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Gallium Nitride Porous Microtubules Self-Assembled from Wurtzite Nanorods

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Abstract

Wurtzite gallium nitride microscale tubules were synthesized through chemical vapor deposition method. The tubules were self-assembled from nano rods without any templates. The self-assemblies were up to one hundred micrometers long and ten micrometers in diameter. The tubules were porous. The unique structures of the tubules caused red-shifts of Raman modes and yellow band in PL spectra. A possible growth mechanism of the porous microtubules was proposed based on experimental observations.

Keywords: B2. Semiconducting III-V materials, A1. Low dimensional structures, A1. Nanostructures, A1. Growth models, A1. Crystal morphology

1. Introduction

For decades, scientists have been interested in self-assemblies of nanomaterials. Since the discovery of C_{60} [1] and carbon nanotubes [2], various nanoparticles [3], nanowires [4], and nanotubes [5] *etc.* have been synthesized. These

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- nanoscaled materials can self-assemble into various macroscopic structures [6], such as carbon nanotube micro-rings [7, 8], gallium nitride nanocrystal-assembled bulks in millimeters [9], and thermoelectric bulk nanocomposites in inches [10, 11], without any templates. Among the self-assembled macroscopic structures, microtubular structures consisting of nanoparticles are expected to facilitate
 wide applications in electrochemistry [12, 13], biosensors [14] and field emis-
- sion [15]. These macroscopic structures possess high surface area and quantum confinement effects associated with their constituent nanomaterials, resulting in superior properties over three-dimensional bulk nanocomposites.

However, it is challenging to synthesize microtubular structures with quantum effects. Various microscaled hollow tubular structures have been synthesized without templates, such as element microtubes (gold microtubes [16], selenium microtubes [17], tellurium microtubes [18, 19], silicon microtubes [20], and carbon microtubes [21]), surfide microtubes (ZnS [22], MoS₂ [23], and PbS [24]), oxides microtubes (ZnO [25–27] and Al₁₈B₄O₃₃ [28]), borate microtubes (AlB

- [29]), pharmaceutical microtubes [30], and organic microtubes [31–33]. The crystalline size of the constituent nanostructures, as well as the walls of these microtubes, were several hundred nanometers to several microns in diameter. Therefore, these microtubes show only limited quantum properties. To date, it is still very challenging to self-assemble zero-dimensional nanoparticles, one-
- ²⁵ dimensional nanowires, or one-dimensional nanotubes into three-dimensional ordered structures to achieve macroscaled tubular materials with quantum confinement effects.

Gallium nitride (GaN) semiconductors have a direct band-gap of 3.4 eV and have been widely applied in blue and UV light emission devices and laser devices

- ³⁰ [34, 35]. To date, many kinds of GaN nanomaterials, including GaN nanoparticles [36], GaN nanorods [37, 38], GaN nanowires [39–42], GaN nanotubes [43–46], and GaN nanocomposites [9] have been synthesized. GaN square microtubes were recently reported using a thermal vapor deposition method [47]. Such square microtubes consisted of zinc-blende GaN nanoparticles. Here, an-
- ³⁵ other kind of GaN microscaled tubes is presented. The presented microtubes

are circular and consisted of wurtzite GaN nanorods. The self-assembly growth mechanism is proposed based on experimental phenomena.

2. Experimental

The synthesis procedures of microtubules are carried out in a hot-walled chemical vapor deposition (CVD) system consisted of a horizontal quartz tube, a resistance tube furnace equipped with a temperature controller, and a molecular pump backed by a mechanical pump. Type-K thermocouples are used to monitor and control temperatures of the CVD system. The gallium metal (99.999 % purity) was purchased from the Sigma-Aldrich Corporation. Polycrystalline quartz substrates are washed by ultrasonicating in acetone and de-

- ⁴⁵ crystalline quartz substrates are washed by ultrasonicating in acetone and deionized water, followed by thorough rinsing with methanol and drying in air. Gallium is placed on the quartz substrates and located at the center of the horizontal quartz tube. Then the reaction system is evacuated by the molecule pump backed by the mechanic pump, and purged / rinsed several times by argon
- $_{50}$ gas before introducing ammonia gas. The gallium / substrates are then heated under a constant flow of argon gas. The temperature gradually increases from room temperature to 820 - 840 °C over 20 minutes. The flowing argon gas is then switched to ammonia gas. The gallium / substrates are maintained at the reaction temperature and kept under the flowing ammonia gas for two minutes.
- As-received analytical grade commercial argon gas and ammonia gas (99.9 % purity) are used without further purification throughout the procedures. Afterwards, the flow of ammonia is stopped and the entire system is rapidly cooled to room temperature.

X-ray diffraction (XRD) data is collected on a Sintag XDS 2000 θ -2 θ diffractometer (Thermo Fisher Scientific Inc.) using a step mode of 0.02° with 5 s per step, operating at 45 kV voltage and 40 mA current with graphite-monochromatized Cu- K_{α} X-ray radiation of $\lambda = 1.5415$ Å. Scanning electron microscopy (SEM) images are taken in secondary electron imaging mode using a CamScan FE 44 SEM (CamScan Electron Optics Ltd., U. K.) operated at 25 kV. Transmission



Figure 1: XRD pattern of the as-prepared GaN microtubules.

electron microscopy (TEM) experiments are carried out on a JEM-2200FS TEM (JEOL Ltd., Japan).

Raman spectra are collected on a WITec CRM200 confocal Raman system (WITec Corp., Germany). An excitation laser with $\lambda = 532$ nm is focused onto individual porous GaN microtubules using a 100 × optical lens (numerical aperture NA = 0.95). The laser spot is about 500 nm in diameter. The Raman signals are routed to a TE-cooled charge-coupled-device cooled to -60 °C.

The micro-PL measurement on the GaN microtubes is performed in a confocal configuration at room temperature using a 532 nm laser as the excitation source, with the power of 0.4 mW. The spectra are obtained by using a Horiba Triax550 spectrometer equipped with a thermo-electrically cooled charge coupled device. The laser beam is focused on individual GaN microtubules with a $50 \times$ objective under an optical microscope when the PL spectra are collected.

3. Results and Discussion

GaN Microtubules. After the synthesis procedures, yellow layers are deposited
on the substrates. X-ray powder diffraction (XRD) patterns are collected di-



Figure 2: SEM images of (a-d) microtubules grown at different regions and (e) wall surface of a microtubule. White arrows mark the closed ends, black arrows the open ends, and the blue arrows the nanopores of the microtubules. (f) Histogram of microtubule diameter.

rectly from the yellow layers deposited on the substrates. Figure 1 shows a typical XRD pattern of the yellow layers. All of the broadened XRD peaks can be indexed on the basis of the hexagonal wurtzite GaN phase with a space group of P6₃mc [48]. The broadening of the XRD peaks possibly come from defects or crystalline size of the synthesized materials. The internal strain is calculated using the Williamson-Hall method from the XRD data, $\epsilon = 0.0022$. The internal stress of the produced materials can be calculated if we assume that the produced nanomaterials are spherical. The calculated internal stress of the synthesized materials is $\sigma = 0.46$ GPa.

⁹⁰ Figure 2a-d show SEM images of the yellow products on the substrates.

The synthesized structures are hollow. The cross-section of the microtubules is circular. The ends of most of the microtubules are open (marked with black arrows) while some are closed (marked with white arrows). The length of the microtubes is up to $100 \ \mu m$.

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Eighty-five microtubules are randomly chosen from ten different regions of the substrate surfaces (some are shown in Figure 2a-d) and their diameters are measured from SEM images. The microtubules grown on the same region are uniform while those grown on different regions are slightly different, especial in diameters. Figure 2f plots the diameter distribution of these microtubules. The statistical analysis indicates that the diameter of the synthesized microtubules ranges from 4 μ m to 15 μ m with an average value of 10 μ m.

By observing the open ends of the microtubules, the thickness of the microtubular walls is measured from fifteen microtubules, and is found to be $0.13 - 0.52 \mu m$ with an average of $0.24 \mu m$.

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High magnification SEM images (*i. e.*, Figure 2e) indicate that the walls of the microtubules consist of short nanorods. Most of the nanorods are 2 μ m long and about 0.3 μ m in diameter. Consequently, the wall is essentially 1-2 nanorods thick, highly defective with many nanopores (as marked with blue arrows in Figure 2e), and have very large surface areas.

As expected, the porous microtubules are brittle. While in some instances the microtubules are picked up carefully using metal tweezers under an optical microscope, most of the microtubules are broken when they are transferred from the substrates to TEM grids. This is especially noticeable for longer microtubules with large diameters and thin walls. Only shorter microtubules with 115 thicker walls and smaller diameter can be transferred to TEM grids.

Figure 3a shows a typical bright-field TEM (BF-TEM) image of an intact microtubule on a TEM grid. The diameter is about 5 μ m and the wall thickness, as suggested by the region of dark contrast at the outer edges of the tubule, is near 0.5 μ m. The microtubule is *in-situ* rotated around its axis from -15° to 15°

 $_{120}$ on TEM. The width of the microtubule and the darker edges are independent on the rotation. The wall thickness ranges from 0.2 µm to 0.5 µm. Therefore



Figure 3: (a) BF-TEM image of a GaN microtubule. Several typical nanopores are marked by arrows. (b) EDS spectrum of the microtubule in (a). Cu signal coming from the TEM grid. (c) SAED pattern of the microtubule in (a). (d) EDS linescan of Ga- K_{α} across the microtubule in (a). (e) BF-TEM image of several adjacent nanorods near a nanopore. (f) SAED of the nanorod circled in (e). (g) HRTEM image of the nanorod circled in (e). (h) IFFT of (g). Inset: FFT of (g). Two green circles mark the diffraction spots used for IFFT.

the microtubule is in fact tubular hollow structure with a nano-wall.

TEM images confirm that the microtubules are porous besides SEM observations. Consequently, the walls display significant roughness. The intensity
variations observed across the images are consistent with large variations in the grey density of the walls of the microtubule, with some nanopores marked with the arrows in Figure 3a. Electron X-ray dispersive spectroscopy (EDS), shown in Figure 3b, indicates that the microtubule is composed of gallium and nitrogen. The chemical composition is in agreement with the XRD data indicating the crystal structure is consistent with that of GaN. Selected area electron diffraction (SAED) patterns, collected from the microtubule and shown in Figure 3c, indicates that the microtubule is polycrystalline.

Figure 3d shows EDS gallium K_{α} intensity across the microtubule. The EDS linescanning indicates that the microstructure is hollow, with a stronger EDS signal near the walls of the microtubule.

Figure 3e shows several adjacent nanorods near a nanopore. These nanorods are overlapped and connected to each other. One nanorod is chosen (marked with a blue circle) to study crystallinity. Figure 3f shows its SAED pattern. The SAED indicates that the individual nanorod is a single crystal. High-resolution

- TEM (HRTEM) images of the nanorod are taken at room temperature and Figure 3g shows the core region of the nanorod. Although the nanorod is crystalline, there is a lot of atomic distortion in the lattice, as shown in Figure 3h which is the inverse fast Fourier transform (IFFT) of Figure 3g along a certain direction. From the core to the edge of the nanorod, the crystallinity is worse and worse. More atomic distortions and dislocations are observed in the edge
 - regions of the nanorod.

Raman scattering. Microstructures of the nanorods affect optical properties of the microtubules. Figure 4 shows a typical Raman spectrum of a GaN microtubule measured at room temperature. The laser beam is focused on one

 $_{150}$ GaN microtube under an optical microscope and the Raman spectrum is collected from the individual microtubule. Wurtzite GaN with P6₃mc space group



Figure 4: Raman scattering of a GaN microtubule. o: experimental; - : fitting. Inset: complete range of Raman scattering of the microtubule (red curve) compared with that of GaN crystalline films (blue curve).

has six active Raman modes: $A_1(TO) + A_1(LO) + E_1(TO) + E_1(LO) + 2E_2$ [49]. Four active modes are observed here. The peaks at 519, 544, 564, and 719 cm⁻¹ correspond to the $A_1(TO)$, $E_1(TO)$, $E_2(high)$, and $A_1(LO)$ symmetries, respectively. Compared with bulk data (532 cm⁻¹ for $A_1(TO)$, 559 cm⁻¹ for $E_1(TO)$, 568 cm⁻¹ for $E_2(high)$, 734 cm⁻¹ for $A_1(LO)$) [49], the four active Raman modes significantly red shift to shorter wavenumbers.

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Two other Raman modes are observed on the low wavenumber side of the $A_1(LO)$ mode. The two peaks at 656 cm⁻¹ and 704 cm⁻¹ should be surface optical (SO) phonon modes corresponding to A_1 and E_1 symmetries and caused by surface effects of the GaN nanorods.

A unusual Raman peak is observed at 414 cm^{-1} (inset of Figure 4). The peak should be the acoustic overtone [50] from wurtzite GaN nanorods.

PL spectrum. Figure 5a shows a typical photoluminescence (PL) spectrum of
an individual GaN circular microtube, excited by 532 nm wavelength radiation.
The laser beam is focused on the individual microtube under an optical micro-



Figure 5: Photoluminescence spectra of (a) a GaN circular microtube with wurtzite structure and (b) a GaN squared microtube with zinc-blende structure.

scope to excite the PL spectrum. The collected PL signals should only come from the circular microtubule, not from other nanomaterials underneat the microtubule. A yellow band, centered at 653 nm, is observed. Similar yellow bands were also observed in GaN nanocomposites [9], nanoparticles [36], and nanowires [39] with wurtzite structure.

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A PL spectrum of zinc-blende microtubes [47] is shown in Figure 5b for comparion. The PL spectrum of the zinc-blende microtubes is centered at 685 nm. The PL spectrum of the circular microtubes blue-shifts to higher energy, reflecting the fact that the wurtzite GaN has a wider band-gap than the cubic GaN [50].

Growth Mechanism. The formation of the porous microtubules can be explained by the Liesegang phenomenon [51] and diffusion limited growth. Gallium has a low melting point of 303 K and a boiling point of 2520 K. Therefore, large amounts of gallium liquid droplets can condense on quartz substrates from gaseous gallium (Figure 6a), as observed on silicon substrates [52]. The diameter of the condensed droplets is usually $5 - 50 \ \mu m$ [53], depending on reaction temperatures and substrates. The behavior of gallium is very similar to that of other low melting point metals, such as selenium [17]. Gallium droplets evapo-

rate at high temperatures to produce gallium vapor during the CVD procedure.



Figure 6: Possible growth mechanism of the self-assembled GaN microtubules. (a) Initial stage. No GaN nanomaterials are synthesized. (b) Template stage. Liesegang rings of GaN nanomaterials are formed. (c) Growth stage. GaN nanorods self-assemble into microtubules. (d) Enclosing stage. Ga sources are exhausted and the ends of GaN microtubules are closed. Top: model of each stage. Middle and bottom: SEM images at each stage.

Once ammonia passes the gallium droplets, gallium vapor would react with ammonia to produce GaN nanoparticles (Figure 6b). The number of the GaN nanoparticles per unit volume is so dense around the gallium droplets that the GaN nanoparticles around the gallium droplets can be considered as a supersaturated aerosol, similar to charged nanoparticles in solutions [54] and nanoparticles in vapor phases [55, 56]. These supersaturated GaN nanoparticles would spontaneously aggregate into Liesegang rings due to thermodynamatic stability, as observed in other kinds of ordered Liesegang nanoparticle-rings [54, 57].

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The proposed growth mechanism is experimentally confirmed by SEM observation. The middle panel in Figure 6b shows an SEM image of a typical GaN nanoparticle Liesegang ring with a diameter of several micrometers. A higher magnification SEM image (bottom panel in Figure 6b) indicates that the microring consists of many GaN nanoparticles with a size below one hundred nanometers. Other size GaN rings are also observed on the substrates. These surviving

GaN Liesegang rings indicate that the Liesegang rings can self-assemble from GaN nanomaterials during the CVD procedures when GaN nanoparticles are supersaturated enough.

Then, porous GaN microtubules grow on the Liesegang ring templates, as shown in Figure 6c. Based on the diffusion-limited aggregation mechanism, the

- ²⁰⁵ protruding parts of the GaN microrings can easily attract the GaN nanorods and grow quickly to build new nanorod-walls from the Liesegang ring edges, leaving the hollow interior. SEM images in Figure 6c show tips of two GaN microtubules, indicating the growth on the Liesegang rings. With the consuming of gallium, supersaturated GaN nanorods are continuously produced from
- the reaction of ammonia and gallium vapor as long as the gallium vapor pressure are high enough, resulting in the continuous deposition of GaN nanorods on the GaN microrings to form GaN microtubules. During the whole growth stage, the gallium droplets evaporate to generate the gallium vapor to keep the microtubules open.
- The gallium droplet size is reduced with the reaction time because of evaporation. Once the gallium droplets vanish, the vapor pressure of the gallium droplets would decrease near the open ends of GaN tubules. As a result, the gallium vapor pressure front should shrink back from the microtubule open tips. Because the GaN nanorods aggregate along the gallium vapor pressure front,
- the aggregating GaN nanorod front would also shrink back to enclose the microtubule ends, forming enclosed GaN microtubes as shown in Figure 6d. SEM images in Figure 6d show two microtubules with half-closed ends.

Additionally, the GaN microtubules are synthesized in a short time – only two minutes. It is the indirect evidence for the supersaturation growth, indicat-

ing rapidity of the Liesegang ring formation and the microtubule growth. These two phenomena (ring formation and rapid growth) are the specific characteristics of super-saturation growth caused by the Liesegang effect.

4. Conclusion

One kind of novel gallium nitride circular tubules are grown from wurtzite nanorods by chemical vapor deposition. The bottom-up grown microtubules are porous, several tens of micrometers long and several microns in diameter. The constituent nanorods are crystalline with lots of defects. The self-assembly of GaN nanomaterials is contributed to the diffusion limited growth of supersaturated GaN nanorods. Compared with bulk crystals, the Raman active modes of the microscale tubules red shift. The red-shift should come from the defects in the microstructure. A yellow band was observed in photoluminescence spectra of the grown nanomaterials.

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