

Various one-dimensional GaN nanostructures formed by non-catalytic routes

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Abstract GaN crystals were nucleated and grown into various one-dimensional forms by the supersaturation of a source gas via non-catalytic routes. Chemical vapor deposition (CVD) was employed for the GaN growth using Ga metal and ammonia gas as sources. The formation of one-dimensional GaN nanostructures including nanocolumns, nano-cakes, nano-flowers, and nano-bundles was identified using scanning electron microscopy (SEM). X-ray diffraction (XRD) was performed to analyze crystallinity of each nanostructure. The growth mechanism of thick nanocolumns was proposed as the epitaxial growth of GaN (002) hexagonal columns with {100} facets from the GaN thick films. The growth of nano-cakes was suggested as the (002) hexagonal plate formation with {100} facets at the first stage followed by the secondary (002) crystal growth from each plate. The growth mechanism of nano-flowers would be the formation of GaN seed particles first and the subsequent nucleation and growth of GaN (101) nanowires with several directions from the seeds. The growth of nano-bundles is the most interesting structure and the formation mechanism was

proposed as the first formation of a GaN (002) nanowire and then subsequent nucleation and growth of GaN (002) and (10-1) nanocrystals at the surface of the primary GaN (002) nanowire.

Keywords GaN · One-dimensional · Nanostructures · Non-catalytic routes

1 Introduction

Gallium nitride is a III-V semiconductor having a wide energy band gap and showing a direct transition behavior. Due to this physical property it shows the effective blue, violet, or UV light emission [1, 2]. Thus, the GaN in thin film forms has been widely used as light emitting diodes (LED) for traffic light, full color display applications, and laser diodes (LD) for high density-digital versatile disk (HD-DVD) applications [3–6]. GaN in nanowire forms, on the other hand, shows the reduced defect density and size confinement effect, and thus showing superior light emitting properties compared to that in thin film forms [7–13]. One-dimensional nanowires have the length in micro-scale, thus the manipulation of nanowires to construct including optical and electronic devices and bio/chemical sensors is relatively easy compared to that of zero-dimensional nanocrystals [14–17].

The vapor phase growth mechanisms of nanowires include vapor-solid (VS) and vapor-liquid-solid (VLS). Contrary to the restricted growth of nanowires from the metal catalysts by the VLS mechanism the vapor solid mechanism can give freedom in the formation of nanowires with various structures. The crystal growth mechanisms vary with each different structure of nanowires. In this study GaN nanowires in various structures of nanocolumns, nano-cakes, nano-flowers, and nano-bundles were grown by VS mechanism

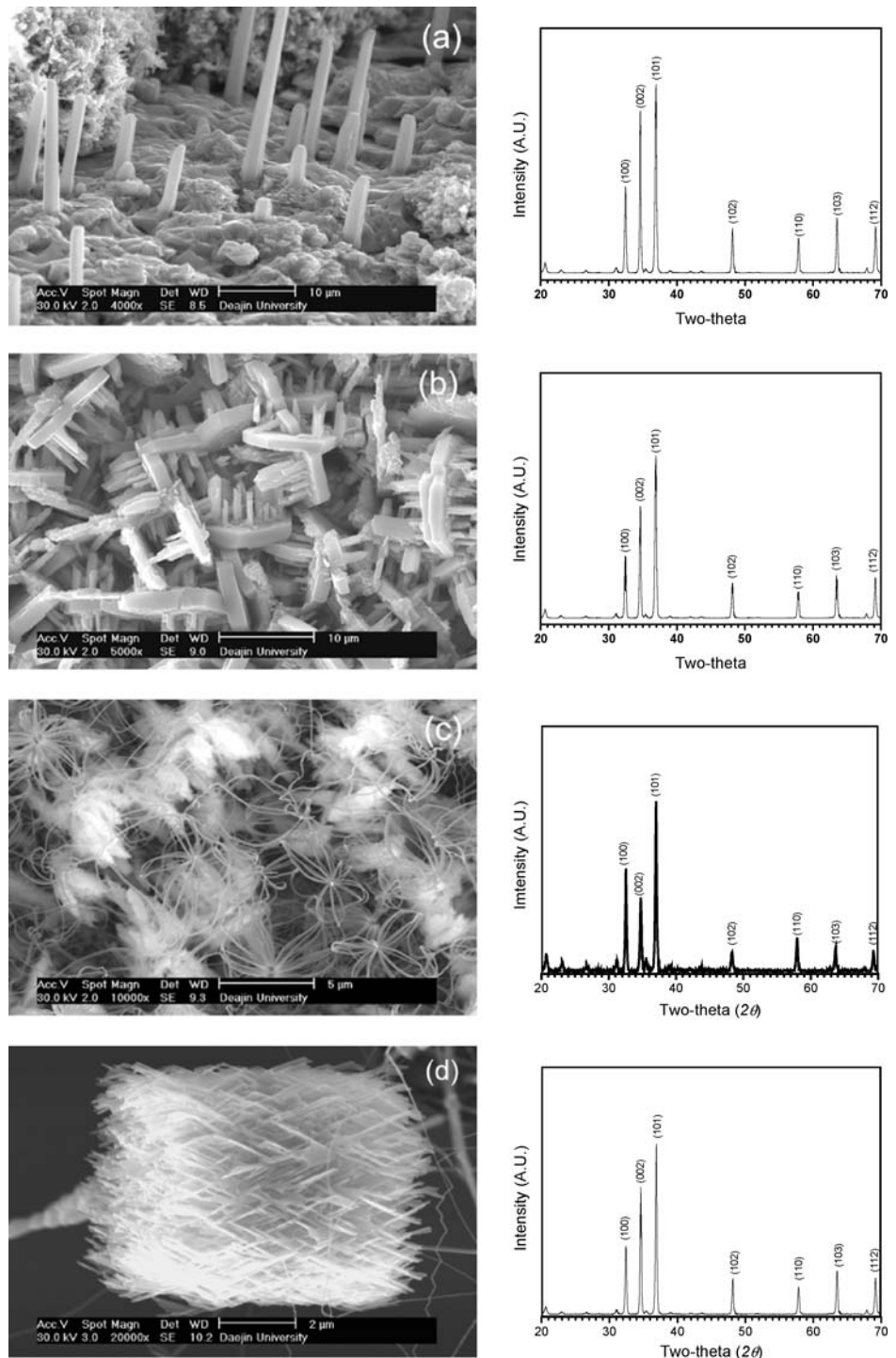
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Fig. 1 Scanning electron microscopy (SEM) images and x-ray diffraction patterns of (a) nano-columns, (b) nano-cakes, (c) nano-flowers, and (d) nanobundles, respectively, grown by the non-catalytic route



and the crystal growth mechanism for each structure was proposed based upon SEM, XED, and TEM analyses.

2 Experimental

A simple thermal chemical vapor deposition (CVD) chamber consisting of a two-zone furnace and a quartz tube was used

for the growth of GaN nanowires. Ga metal (99.999%) and NH_3 gas (99.9999%) was used as source materials, and Si (111) wafer was used as substrates for the growth. Ga metal was loaded inside an alumina boat and Si wafer was located right above the Ga metal. Ar gas (99.9999%) was introduced into the reaction chamber as a carrier gas. The temperature of the first zone including the Ga source was 1000°C and that of the secondary zone including substrates was varied from 800

to 1000°C. The gas flow rate of NH₃ was 150 sccm and the chamber pressure was 200–400 torr. The time period for the growth of GaN nanowires was 10–20 min and the substrate temperature was 800–900°C.

The scanning electron microscopy (SEM: Philips XL-30 E-SEM, Eindhoven, the Netherlands) was employed to observe the morphological features of GaN nanowires. The crystallinity of GaN nanowires were examined by the x-ray diffraction (XRD: Rigaku 2000, Japan). Cu-K α radiation was used at 40 kV and 40 mA, and 2θ - θ scans covered from 10 to 70° at a theta offset of 4° and a step size of 0.5° per min. The high-resolution transmission electron microscopy (HRTEM: JEM4010, JEOL, Japan) was used to investigate the crystal orientation, defects, and detail morphology of GaN nanostructures. The optical characteristics of GaN nanostructures were examined by photoluminescence (PL: F-450 Hitachi, Japan).

3 Results and discussion

GaN nanowires with various structures were grown by non-catalytic routes. Figure 1 shows scanning electron microscope (SEM) images of GaN nanowires with different morphologies and corresponding XRD patterns. It was found that thick GaN films were deposited on the Si wafers first, and then GaN columns could grow from the thick GaN films by nucleation and subsequent growth possibly due to the high vapor pressure of Ga both from the Ga metal source and from the thick GaN films. The direct growth of GaN columns from the thick GaN films without any catalytic assistance supports the high vapor pressure at the surface region. The GaN nanocolumns show formation of clear hexagonal facets at the radial surface and they were almost well aligned. The growth orientation would be [001] since they show hexagonal facets. The tip portion shows secondary facets with an angle with {100} planes, which would be {110} planes. The top surface of the GaN columns has exact hexagonal shape presenting the formation of (002) planes. The nucleation of GaN columns would occur to reduce the free energy of the supersaturated Ga vapor inside the reaction chamber, especially at the surface region of GaN films. Once the facets form in the radial direction the nanowires will grow into facet as well as longitudinal directions, and thus thick columns can form instead of thin cylindrical-shape nanowires. If the facets are not formed the cylindrical nanowires with much smaller diameters will grow mostly into the longitudinal [001] direction since the vapor pressure of the cylindrical-shape convex surface of the nanowires would be higher than the vapor pressure inside the chamber, while that of the flat top-edge of the nanowires is much lower. XRD patterns from these GaN columns in Fig. 1 (a) show strong (002) and (101) diffraction. The strong (002) deflection comes from the [001] growth direction of GaN

columns and the strong (101) diffraction comes from the highest XRD diffraction intensity of GaN listed in JCPDS card. Due to the c-axis growth the relative diffraction intensity of (002) to that of (101) is very high in the GaN columns.

The possible mechanism of GaN nano-cake structure formation, shown in Fig. 1(b), could be elucidated by employing the two-stage crystal growth. First, primary {002} platelets can nucleate and grow randomly. This disordering in the crystal growth of GaN platelets is possibly due to the random formation of GaN nuclei. The platelets have exact hexagonal facets at the side surfaces and would be {100} faces. The secondary nucleation and growth of GaN can occur at the top surfaces of GaN platelets due to higher vapor pressure of Ga and the low energy sites for nucleation. The crystal growth direction would be [001] since this is the vertical growth from the (002) planes and the GaN nano-columns on the platelets are also faceted. The XRD patterns in Fig. 1(b) also show strong reflection from (002) planes, but they were relatively weak compared to those from (101) planes most probably due to random orientation of nano-cakes.

The GaN nano-flowers shown in Fig. 1(c) could be formed by the formation of small-size GaN seed particles first and then growth of thin nanowires from the seeds. Many nanowires from the seeds can grow into a flower structure. In this case, the nanowires were not faceted and cylindrical-shape nanowires were formed. The diameter of nanowires was about 50–100 nm. The XRD patterns from the nano-flower structure shown in Fig. 1(c) reveal the relatively strong reflection from (101) planes compared to other nanostructures. High-resolution transmission electron microscopy (HRTEM) was performed for the nano-flowers and the image is shown in Fig. 2. High crystallinity was found in the nanowire and the defect such as stacking fault was not detected. The interplanar d -spacing was about 2.057 Å, corresponding to (101) planes. Thus, the growth orientation of each nanowires in the nanoflower was determined as the <101> family.

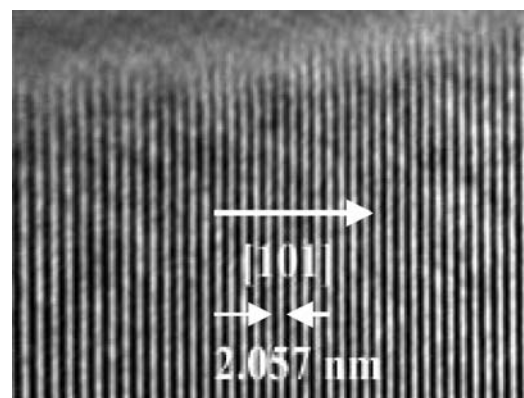


Fig. 2 High-resolution transmission electron microscope (HRTEM) image of GaN nanoflower

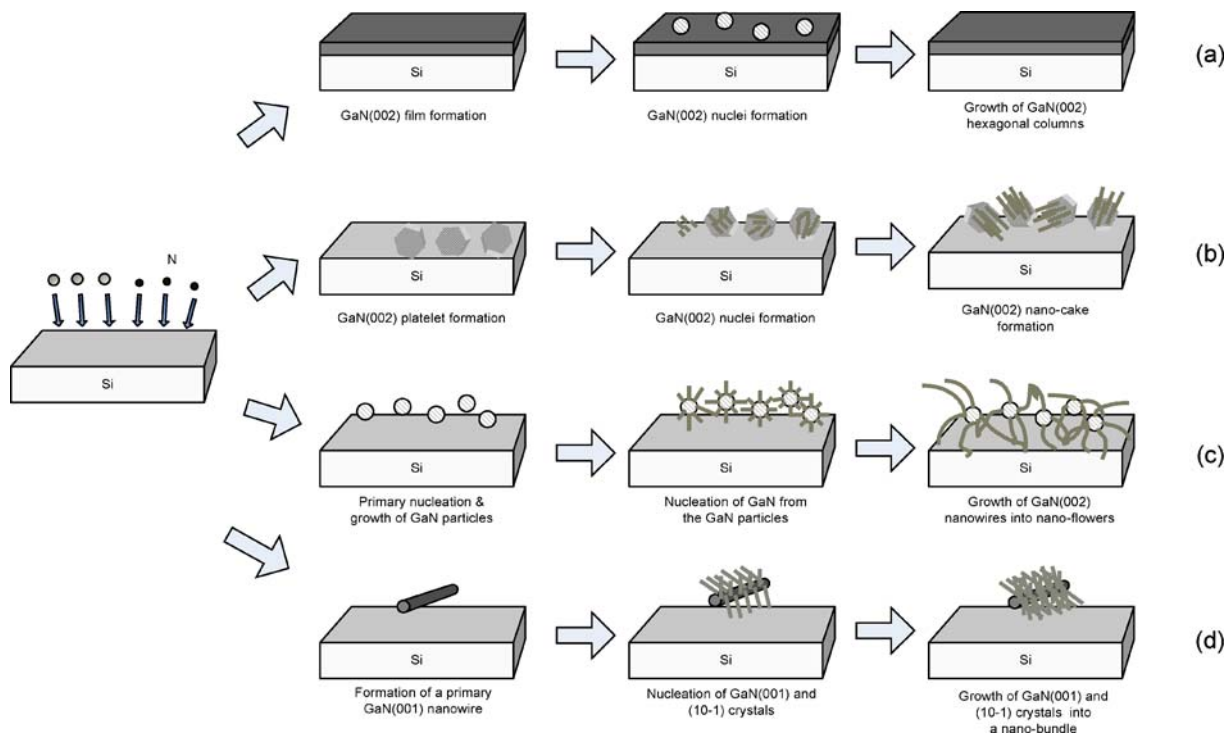


Fig. 3 Schematic diagrams showing the possible crystal growth mechanisms of (a) nano-columns, (b) nano-cakes, (c) nano-flowers, and (d) nano-bundles

The growth mechanism of nano-bundles is not clear, however, it is suggested that a thin primary GaN nanowire forms first and subsequently many nuclei form around the nanowire surface. The secondary nanowires with ~ 100 nm thickness can grow from the nuclei. The crystal growth planes would be (101) and (002) which are 60° to each other and well agree with the angle between the two growth orientations observed in the SEM photographs. This crystal growth orientation was confirmed by the strong reflections from (101)

and (002) planes in XRD patterns as shown in Fig. 1(b). The diagrams presenting each of the formation mechanism of GaN nanostructures are schematically shown in Fig. 3.

Photoluminescence (PL) properties were analyzed for each GaN nanostructure and shown in Fig. 4. The GaN nano-bundles showed the highest PL intensity possibly due to the high density, large length, and high crystallinity of nanowires. Also, the GaN nano-flower structure showed high PL intensity, while the nano-cake and nano-column structures showed low PL intensity. The PL peaks from nano-bundles and nano-flowers were slightly blue-shifted possible due to the size confinement effect. Therefore, it can be concluded that the high-density nano-bundle or nano-flower structure would be desirable to obtain high intensity light emission.

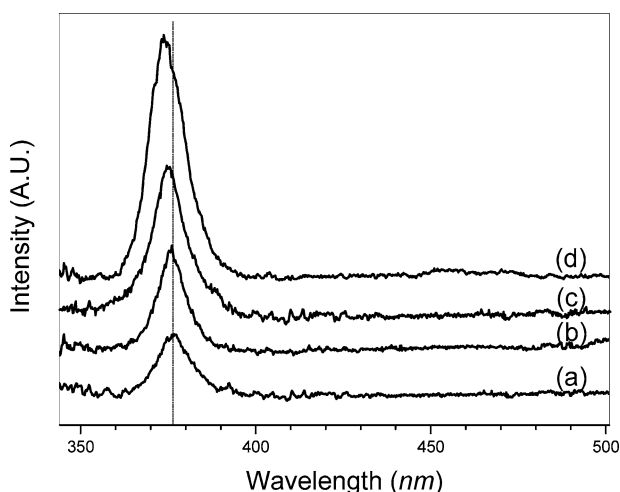


Fig. 4 Photoluminescence (PL) emission spectra from (a) nano-columns, (b) nano-cakes, (c) nano-flowers, and (d) nano-bundles

4 Summary

Various one-dimensional GaN nanostructures were fabricated using chemical vapor deposition via non-catalytic route. The column structure would be the result of supersaturation of gallium vapor inside the reaction chamber and the {100} facet formation. The nano-cake structure would come from primary formation of (002) platelets and subsequent growth of GaN (002) crystals. The nano-flower structure could be originated from the nucleation of GaN seeds, followed by nucleation of several (101) GaN crystals at the surface of the seeds. The nano-bundle structure would be

caused by primary formation of GaN nanowires and subsequent nucleation of GaN (002) and (101) crystals at the nanowire surface. Due to the high-density, high-crystallinity, and large length nanowires nano-flower and nano-bundle showed higher PL emission. The non-catalytic route is a simple method to grow nanowires and it gives a freedom to fabricate various structures compared to the catalyst-confined vapor-solid-liquid (VLS) mechanism.

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