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Synthesis and Characterization of One-Dimensional GaN Nanostructures Prepared via Halide Vapor-Phase Epitaxy

Yun-ki Byeun, Do-Mun Choi, Kyong-Sop Han,* and Sung-Churl Choi†

Department of Ceramic Engineering, Hanyang University, Seoul 133-791, Korea
**Korea Institute of Science and Technology, Seoul 136-791, Korea*
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ABSTRACT

High-quality one-dimensional GaN nanorods and nanowires were synthesized on Ni-coated c-plan sapphire substrate using halide vapor-phase epitaxy (HVPE). Their structure and optical properties were investigated by X-ray diffraction, scanning and transmission electron microscopy, and photoluminescence techniques. Full substrate coverage of densely packed, uniform, straight and aligned one-dimensional GaN nanowires with a diameter of 80nm were grown at 700~900°C. The X-ray diffraction patterns, transmission electron microscopic image, and selective area electron diffraction patterns indicate that the one-dimensional GaN nanostructures are a pure single crystalline and preferentially oriented in the [001] direction. We observed high optical quality of GaN nanowires by photoluminescence analysis.

Key words*: *GaN, Single crystalline, One-dimensional, Nanostructure, Photoluminescence

1. Introduction

The discovery of carbon nanotubes[1)] has drawn great attention to fabrication of one-dimensional (1-D) nanostructures, such as wires and rods.[2,3)] Understanding of such one-dimensional nanostructures will be essential in testing the role of dimensionality and size in optical, electrical, mechanical, and magnetic properties.[4)] The miniaturization of devices represents a trend for both industrial manufacture and academic research. In this regard, 1-D nanostructures are interesting as building blocks toward the fabrication of various nanometer scale devices.[9,10)] Furthermore, theoretical calculations indicate that the 1-D nanostructures are of superior crystalline quality to those of bulk or thin film.[11)] The combination of the distinctive physical and chemical properties of GaN and the unique advantages of nanostructures make GaN an excellent candidate for designing and fabricating nanodevices. Ga-based nitride semiconductors having a large band gap and strong chemical bonding have been extensively studied due to their versatile optoelectronic and electronic device.[5)] Various methods for forming 1-D GaN structures have been reported in literature.[6-8)] Among these methods, halide vapor-phase epitaxy (HVPE) has been widely used for growing high quality, high growth rate GaN thin films with transfer of native defect concentrations to non-degenerate levels. This enables p-type doping, because HVPE growth occurs near thermodynamical equilibrium condtions.[12,13)] Despite these advantages, the growth of sub-100 nm films of 1-D GaN nanowires via HVPE has been rarely demonstrated and reported. To control growth using this technique, we have developed a framework for understanding the growth conditions with a vapor-liquid-solid (VLS) mechanism of formation for 1-D GaN and the fabrication of defect-free single crystalline GaN.

In this work, we study the formation of 1-D GaN nanostructures using Ni-coated single crystalline sapphire. Using the HVPE technique, we were able to effectively control diameter size and type of 1-D GaN growth.

†Corresponding author : Sung-Churl Choi
E-mail : choi0505@hanyang.ac.kr
Tel : +82-2-2220-0505 Fax : +82-2-2291-6767

2. Experimental Procedures

The growth of GaN nanowires was carried out in a horizontal hot-wall HVPE system. Fig. 1 shows the schematic diagram for the growth system of 1-D GaN nanostructures using the Ga metal source and HCl, NH_3, and N_2 gas flow system. The substrate used was c-plane sapphire, which was sputter-coated with Ni catalyst. The Ga source was located 0.5 inch from the center of the hot zone. The source reaction with HCl and N_2 carrier gas was controlled by infusion of HCl and N_2 into the reaction tube, leading to the conversion of the gallium metal source to gallium chloride. The reacted vapors were then transported to the substrate area, where they were mixed with NH_3 gas. They are deposited to form single crystalline GaN on the substrate coated Ni catalyst. In this process, the HCl flow rate was in the range of 1~10 sccm, and the NH_3 flow rate was 10~200 sccm at various temperatures. The total gas flow rates were kept at 1000 sccm for all experiments. After the furnace was cooled to room temperature, a light yellow deposited layer was

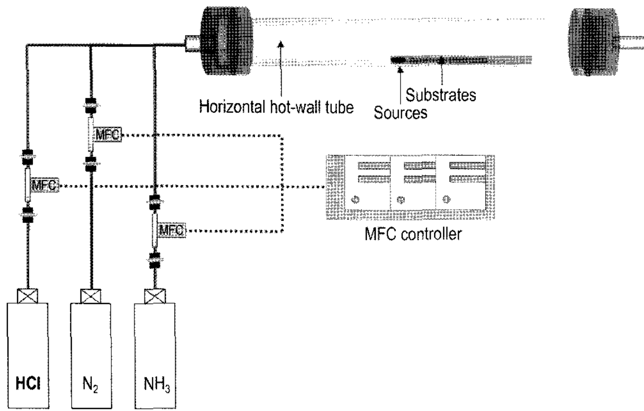


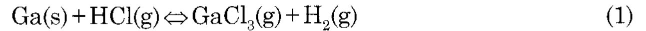
Fig. 1. Schematic diagram showing the home made growth system of 1-D GaN nanostructures.

found on the surface of the substrate.

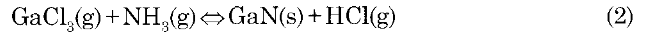
The morphologies and crystalline structure of the 1-D GaN films deposited on the substrate were characterized by scanning electron spectroscopy (SEM), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM) and selective area electron diffraction (SAED). Photoluminescence (PL) spectra were also measured at room temperature using a He-Cd laser with 325 nm excitation to study the optical properties of the nanowires.

3. Results and Discussion

The presence of an HVPE has been recently considered critical to the study of 1-D GaN nanostructure. The transported Ga elements evaporated with the reacted chlorine gas through the reaction of HCl gas, and NH_3 can produce GaN crystalline phases along the following schematic reaction.



$$Ga(s) + HCl(g) \Leftrightarrow GaCl_3(g) + H_2(g) \quad (1)$$



$$GaCl_3(g) + NH_3(g) \Leftrightarrow GaN(s) + HCl(g) \quad (2)$$

In this reaction, the $GaCl_3$ serves as a thermodynamically favorable transport agent for the formation of GaN phase as well as acting as a doping reactant. More importantly, this process can produce single crystalline GaN nanowires without defects, providing a solution to common problems associated with defects in previous studies of GaN thin films.

Fig. 2 shows typical SEM images of GaN rod growth as a function of the gas flow rate of P_{HCl}/P_{NH3} under growth conditions of 900°C for 0.5 h. The gas flow rates were controlled by a mass flow controller (MFC) with nitrogen gas, which took on the role of carrier and diluter for the reaction gases. The gas flow rates of P_{HCl}/P_{NH3} were as follows: 0.002 (Fig. 2(a)), 0.01 (Fig. 2(b)), and 0.05 (Fig. 2(c), (d)). Here, total gas flow rates are fixed at 1000 sccm to reduce the parameter of the gas conditions. As the HCl gas was released for reaction in the condition with the lowest P_{HCl}/P_{NH3} concentration (Fig. 2(a)), the initially formed shiny metallic coating was observed on the substrate. However, as the rate value increased beyond 0.01, a light yellow layer was observed. This layer was analyzed and found to be composed of GaN single crystal grains and rods. We found that increasing the holding time (Fig. 2(d)) increased rod length.

Fig. 3 shows the SEM images indicating the effect of temperature on growth, with temperatures ranging from 700~900°C. These figures show that the diameter of 1-D GaN

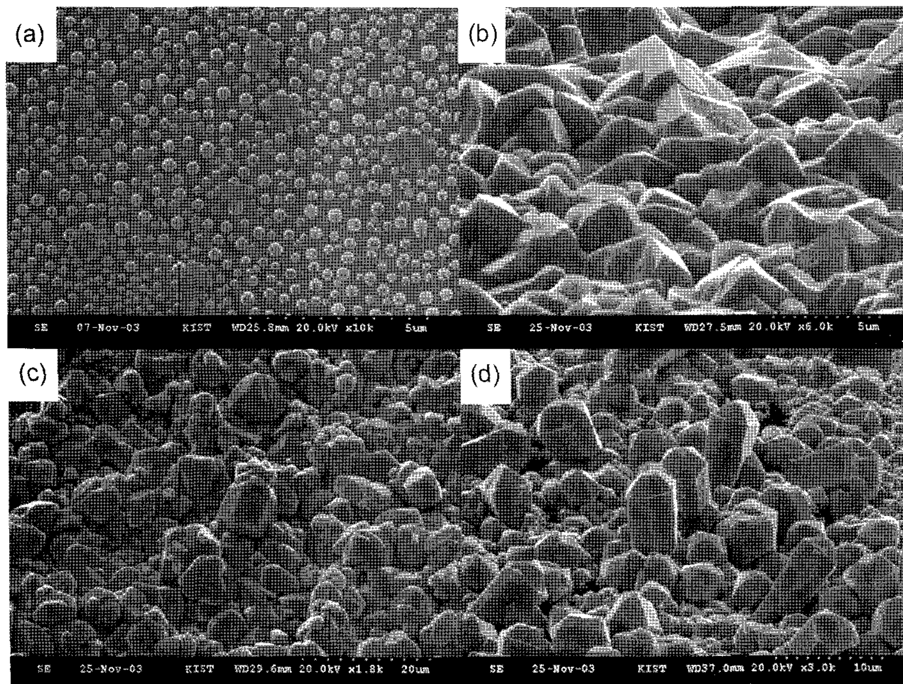


Fig. 2. SEM image of GaN rods grown as a function of flow rate of P_{HCl}/P_{NH3}; (a) 0.002, (b) 0.01, (c) 0.05, and (d) only during 1.5 h holding.

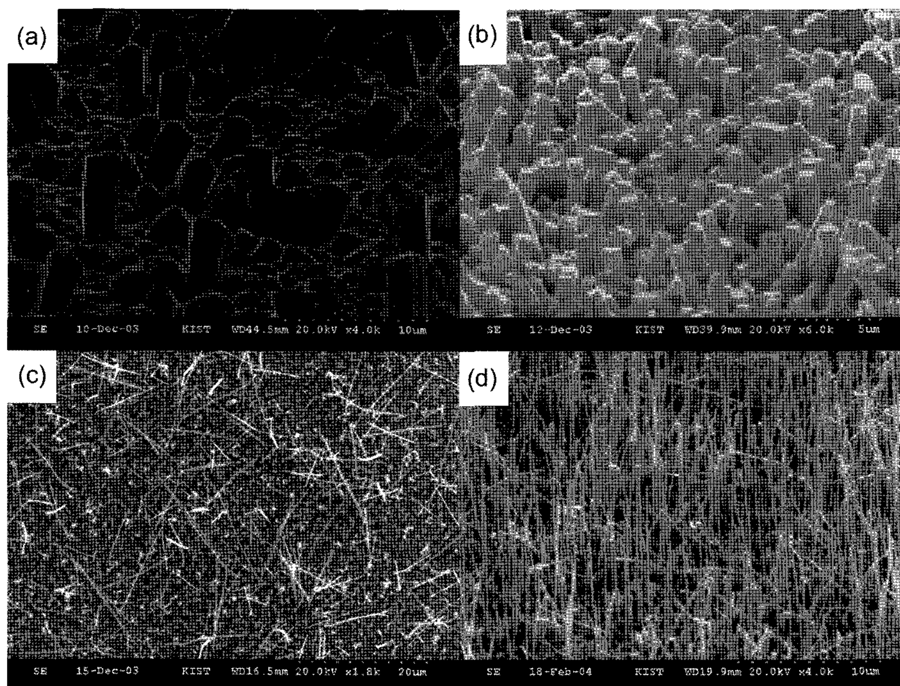


Fig. 3. Typical SEM images of 1-D GaN rods and nanowires were grown on c-plan sapphire substrate at (a) 900, (b) 850, (c) 800, and (d) 700°C, respectively.

decreased as the growth temperature decreased. This result suggested that the primary growth direction was dependent on growth temperature. At higher temperatures, growth in the [110] direction was preferred over [001] directional growth.

As shown in Fig. 2(c), (d), rod growth rate can be defined as growth direction with 11.5 μm/h ([001] direction) and 0.36 μm/h ([110] direction), respectively. Fig. 4 shows that the aspect ratio ($Length_{[001]}/Diameter_{[110]}$) increased steeply with decreasing growth temperature. Vertical growth of GaN was dependent on the growth time, and lateral growth of GaN was dependent on the growth temperature. It could be understood that nanowire diameter was decreased with decreasing temperature accompanying change of dilution degree of inert gas pressure. Namely, $GaCl_x$ partial pressure (P_{GaCl3}) was reduced with decreasing growth temperature. A theoretical study by W. Seifert was conducted on the growth of GaN thin films in a VPE system.[14] However, no growth mechanism was reported for 1-D GaN.

Fig. 5 shows low angle XRD patterns of GaN nanowires grown on c-plan sapphire substrate by HVPE. The sharp diffraction peaks in the pattern correlate with a hexagonal wurtzite structure of lattice constants of a=0.3189 nm and c=0.5183 nm, which agree with the reported values of GaN

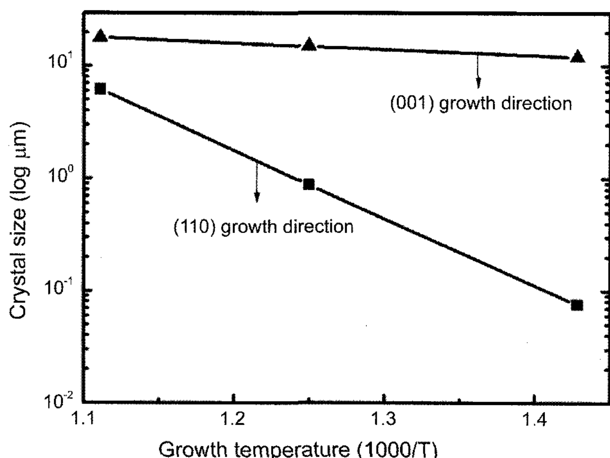


Fig. 4. Growth and reduction rate of one dimensional GaN along the different growth directions as a function of growth temperature.

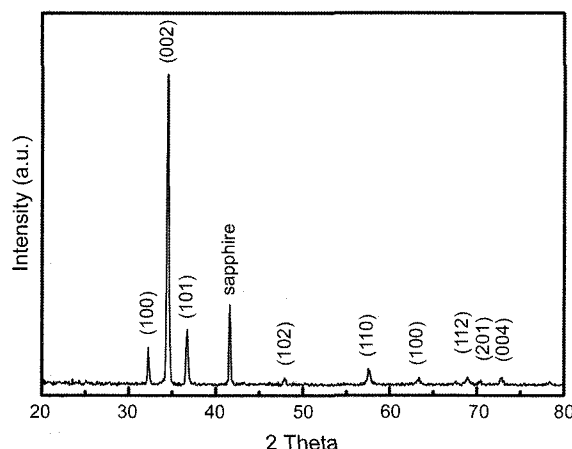


Fig. 5. XRD pattern of 1-D GaN nanostructure on the sapphire substrate by HVPE. The pattern is indicative of a hexagonal wurtzite structure.

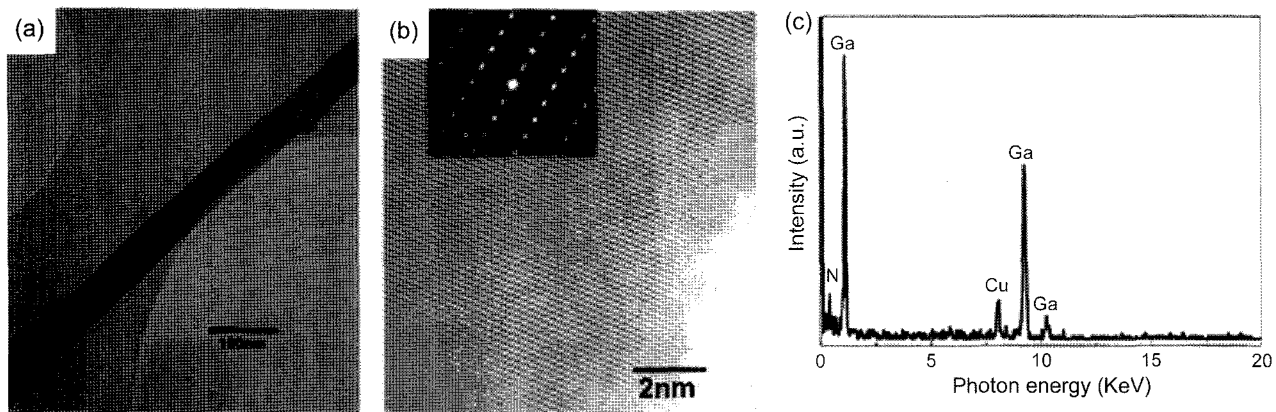


Fig. 6. (a) TEM image of GaN nanowires, (b) High resolution TEM image of single crystalline GaN nanowire and inset is the corresponding electron diffraction pattern taken along the <100> zone axis, and (c) EDS spectrum of the nanowire.

bulk. It should be noted that in the XRD data, the intensity of the (002) plane is higher than that of bulk crystals, because it was grown as the preferred orientation of c-plan growth direction in hexagonal GaN structures. Generally, nanowire for the metal catalyst (Ni is used in our experiment), because of the mechanism of VLS growth, formed metal tips on the top of nanowires. However, the metal tips don't retain after finished process, because they are etched out by formation of HCl gas produced from Eq. (2). Therefore, impurities of metal alloys do not appear in XRD analysis.

Fig. 6 shows the low magnification images of a GaN nanowire with a crystalline linear segment whose diameter is about 80 nm. The HR-TEM image (Fig. 6(b)) was parallel to the long axis of the wire with the [001] direction. The inset shows SEAD patterns taken along the <100> zone axis, which show that the nanowires have wurtzite structures with a [001] growth direction. This is in good agreement with former results of XRD. The Fig. 6(c), the EDS analysis, indicates that the nanoparticle on the tip mainly consisted of Ni, Ga, and N, but that the nanowire was composed of only Ga and N. The molecular ratio of Ga/N of the nanowire calculated from the EDS data was similar to that of a bulk GaN crystal. The collective data from SEM, EDS, and TEM analyses altogether were consistent. In general for VLS growth, diameter size of nanowires is mostly dependent on the particle size of the metal catalyst.[4] In contrast, our study seems to indicate that the diameter of 1-D GaN rods are more influenced by growth temperature. We observed that growth of our nanowires were more characteristic of direct vapor-phase growth than the proposed mechanism of VLS growth. However, our nanowires were not grown without the catalyst. This phenomenon has not yet been addressed.

Finally, we carried out studies of the optical properties of the GaN nanowires. Fig. 7 shows the PL spectrum of GaN nanowires at room temperature. After exciting the nanowires with a He-Cd laser at 325 nm, a band-edge emission at 374 nm (3.31 eV) is observed. Importantly, the well-known defect-induced yellow emission band is not observed here,

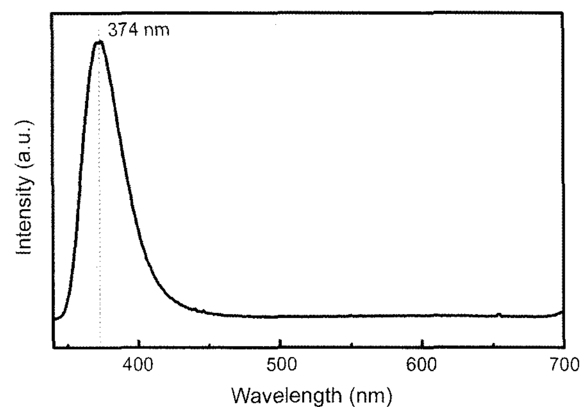


Fig. 7. PL spectrum of GaN nanowire excited at 325 nm by a He-Cd laser with a band-edge emission at 374 nm (3.31 eV).

indicating the high optical quality of GaN nanowires obtained in the present study.

4. Conclusions

In this study, high-quality 1-D GaN rods and nanowires were synthesized on Ni-coated c-plan sapphire substrate using the HVPE system. The high density of the straight and aligned 1-D GaN nanowires was grown at 700°C. We have optimized the synthetic growth conditions, so as to minimize the diameter of 1-D GaN nanowires via growth temperature. The resulting nanowires have a preferred [001] growth direction. The strong photoluminescence of the nanowires in the blue region suggests possible applications in optoelectronic nanodevices. Therefore the GaN with well-controlled 1-D nanostructures offers good opportunities for direct nanodevice applications, such as nanowire-based FETs, LEDs, and sensors.

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