High quality GaN nanowires synthesized from Ga$_2$O$_3$ with graphite powder using VPE method

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Abstract

Synthesis of single-crystalline GaN nanowires on C-Al$_2$O$_3$ substrates in a vapor phase epitaxy process by the help of a Ni catalyst was realized. The GaN nanowires were grown at 1000–1100 °C using a mixed powder of Ga$_2$O$_3$ and graphite. GaN nanowires were found to have a single-crystalline hexagonal structure in a high-resolution transmission electron microscopy and X-ray scattering measurements in spite of atmospheric pressure growth. Diameters of the grown nanowires range from 60 to 120 nm, which are comparable to the diameters (10–80 nm) of hydrothermally prepared Ni nanoislands acting as a seed. This fact indicates that the diameter of GaN nanowires can be effectively tuned by controlling that of Ni catalysts.

Keywords: GaN; Nanowires synthesis; VPE method; Ga$_2$O$_3$ powder

1. Introduction

Gallium nitride (GaN) and related III-nitrides can be applied not only to optical devices such as light emitting diodes (LEDs) and laser diodes (LDs), but also to high power or high temperature microelectronic devices [1]. Recently, many research groups have extensively studied the synthesis, microstructure and physical properties of GaN [2,3]. Also, one-dimensional nanostructures such as nanowires and nanotubes are attractive building blocks for nanoelectronics since their morphology, size and an electronic property make them suitable for fabricating both nanoscale devices and interconnects [4].

GaN nano-materials have an interesting and potentially important role both in demonstrating new theoretical concepts and in practical applications [5], and they have attracted a great deal of attention due to their unique physical properties and potential applications in GaN nanowires-based electronic devices [6,7]. One-dimensional GaN crystals such as nanowires and nanorods, have been synthesized by many different methods in recent years. However, the direction and diameter control of GaN nanowires is the key to their synthesis, in which the synthetic process itself plays a role when it comes to the large-scale synthesis of GaN nanowires with good quality.

In the present work, we report a novel approach to the synthesis of single-crystalline GaN nanowires through the reaction of Ga$_2$O$_3$ and graphite mixed powder with NH$_3$ gas at an atmospheric pressure. We synthesized high quality GaN nanowires with uniform size and clear surface. In addition, formation mechanism of GaN nanowires is also presented by structural analysis.

2. Experiment

We deposited Ni (0.5, 1 nm) on c-plate Al$_2$O$_3$ substrate using radio-frequency magnetron sputtering in order to prepare the Ni catalyst. After their deposition, the Ni thin films were pretreated with ammonia (NH$_3$) gas at a flow ratio of 400 sccm for 20–40 min at 600–800 °C, in order to form the nanometer sized catalyst particles on the substrate.

The GaN nanowires were synthesized using the vapor phase epitaxy (VPE) method. Fig. 1 shows a schematic diagram of the VPE method used to synthesize the GaN nanowires. As shown in Fig. 1, a SiC heater was used to achieve a temperature gradient and the furnace consisted of three zones. In the source part, the...
starting materials were: Ga$_2$O$_3$ (>99.99% purity) and graphite powder (99.99% purity). They were mixed at mole ratios of Ga$_2$O$_3$:C = 1:20 and 25. The powder boat used was made of sintered Al$_2$O$_3$ which was placed in the center of a quartz tube with an outer diameter of 100 mm and a length of 1000 mm. In the substrate part, the Al$_2$O$_3$ crystal plate utilized as the substrate was placed at a distance of 10–40 mm from the boat. The nanowires synthesis experiments were performed for 90 min at 1000–1100 °C. High purity Ar (99.999%) gas was used as the carrier gas. While heating the substrates for 90 min, Ar gas with a flow rate of 2000–2500 sccm was introduced into the quartz tube at an atmosphere pressure of 760 Torr. NH$_3$ (99.99%) was used as the reaction gas, and was sprayed downstream between the source and substrate with a flow rate of 200–600 sccm. After the synthesis, the sample was allowed to cool down naturally to room temperature, and was then analyzed by X-ray diffraction (XRD) using Cu K$_\alpha$ radiation. The shape of the GaN single crystals was observed using field-emission scanning electron microscopy (FESEM). Their chemical composition was investigated using energy-dispersive X-ray spectroscopy (EDX). The crystallinity and structure of the GaN nanowires were studied by high-resolution transmission electron microscopy (HRTEM).

3. Results and discussion

The catalyst films were etched by introducing NH$_3$ gas into the quartz reactor at 600–800 °C and were agglomerated on the substrate, resulting in the formation of nanosize particles. In the case of the treatment with NH$_3$ at 800 °C, the size of the Ni catalyst particles was less than 100 nm. Fig. 2 shows the FE-SEM images revealing the general morphologies of the Ni catalyst on the Al$_2$O$_3$ substrates. As shown in Fig. 2, Ni nanoislands with diameters of 10–80 nm were formed on the surface of the substrate during the treatment at 800 °C for 40 min. The GaN nanowires were successfully synthesized by Ni-catalyst driving using the VPE method. Fig. 3(a) shows an FE-SEM image of the GaN nanowires grown by the help of the Ni catalyst on the Al$_2$O$_3$ surface. These nanowires were synthesized for 90 min at 1050 °C with an NH$_3$ flow rate of 400 sccm and ranged from 60 to 120 nm. Diameters of the grown nanowires are comparable to those of hydrothermally prepared Ni nanoislands acting as a catalyst for nanowire growth, indicating that the diameter of GaN nanowires can be effectively tuned by controlling that of Ni catalysts.
Fig. 4. FE-SEM images of GaN nanowire and its chemical composition: (a) FE-SEM image of GaN nanowire and (b) its chemical composition by EDX analysis.

Fig. 3(b) shows an FE-SEM image of the cross-section of the nanowires. The shape of the GaN nanowires was straight. As shown in Fig. 3, the GaN nanowires were synthesized together with Ga2O3 polycrystals. According to this image, the following reaction mechanism can be confirmed, consisting of two chemical routes:

\[
\text{Ga}_2\text{O}_3 + 2\text{C} \rightarrow \text{Ga}_2\text{O} + 2\text{CO} \quad (\text{reaction}) \quad (1)
\]

\[
\text{Ga}_2\text{O} + 2\text{NH}_3 \rightarrow 2\text{GaN} + \text{H}_2\text{O} + 2\text{H}_2 \quad (\text{growth}) \quad (2)
\]

Eq. (1) shows that the Ga2O3 in the boat first reacts with graphite to form Ga2O which is then carried to the growth zone by Ar gas. Next, in Eq. (2), Ga2O reacts with NH3. Therefore, the GaN nanowires are synthesized on the Ni catalyst. Eq. (2) is thermodynamically favorable at the synthesis temperature of 1000 °C [8]. If the reaction could not occur in the boat, the Ga2O3 nanocrystals were synthesized on the substrate.

In addition, Ni catalyst was observed on the tip of the synthesized GaN nanowires. This fact means that the GaN nanowires were mainly synthesized via the vapor–liquid–solid (VLS) process. The Ga2O vapor and decomposition N form NH3 gas are dissolved in the Ni catalyst to form a Ni–Ga–N alloy. After a certain time, concentration of Ga and N in the alloy are saturated and then, GaN precipitates out from the Ni catalyst.

Fig. 5 shows the XRD pattern used for the structural characterization of the synthesized GaN nanowires. All of the diffraction lines were indexed and identified by X-ray powder diffraction as the hexagonal wurtzite type with the lattice parameters: \( a = 3.2040 \) Å and \( c = 5.2080 \) Å, while no cubic phase was found. All of the diffraction peaks are broadened due to the size effect.

Fig. 6 shows the URTEM and SAED images of the GaN nanowires along the \( \langle 0001 \rangle \) zone axis. Fig. 6(a) shows that the
synthesis direction of the GaN nanowires was [1 2 1 0] direction, and the morphology of the side edge part was mainly smooth. Fig. 6(b) shows an enlarged photographic high-resolution TEM image of the GaN nanowires. The distance between neighboring atoms was 0.263 nm, which is coincident to corresponding to the plan distance of hep GaN (0 0 2). The lattice was good crystallographic structure and its orientation was clear and uniform. Fig. 6(c) shows the selected area diffraction pattern of the GaN nanowires, which demonstrates that they are single-crystalline and of good quality, and which could be indexed to the diffraction pattern of hep (wurtzite) GaN. The clear and regular spots indicate that the synthesized GaN nanowires are of high quality. Also, the selected area diffraction pattern is in good agreement with the wurtzite XRD data.

4. Conclusion

We synthesized GaN nanowires of high quality using the VPE method. The GaN nanowires were obtained in the temperature range of 1000–1150 °C. The Ar and NH3 flows were 2000–2500 and 200–600 sccm, respectively. The thickness of the GaN nanowires was below 100 nm. The shape of the GaN nanowires was confirmed through SEM analysis. In addition, the XRD data was in agreement with the selection rules for the wurtzite structure. The HRTEM image and SAED pattern indicated that the GaN nanowires are single crystal structures with a perfect lattice. All of these results confirm the good crystallinity of the synthesized GaN nanowires. The results of this experiment confirm the direct and high quality synthesis of GaN nanowires using the VPE method.

References