a gas interface reaction route. Recently it was reported that wurtzite GaN nanorods were successfully assembled into micron scale tubular structures with diameters of about 10 μm [21] under supersaturated conditions. All these bulky assemblies inhibited quantum confinement effects of nanomaterials.

Here we report another kind of GaN self-assemblies: porous GaN square microtubes. Such porous microtubes were found to be consisted of GaN submicron irregular structures with a zincblende structure. The self-assembled GaN square microbes possess both advances of bulks (macroscale size) and nanomaterials (quantum confinement effect).

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Experimental

The synthesis of the microtubes was carried out in a horizontal quartz tube furnace. Gallium metal (99.999%

purity) was purchased from Sigma-Aldrich Corporation. Quartz substrates were washed by ultrasonicing in acetone and then in de-ionized water, followed by thorough rinsing with methanol and drying in air. Gallium was placed on quartz substrates and positioned at the center of the horizontal tube in a hot-walled chemical vapor deposition (CVD) furnace. The CVD system was evacuated by a mechanical pump backed molecule pump, and purged several times with argon gas before introducing ammonia gas. As-received analytical grade (purity of 99.9%) commercial argon and ammonia gas were used without further purification. The entire system was heated from room temperature to 800°C in about 20 min and maintained at the reaction temperature for 2 min. Afterwards, the flow of ammonia was stopped and the entire system was cooled to room temperature.

Scanning electron microscopy (SEM) images were taken on a CamScan FE 44 SEM at 25 kV. Transmission electron microscopy (TEM) experiments were carried out on a JEOL 2200FS TEM equipped with an in-column energy filter and electron energy-loss spectroscopic (EELS) spectra were collected in scanning transmission electron microscopy mode. The room temperature photoluminescence (PL) of GaN microtubes was performed using a 337-nm UV laser and a single-grating spectrometer (Horiba HR320).

Results and discussion

After reactions yellow deposits were observed on the substrates. SEM observation indicated that the yellow deposits consisted of many microtubes. Figure 1a–c shows

SEM images of some microtubes grown on the substrates. The synthesized structures were hollow microtubes with cross sections about 3 μm and lengths up to 100 μm . The ends of most of these microtubes were open, but some were closed (Fig. 1a). SEM images also indicated that all tube walls were nearly equal in width (Fig. 1a–d) and all face angles were at right angles (Fig. 1a–e). That is, the synthesized microtubes were square in cross-section.

From the open ends of the microtubes (Fig. 1a–c), the thicknesses of the microtube walls were found to be about 100 nm. More detailed examination (Fig. 1d) indicated the walls consisted of single layer of randomly oriented sub-micron irregular structures. The diameters of the submicron irregular structures were about 100 nm and their lengths were about 1 μm (Fig. 1d–f).

High magnification SEM images (Fig. 1d–f) indicated that, as a result of the random packing of the submicron irregular structures, the thin walls of the microtubes were porous. Some nanopores of these walls are noted by the arrows in Fig. 1d–f. Such porous structures should have large surface areas. Unfortunately, it is very difficult to remove the synthesized microtubes from the substrates because of brittleness and their surface area was not measured experimentally.

Figure 2a shows a typical TEM image of the square microtubes at low magnification. The thin wall of the microtube is porous. Selected area electron diffraction (SAED) patterns (Fig. 2b) collected from the microtube indicated that the microtube was polycrystalline. The electron diffraction pattern can be indexed to cubic GaN.

In order to confirm the cubic crystallographic structure of the thin wall further, SAED patterns were also taken at nanoscale. Figure 2c shows a typical TEM image of a

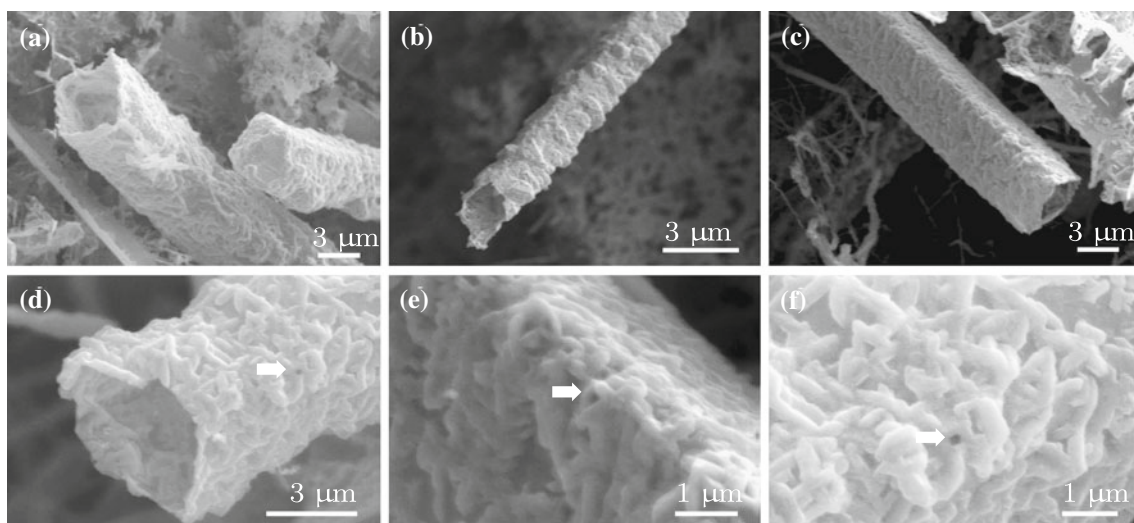
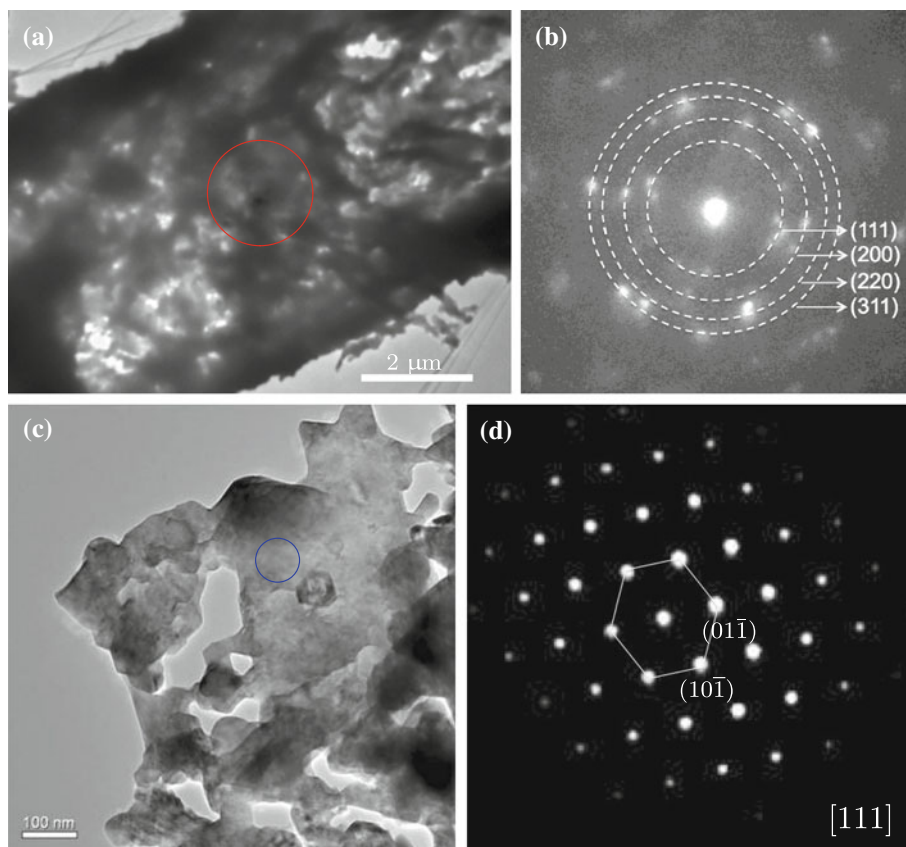


Fig. 1 SEM images of GaN square microtubes. **a–c** Microtubes grown at different regions. **d** End of one microtube. **e** Edge of a square microtube. **f** Enlarged surface of a microtube. White arrows mark the nanopores of the microtubes

Fig. 2 **a** TEM image of a square microtube at low magnification. **b** SAED pattern of the circled region in **a**. The pattern is indexed as the cubic GaN phase. **c** TEM image of a GaN square microtube end at higher magnification. **d** SAED pattern of the circled region in **c**. The pattern is indexed as the cubic GaN phase with a zone axis of [111]



microtube square end at higher magnification. Nanopores were also observed from the TEM image. Figure 2d is the SAED pattern of a nano-region. The nano-region is single crystalline. The pattern has a threefold symmetry and can be indexed as the cubic GaN (c-GaN) phase (space group of $F\bar{4}3m$ with a lattice parameter of 4.503 \AA) with a zone axis of [111] or the hexagonal GaN (h-GaN) phase (space group of $P6_3mc$ with lattice parameters of $a = 3.18907 \text{ \AA}$ and $c = 5.1855 \text{ \AA}$) with a zone axis of [001]. The inter-plane distance d corresponding to the diffracted spots was carefully measured from Fig. 2d. The measured d values of the diffracted spots are 3.3 and 1.6 \AA , corresponding to that of (110) ($d_{(110)} = 3.18 \text{ \AA}$) and (220) ($d_{(220)} = 1.59 \text{ \AA}$), respectively, of c-GaN with the zinc blende structure, while far from that of (100) ($d_{(100)} = 2.76 \text{ \AA}$) and (200) ($d_{(200)} = 1.38 \text{ \AA}$) of the h-GaN with the wurtzite crystal structure. Therefore, the SAED pattern confirmed that the wall nanoregion is of c-GaN with a zone axis of [111], not h-GaN with a zone axis of [001]. Therefore the entire microtubes are polycrystalline while the consisting irregular nanostructures are single crystalline c-GaN.

Figure 3a shows an EELS spectrum revealing the low-loss region and the zero-loss peak (ZLP) of a GaN microtube. The energy resolution of the EELS spectrum is 1.75 eV , according to the full-width at half-maximum of the zero loss peak. A plasmon excitation is determined at

$\sim 25 \text{ eV}$. This plasmon peak position is very close to that of GaN bulks [22, 23]. It has been reported that the plasmon peak position shifts linearly with strain [24] caused by confinement size and defects in GaN nanomaterials (0.168 eV per 1% volume change). However such subtle plasmon peak shifts are not observed here because of the limited EELS energy resolution.

Figure 3b shows the electron-energy loss near-edge fine structures (ELNES) of the nitrogen K edge. Three main peaks are observed, at 403, 405, and 407 eV. Compared with the standard data of GaN crystals (400, 403.5, 405.5 eV [25, 26]), the loss peaks shift slightly. Figure 3c shows the ELNES of the gallium $L_{2,3}$ edge, which arises from the excitation of electrons from the $2p_{3/2}$ and $2p_{1/2}$ states to ($4s$, $4d$) states in the conduction band. The Ga- $L_{2,3}$ edges reflect the s and d partial unoccupied density of states. The energy of the L_3 edge is very close to the reported value of single crystalline GaN (1125 eV) [22]. However, the observed peak position of the Ga- L_2 (1175 eV) was very different from the reported values for bulk GaN (1126 eV [26] or 1155 eV [22]). The difference in the Ga- L_2 edge should come from the confinement effect of the GaN submicron irregular structures, which change the s unoccupied density of states of the microtubes.

Figure 4 show a PL spectrum of the square microtubes. A strong and wide yellow band was observed at

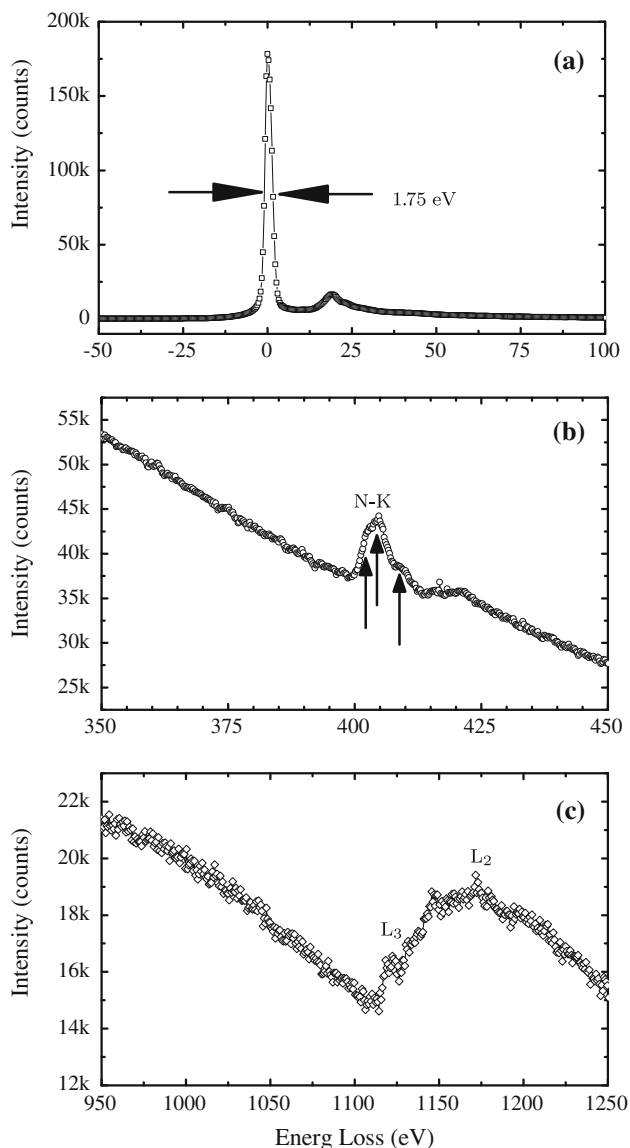


Fig. 3 EELS spectra of a GaN microtube. **a** Low loss EELS including the ZLP. ELNES of **b** nitrogen K edge and **c** gallium $L_{2,3}$ edge. The *arrows* mark the main three peaks of N–K edge

550–750 nm. The yellow band was usually observed in GaN nanocomposites [19, 20], nanoparticles [3], and nanowires [6]. It is generally accepted [27] that nitrogen vacancies and deep level impurities contribute to the yellow band. No any blue band was detected below 400 nm (>3.1 eV).

The formation of the porous square microtubes may result from supersaturation growth, similar to that of tubular microtubes consisting of wurtzite GaN nanoparticles [21]. It is known that gallium has a low melting point of 303 K and a boiling point of 2520 K. Therefore large amounts of gallium droplets can form on the quartz substrates, as observed on silicon substrates [28]. The gallium droplets react with the flowing ammonia to produce GaN

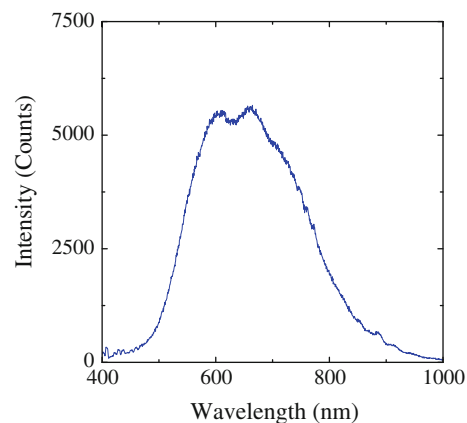


Fig. 4 PL spectrum of square microtubes

submicron irregular structures with a zincblende (cubic) structure. These zincblende GaN submicron irregular structures are so dense that they can be considered as a supersaturated aerosol, as observed in charged nanoparticles in solutions [29] or in vapor phases [30, 31]. The zincblende GaN submicron irregular structures then spontaneously aggregate into square microtubes.

It was reported that h-GaN nanostructures with a hexagonal wurtzite structure self-assembled into circular microtubes [21], not square microtubes as observed here. At present we do not know why c-GaN nanostructures self-assembled into square microtubes, while h-GaN nanostructures self-assembled into circular microtubes. A most possible explanation is that c-GaN nanostructures trend to square microtubes, while h-GaN nanostructures trend to circular microtubes in order to lower the total surface free energy of self-assembled microtubes. Thermodynamic calculations of the nanoporous microtubes consisting of GaN nanostructures should give more detailed information on total surface free energy of the microtubes and will be carried out in the future.

Summary

In a summary, a new kind of GaN self-assemblies was synthesized. The self-assemblies were nanoporous and square. These square microtubes were consisted of zincblende GaN submicron irregular structures and emitted broad yellow light centered at 550–750 nm. A shift of Ga- L_2 electron-energy loss edge was observed in the GaN square microtubes.

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