Preparation and characterization of carbon nanotubes encapsulated GaN nanowires

C.-C. Chen\textsuperscript{a,}\textsuperscript{*}, C.-C. Yeh\textsuperscript{b}, C.-H. Liang\textsuperscript{c}, C.-C. Lee\textsuperscript{b}, C.-H. Chen\textsuperscript{a}, M.-Y. Yu\textsuperscript{a}, H.-L. Liu\textsuperscript{d}, L.C. Chen\textsuperscript{c}, Y.-S. Lin\textsuperscript{e}, K.-J. Ma\textsuperscript{e}, K.H. Chen\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, National Taiwan Normal University, 88 Tingchow Road Sec. 4, Taipei 116, Taiwan
\textsuperscript{b}Institute of Atomic and Molecular Science, Academic Sinica, Taipei, Taiwan
\textsuperscript{c}Center for Condensed Matter Science, National Taiwan University, Taipei, Taiwan
\textsuperscript{d}Department of Physics, National Taiwan Normal University, Taipei, Taiwan
\textsuperscript{e}Department of Mechanical Engineering, Chung-Cheng Institute of Technology, Tao-Yuan, Taiwan

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Abstract

A novel two-step catalytic reaction is developed to synthesize gallium nitride nanowires encapsulated inside carbon nanotubes (GaN@CNT). The nanowires are prepared from the reaction of gallium metal and ammonium using metals or metal alloys as a catalyst. After the formation of the nanowires, carbon nanotubes are subsequently grown along the nanowires by chemical vapor deposition of methane. The structural and optical properties of pure GaN nanowires and GaN@CNT are characterized using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, energy dispersive X-ray spectroscopy and Raman spectroscopy. The results show that GaN nanowires are indeed encapsulated inside carbon nanotubes. The field emission studies show that the turn-on field of GaN@CNT is higher than that of carbon nanotubes, but substantially lower than that of pure GaN nanowires. This work provides a wide route toward the preparation and applications of new one-dimensional semiconductor nanostructures. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the discovery of carbon nanotubes by Iijima [1], the materials always offer intriguing possibilities for fundamental studies of nanoscale well-defined structures and provide high potential for technological applications. Significant progresses have been made recently on the studies of mechanical, electronic transport and structural properties of individual carbon nanotubes and the results indicated that they exhibited high tensile strength [2,3], discrete electronic states [4] and structural helicity [5]. On the application side, carbon nanotubes have been applied in the fabrications of various devices, for examples, scanning probes [6], biological sensors [7,8], electronic transistors [9,10], field emitting devices [11,12], and energy storage [13].

\textsuperscript{*} Corresponding author. Tel.: +886-2-8931-6151; fax: +886-2-2932-4249.
E-mail address: t42005@cc.nctu.edu.tw (C.-C. Chen).

Filling materials into the inner hollow cavity of carbon nanotubes have brought great attention because the new filled one-dimensional (1-D) structures are expected to exhibit different physical properties than those of empty nanotubes [14]. Many attempts have been made to encapsulate various materials into carbon nanotubes. For example, capillary force has been utilized to fill lead and bismuth into an open nanotube [15,16]. Also, different transition metals such yttrium, manganese, iron or gadolinium have been encapsulated into nanotubes using an arc-discharge method [17,18]. In addition, a direction chemical vapor deposition (CVD) of metal organic complexes of Fe(CO)_5 and Co(CO)_5 has been used to generate the carbon nanotubes filled with Fe and Co nanoparticles [19,20]. However, in those methods, the overall yield of the encapsulated nano-materials is rather low and they are difficult to scale up. Moreover, to our knowledge, still there are few reports on how to fill binary semiconductor materials into carbon nanotubes, although it has been known that 1-D semiconductor nanostructures (nanowires)
are electronic confined systems ideal for fundamental studies of their physical properties and for the fabrications of optoelectronic nanodevices [21,22].

One of the III–V 1-D semiconductor nanostructures, GaN nanowires, has attracted much interest because of its great potential for new visible and UV optoelectronic applications [23,24]. Recently, we have developed a large-scale synthesis of GaN nanowires from the catalytic reaction of gallium and ammonium using various metals as a catalyst [25]. Subsequently, breakthroughs have been made to achieve high purity and high quality synthesis of the GaN nanowires by careful optimizing the growth conditions [26]. From our previous results, we found that the resulting GaN nanowires from the catalytic reaction are usually terminated with a nanoparticle on the tip of each individual nanowire and the mechanism of the nanowire formation can be attributed to vapor–liquid–solid (VLS) growth. It has been well known that single-wall and multi-wall carbon nanotubes can be prepared by a CVD of methane or ethylene using iron, nickel, cobalt or their alloys as a catalyst [27–29]. There are several similarities between the proposed mechanisms and growth conditions of GaN nanowires and carbon nanotubes. First, the growths of the nanowires and nanotubes are both performed in a gas phase with the presence of metal catalysts. Second, the catalysts of cobalt, nickel and iron can commonly serve in either one of the growths. Third, after the growth, catalytic nanoparticles were generally found on the tip of individual nanowires and nanotubes. Thus, on the basis of the similarities between their growth conditions, we propose a two-step catalytic reaction (Fig. 1) in a gas phase for the growth of GaN nanowires encapsulated inside carbon nanotubes (GaN@CNT). The resulting materials of GaN@CNT were characterized using electron microscopy and Raman spectroscopy. In addition, their field emission properties were measured to demonstrate their potential in an electronic device application.

2. Experimental

2.1. Materials, reagents and catalysts

All chemicals were reagent grade and used as received. Silicon (100) wafers (2 × 2 cm², semiconductor grade) were used as substrates. The substrates were cleaned by a standard treatment in piranha solution (H₂O₂/H₂SO₄ = 3/7) and then washed several times with deionized water. Before the reaction, the substrates were completely dried in the furnace at 150°C under an argon flow. Molten gallium (1 ml, 99.999%) were transferred to a silicon substrate (Substrate A) by a syringe inside a dried box. A catalyst solution was prepared by dissolving either metal nitrate (0.002 mole, 99%, M(NO₃)₃, M = Fe, Ni, Co) or two kinds of metal nitrates (molar ratio = 1:1) in ethanol. The solution was dropped onto a silicon substrate (Substrate B) and dried at 150°C for 12 h. Ammonium and methane were purified through a gas purifier to remove water and oxygen before the reaction.

2.2. Growth of GaN nanowires encapsulated inside carbon nanotubes

The detailed experimental procedures for the preparation of pure GaN nanowires at the first-step growth have been described in our previous publication [26]. The experimental setup for the two-step growth of GaN@CNT is described schematically in Fig. 2. Substrates A and B were deposited...
with an excess amount of molten gallium and catalyst (1–5 mg), respectively. Both substrates were inserted into the center of a quartz tube (1 in. diameter) inside a tube furnace and Substrate B (downstream) was placed away from Substrate A (upstream) with a distance of ~1 cm. The quartz tube was degassed by purging with a flow of argon. At this stage, the first-step reaction began. The temperature of the furnace was increased from room temperature to 915°C at a rate of 100°C/min and kept under a constant flow of ammonia (18 sccm). After 10 h, GaN nanowires were produced from the reaction of gallium and ammonium. The quartz tube was purged with argon (500 sccm) for 10 min to remove residual ammonia. Then, the second-step reaction started. The temperature of the furnace was increased from 915 to 1000°C at a rate of 100°C/min. As soon as the temperature of the furnace reached to 1000°C, a constant flow of methane (1000 sccm) was purged into the quartz tube. The reaction temperature was kept at 1000°C for 5–20 min. Afterwards, the quartz tube was purged with argon (100 sccm) and the furnace was cooled to room temperature at a rate of 10°C/min. Finally, the materials deposited on Substrate B were collected for further characterization.

2.3. Material characterization

The morphologies and crystal structures of the resulting materials on Substrate B were examined using scanning electron microscopy (SEM, JOEL-JSM-6300) and X-ray powder diffraction (XRD, Toshiba, A-40-Cu). Transmission electron microscopy (TEM, Zeiss-10C at 100 kV), high-resolution TEM (HRTEM, JOEL-4000 EX at 400 kV), selected-area electron diffraction, and energy dispersive X-ray spectroscopy (EDX) were used to inquire structure and stoichiometry information of individual GaN nanowire. The TEM samples were prepared by a direct observation on the cross section of Substrate B or by depositing an aliquot of resulting materials dispersed in toluene onto an amorphous carbon film on a Cu grid.

2.4. Raman spectroscopy

All Raman spectra were taken at room temperature using 514.5 nm incident photons from an Ar+ ion laser (Spectra Physics Model 2017). The linearly-polarized light was focused on the sample through a 100 × optical microscope objective (0.95 N.A.) with a spatial resolution of <2 μm in a backscattering geometry. Several locations of each sample were probed to ensure reproducibility of the data. The laser power used was less than 1.5 mW. The possible effect of local heating was checked by varying the excitation power and no appreciable change in the Raman spectra was observed for powers up to ~5 mW. The scattered light without polarization analysis was collected and dispersed using a Dilor XY 800 triple spectrometer equipped with 1800 grooves/mm gratings and a liquid-nitrogen cooled 1024 pixel wide charge-coupled detector (Jobin Yvon Model Spectrume One). The spectral resolution with these instruments was typically less than 1 cm⁻¹.

2.5. Field emission measurements

Field emission properties of GaN@CNT were carried out using a parallel-plate I–V measurement configuration at room temperature under a base pressure of 1 × 10⁻⁷ Torr. As shown in Fig. 3, a Keithley 237 electrometer was employed for supplying the voltage and measuring the current. The measurement was performed by collecting electrons emitted from the sample while applying a positive voltage on an indium–tin–oxide-coated (ITO) glass electrode. The electrode was placed 90 μm above the sample.

Fig. 3. Schematic illustration of the field emission measurement setup. Indium tin oxide (ITO) glass was used as anode to monitor the uniformity of the emitted current.
The area of the anode was restricted to be smaller than that of the sample to avoid the emission at the sample edges due to structural enhancement, which would lead to false analyses of field emission characteristics. Precaution is required to clean the sample before measurement in order to eliminate dust particle on the surface that would also cause false emission current signals.

3. Results and discussion

3.1. Formation of GaN encapsulated inside carbon nanotubes

In previous work, we have shown that metal (Fe, Co, Ni) and their metal alloys are efficient catalysts for the growth of GaN nanowires [26]. Fig. 4 shows typical SEM and TEM images of resulting materials obtained on the Substrate B after the first-step growth. A high yield (>95%) of nanometer wire-like structures (nanowires) with a diameter in the range of 20–50 nm is produced from the reaction of Ga metal and NH₃ [Fig. 4(a)]. These nanowires are distributed over a large area of the substrate and have quite uniform diameters. The lengths between two entanglement points are up to several micrometers. The structural analysis on the nanowires using XRD and HRTEM showed that they can be indexed to a hexagonal wurtzite structure [30]. The strong intensities of X-ray and electron diffraction peaks relative to the background signal suggested that the resulting products have high purity of GaN wurtzite phase [26]. Fig. 4(b) shows the TEM image that a single GaN nanowire is terminated with a nanoparticle on its tip. The structure and stoichiometry analyses using TEM and EDX on the nanowire suggested that the nanoparticle on the tip consists of GaN and catalyst, whereas the nanowires only contains gallium and nitrogen. The result agrees with the proposed mechanism of VLS growth of the nanowires as described in Fig. 1.

The catalytic nanoparticles terminated on the end of GaN nanowires can also served as a good catalyst for the growth of carbon nanotubes in methane. Fig. 5 shows the SEM and TEM images of resulting materials on the Substrate B after the second-step growth. A thin layer of crystalline materials of light contrast is coated outside the surface of wire-like structures of dark contrast [Fig. 5(a)]. The structural and stoichiometry analyses using HRTEM, EDX and Raman (see below) indicate that the outer thin layer structures and inner wire-like materials in the images are indeed consisted of carbon nanotubes and GaN nanowires, respectively. The nanowires encapsulated inside the hollow core of the carbon nanotubes can extend over a substantial portion of the length (up to μm). The growth direction of carbon nanotubes follows the long axis of GaN nanowires [Fig. 5(b)]. The diameters of nanotubes were generally varied with the diameters of GaN nanowires. The number of graphite layers of carbon nanotubes depended on the total reaction time of the second-step growth. The longer reaction time, the more layers of carbon nanotubes outside the nanowires were obtained. Typically, the number of graphite layers calculated from HRTEM image (see below) are 15–20 under a reaction time of 10 min. Some parts of GaN nanorods are not successively connected inside carbon nanotubes and exhibited linear segments from several tenths to hundred nano-meters [Fig. 5(c)]. The linear segments of GaN nanowires can be found either in the middle or at the end of carbon nanotubes. The structural analysis showed the segment is still a hexagonal structure, which suggests that GaN nanowires may be dissected into several segments without changing their crystal structures during the second-step growth at high temperature (1000°C).

Fig. 6 shows a typical HRTEM image and its corresponding electron diffraction (inset) of the GaN@CNT. A core-shell type structure is observed. The clear cross lattice fringes observed in the core indicated that GaN nanowires have a single crystal structure. In our previous report, both [001] and [110] directions were observed to be in parallel to the long axis of the wires, suggesting that they are common growth directions of the nanowires [26]. A selected-area electron diffraction (inset) on the nanowires shows that they still keep a hexagonal wurtzite structure after the second heating process. The shell of the GaN@CNT consists of about 15 graphene concentric layers with a uniform spacing of 0.34 nm between two consecutive layers, which consistent with previous experimental data measured from multi-wall carbon nanotubes [1]. The interface between nanowires and nanotubes was sharp with no gap or other phases under HRTEM. The result suggests that the first layer of carbon nanotubes could be directly formed on the surface of GaN nanowires.

3.2. Growth mechanism of GaN@CNT

As described above, after the first-step reaction we have observed catalytic nanoparticles terminated on the tip of individual GaN nanowires [Fig. 4(b)] and they can also served as a good catalyst for the growth of carbon nanotubes. The result has provided a clear evidence that the growth of GaN nanowires agree with the proposed mechanism of VLS growth, which is applicable to that in some ceramic whiskers such as AlN, SiC and TaC [31–33]. For the catalytic growth of carbon nanotubes, two formation mechanisms, ‘base growth’ and ‘tip growth’, have been proposed in 1994 [34]. In both growth mechanisms, the formation of carbon nanotubes was briefly interpreted as following: carbon source from the decomposition of hydrocarbon gas (methane in this case) keeps feeding into catalytic nanoparticles and forming small droplets. Each individual droplet acts as a nucleation site for the growth of carbon nanotubes. After the
Fig. 4. (a) A top-view SEM image of GaN nanowires grown on Substrate B. The lengths of the nanowires here are up to several μm and their diameters are approximately 20–50 nm. The nanowires show smooth surface and no ramification over their length. (b) The TEM image of a single GaN nanowire. A nanoparticle as indicated by an arrow in the image is terminated on the tip of the nanowire.

concentration of carbon reaches saturation, graphite layers started to grow. Finally, nanotubes stop growing while both ends closed up and catalytic particles stay in either ‘base’ or ‘tip’ relative to the growth direction of carbon nanotubes. Thus, on the basis of those proposed mechanism, we would expect in our experiment that either carbon nanotubes form at the opposite side of GaN nanowires [35] or grow along the nanowires during
Fig. 5. (a) The SEM image of resulting materials from Substrate B after the second-step growth. The layers of carbon nanotubes (light contrast) were covered on the surface of the nanowires (dark contrast). This sample was particularly prepared under a condition that the second-step reaction was performed for 20 min. Thus, the layers of nanotubes in the image are much thicker than that we usually obtained (the reaction time of 5–10 min). (b) The TEM image of GaN@CNT shows that carbon nanotubes were grown along the long axis of GaN nanowires. The inset shows a magnified TEM image of the tip of a single GaN@CNT. (c) The TEM image of a single GaN@CNT shows that there are linear segments of GaN nanowires encapsulated inside carbon nanotubes.
the second-step growth as described Fig. 1. However, only the latter case was observed in our experiment and no carbon nanotubes were found on the opposite direction of the nanowires. Also, our results showed that a closed structure of both ends of nanotubes was always observed, and no discontinuous or open layer structures were found on the tip or in the middle of GaN@CNT. All those results suggest that ‘base growth’ may be more likely the pathway during the second-step growth of GaN@CNT.

The growth mechanism of GaN@CNT may not be completely interpreted based on the VLS and ‘base and tip growth’ models. There was a possibility that, at the beginning of the second-step growth, carbon source was also adsorbed on the surface of GaN nanowires besides feeding into the catalytic nanoparticle terminated on the tip of the nanowires. Sequentially, the amorphous carbon layer adsorbed on the nanowires was transformed into a graphite layer at high temperature (1000°C). Although further experiments should be addressed on our proposed mechanism of GaN@CNT growth, here we suggest that the nanowires themselves may also act as a nucleation site or as a template at the second-step growth. Currently, we are trying to grow carbon nanotubes with only existence of the nanowires without catalytic particles.

No nano-composite (GaN@CNT) or nano-junction (nanotubes-catalyst-nanowires junction, see Fig. 1) was observed when the two-step growth was executed in a reversed process (the growth of carbon nanotubes at 1000°C first and then GaN nanowires at 915°C). The unsuccessful growth of nano-junction may be due to the loss of catalytic abilities of the nanoparticles after carbon nanotubes formation at the first step growth. Previous reports have indicated that catalytic nanoparticles were encapsulated inside graphite layers after the CVD growth [34]. Thus, the nanoparticles cannot serve as good catalysts any longer for the second-step growth of GaN nanowires.

3.3. Raman spectroscopy

In the main plot of Fig. 7 we show the Raman-scattering intensity of the GaN nanowires sample [26]. The Raman-scattering response, obtained by dividing the measured spectra by the Bose–Einstein thermal factor, is dominated by a number of optical phonons and a broad photoluminescence background. We fit the phonon peaks using a standard Lorentzian profile. Additionally, the broad luminescence background was fitted to a polynomial and subtracted out from the spectrum. The frequencies and assignments of the phonon modes shown in Fig. 7 are listed in Table 1. One first observes five first-order phonon bands near ~144, 537, 562, 569, and 728 cm⁻¹ in the Raman spectrum of the GaN nanowires. These phonons are identified as having $E_2$(low), $A_1$(TO), $E_2$(TO), $E_2$(high), and $A_1$(LO) symmetries.
Table 1
Raman peaks observed in GaN nanowires and GaN@CNT spectra at 300 K and the corresponding symmetry assignments. Units are cm$^{-1}$.

<table>
<thead>
<tr>
<th>GaN</th>
<th>GaN@CNT</th>
<th>Symmetry assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>144</td>
<td>140</td>
<td>$E_2$(low)</td>
</tr>
<tr>
<td>252</td>
<td>248</td>
<td>Zone-boundary phonon</td>
</tr>
<tr>
<td>421</td>
<td>413</td>
<td>Zone-boundary phonon</td>
</tr>
<tr>
<td>537</td>
<td>523</td>
<td>$A_1$(TO)</td>
</tr>
<tr>
<td>562</td>
<td>552</td>
<td>$E_1$(TO)</td>
</tr>
<tr>
<td>569</td>
<td>561</td>
<td>$E_2$(high)</td>
</tr>
<tr>
<td>670</td>
<td>655</td>
<td>Defect-induced phonon mode</td>
</tr>
<tr>
<td>728</td>
<td>711</td>
<td>$A_1$(LO)</td>
</tr>
<tr>
<td>1347</td>
<td></td>
<td>$D$ band</td>
</tr>
<tr>
<td>1584</td>
<td></td>
<td>$G$ band</td>
</tr>
<tr>
<td>1614</td>
<td></td>
<td>$D'$ band</td>
</tr>
</tbody>
</table>

Secondly, we observe phonons at $\sim 252$ and $421$ cm$^{-1}$, which we ascribe to the zone-boundary phonons activated by the finite-size effects. Finally, the appearance of the broad structure near $\sim 670$ cm$^{-1}$ is likely associated with to a defect level below the GaN conduction band minimum.

The inset of Fig. 7 illustrates the Raman spectrum of GaN@CNT with eight phonon resonances (see Table 1), which are associated with the vibrational modes of the GaN nanowires. However, the position of all these phonon peaks are perturbed to some extent due to the encapsulation of carbon nanotubes. Additionally, the broad bands are seen at $\sim 1347$, 1584, and 1614 cm$^{-1}$. We believe that these features are connected with the amorphous carbon ($D$ band), carbon nanotubes ($G$ band) and by products in carbonaceous materials ($D'$ band) [20,36-38].

Fig. 6. A typical HRTEM image of the GaN@CNT showing the core-shell type structure. The corresponding electron diffraction of the nanowire is shown in the inset.
3.4. Applications of GaN@CNT in field emission device

Typical field-emission characteristics of the GaN@CNT, specifically emission current density $J$ as a function of applied field, are shown in Fig. 8. To determine the current density in the measurement, one needs effective emission area as well as the total emission current. However, it is difficult to determine the emission area for samples of irregular morphology like nanotubes and nanowires. In this paper, since the anode area is smaller than that of sample and uniform fluorescence from emitted electron was observed throughout the ITO anode, the emission current densities were obtained by dividing the measured current by the anode area. As shown in Fig. 8, the turn-on field of the GaN@CNT, which is defined as the field required to draw an emission current density of 0.01 mA/cm$^2$, is 5 V/μm. Moreover, the reproducible result from the two repetitive measurements in Fig. 8 indicates that GaN@CNT exhibit promising field emission properties of 0.5 mA/cm$^2$ at an electric field of 9 V/μm. A ten-fold increase of the emission current was observed at 4 V/μm, which is reproducible at the two emission measurement runs. While the detailed mechanism of the emission jump is to be investigated, it might be related to the tube-encapsulated wire structure of the material. In comparison to the field emission characteristics of the GaN-nanowires and CNTs, the 5 V/μm turn-on field is higher than the 3 V/μm for CNT; but substantially lower than the 12 V/μm for pure GaN nanowires as described in our earlier report [26].

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