Microstructures of gallium nitride nanowires synthesized by oxide-assisted method

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Abstract

Gallium nitride (GaN) nanowires were synthesized using the recently developed oxide-assisted method by laser ablating a target of GaN mixed with gallium oxide (Ga$_3$O$_5$). Transmission electron microscopic characterization showed that GaN nanowires were smooth and straight with a core-sheath structure of 80 nm in average diameter and tens of micrometers in length. Both hexagonal and cubic structured GaN nanowires were produced. The growth mechanism was discussed. © 2001 Published by Elsevier Science B.V.

In recent years, considerable effort has been attracted to synthesize gallium nitride (GaN) because of its potential applications in blue and ultraviolet light emission and high-temperature/high-power electronic devices [1–3]. Due to the continual demand for reduction in device size, it is naturally of interest to fabricate nanodevices based on nanoscale materials with novel properties. GaN in nano dimensions, in particularly the nanowires, is a good candidate for this need [4–6]. Several methods have been developed to prepare GaN nanowires. Fan and coworkers employed carbon nanotubes as nano reactors to grow GaN nanowires, from which blue light emission was observed [5]. Recently, highly ordered GaN nanowires were obtained by Zhang and coworkers [7] by assembling the nanowires into anodic alumina membranes. Lieber and Duang [4], based on the vapor–liquid–solid (VLS) growth mechanism, developed a method to prepare GaN nanowires by laser abating a metal-containing target, in which the metal nanoparticles were used as catalysts. Recently, Lee and coworkers [8–10] reported an oxide-assisted method to synthesize several semiconductor nanowires, including silicon (Si), germanium (Ge), gallium arsenide (GaAs) and gallium phosphide (GaP). In the fabricating process, oxides played a central role in the nucleation and growth of nanowires via a series of oxidation–reduction reactions, but no metal catalyst was needed. The absence of catalysts simplifies nanowire fabrication and is highly beneficial to the consequential applications of the nanowires. In this work, the oxide-assisted method was used to synthesize GaN nanowires. The microstructures of the GaN nanowires thus obtained were characterized in detail. Apart from the previously re-
ported hexagonal structured nanowires [4]. GaN nanowires with the cubic lattice structure were also observed for the first time.

The experimental setup is similar to the previous system used for the synthesis of the Si, Ge, GaAs and GaP nanowires via the oxide-assisted method [8–10]. The synthesis of the GaN nanowires was carried out in a quartz tube placed in a tube furnace and an excimer pulsed laser (Lambda Physik) was used for ablation. A target with size of 25 (length) × 25 (width) × 5 (thickness) mm³ and made of GaN powders mixed with 25 (mol) % of gallium oxide (Ga₂O₃) was placed inside the tube at the center which was in central region of the high-temperature zone of the furnace. A polished silicon wafer was placed at the downstream end of the furnace as the substrate. There is a distance of about 25 cm from the target to the substrate. The temperature at the middle of the furnace and the substrate were 1000 and about 900 °C, respectively. The working pressure was around 400 Torr, and the carrying gas of Ar + 5% H₂ was kept flowing through the tube in a direction from the target to the substrate with a flow rate of 50 standard cubic centimeters per minute. The KrF excimer laser beam (wavelength 248 nm, energy 400 mJ/pulse, frequency 10 Hz) was focused by a quartz lens to a spot size of 0.5 × 4 mm² onto the target and the ablation lasted for 2 h. The morphology, structure and chemical composition of the nanowires were characterized by scanning electron microscopy (SEM, Philips XL 30 FEG), transmission electron microscopy (TEM, Philips CM20), high-resolution TEM (HRTEM, Philips CM200FEG), energy dispersive X-ray (EDX) spectrometer attached to the TEM and electron energy-loss spectrometer (EELS) (Gatan GIF200) attached to the HRTEM.

Fig. 1 shows a typical SEM image of the product. Straight and smooth nanowires can be observed from the image. Analysis of a number of the nanowires shows that the diameters vary from 20 to 120 nm, with an average value at 80 nm, and the lengths are up to tens of micrometers. Comparing to the nanowires synthesized by the confined-template growth [7], the diameter of individual nanowires produced by us is very homogeneous, and no nanoparticles attached to the nanowires were observed. Fig. 2 shows a typical TEM image of a nanowire with a diameter of about 75 nm and the inset is the corresponding selected area electron diffraction (SAD) pattern. The nanowire is very smooth and the SAD pattern recorded along [2 1 1 0] direction shows that the nanowire has a hexagonal structure. Detailed structures of the nanowire were further revealed by HRTEM observation. Fig. 3 is a typical HRTEM image of the nanowire. The nanowire has a core-shell structure, which is a typical feature of the wires synthesized by the oxide-assisted method. According to the lattice spacing and the intersection angles between the lattice planes measured from the image, it can be concluded that the crystal core is GaN with a hexagonal structure [11]. The structure observed here is the same as that of the GaN nanowires synthesized by other methods [5–8]. The growth direction of the nanowire is along ⟨0 0 0 1⟩ as determined from this im-
age. The sheath consisted of an amorphous layer, the chemical composition of which was gallium oxide (Ga$_2$O$_3$) as determined by the EELS. Analysis of a number of nanowires indicated that the oxide thickness varied from 2 to 10 nm with an average of about 4 nm.

In addition to the GaN nanowires of hexagonal structure as observed previously, GaN nanowires with a cubic structure were also observed in the product. Fig. 4 shows a TEM image of a cubic GaN nanowire, and the corresponding SAD pattern (inset in Fig. 4). The SAD pattern shows unambiguously that the nanowires has a cubic structure [12], and the incident electron beam in this observation was parallel to the $\langle 110 \rangle$ zone axis. An enlarged lattice-resolved image of the nanowire is shown in Fig. 5. From the lattice spacing and the intersection angles between the lattice planes, the wire was further confirmed to be cubic structured GaN with a $\langle 111 \rangle$ growth direction. Like the hexagonal nanowires, Figs. 4 and 5 also reveal that the crystal core was sheathed with atomically sharp interfaces by an amorphous layer of about 4 nm in thickness. The chemical composition of the amorphous layer is also gallium oxide (Ga$_2$O$_3$) as determined by EELS. It appears that there is no significant difference in the morphology between hexagonal and cubic structure nanowires. It is not clear which parameters determined the crystal structure of the nanowires during the growing process, although nucleation process and temperature may be two possible factors [3]. The detailed mechanisms need to be further studied and understood.

The oxide-assisted growth mechanism of the nanowires has been discussed in detail in previous publications [5,8,13]. Briefly, in the present synthesis of GaN nanowires, we propose that the nucleation and growth of nanowires took place via the oxidation-reduction reaction: 3Ga$_2$O+4N = 4GaN+Ga$_2$O$_3$ at the low temperature zone near the substrate. The Ga$_2$O source was produced
from a reaction between $\text{Ga}_2\text{O}_3$ and Ga, and transported by the carrying gas from the high-temperature zone to deposition zone. The Ga as well as the N originated from GaN decomposition within the target upon laser ablation at high temperature (middle of furnace). It is considered that the series of oxidation–reduction reactions play a crucial role in the oxide-assisted growth mechanism. To verify the proposed mechanism, an experiment was done with a target made of pure GaN powder instead of previous one containing $\text{Ga}_2\text{O}_3$. No nanowires were obtained in product except some particles with micrometers in size. These results revealed that the oxide within target as well as related oxidation–reduction reactions are necessary for the formation of the one-dimensional structure by oxide-assisted growth. The representative features of the nanowires so obtained differ significantly from those grown from the metal-catalyzed VLS growth, laser-assisted metal-catalytic growth, or template-confined growth. The present successful synthesis of GaN nanowires by the oxide-assisted method offers additional support for the oxide-assisted model [8,13]. It is worthwhile noting that oxide also played an important role in the synthesis of GaN nanowires via the hot-filament chemical vapor deposition of gallium oxide ($\text{Ga}_2\text{O}_3$), graphite and ammonia, where metal-catalysts were not used either [5].

In summary, the oxide-assisted method was used to synthesize GaN nanowires by laser ablating a GaN target mixed with the $\text{Ga}_2\text{O}_3$. GaN nanowires of both the hexagonal and cubic structures were produced as identified by transmission electron microscopy observation. The GaN nanowires had an average diameter of 80 nm and length of tens of micrometers. It is considered that a series of oxidation–reduction reactions plays an important role in the nucleation and growth of the GaN nanowires during the oxide-assisted growth process.

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References