

# Synthesis and properties of triangular-shaped GaN nanorods via growth mode control

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## ABSTRACT

The synthesis of wurtzite gallium nitride (GaN) nanorods with triangular shape on *c*-Al<sub>2</sub>O<sub>3</sub> substrates using a thermal chemical vapor deposition process was investigated. It was possible to control nanorod shape and growth mode of GaN nanorods by change of sample geometry in the chamber using a mixture of GaN powder and Ga metal with ammonia gas reaction. It was found that the GaN nanorods were grown via both vapor–liquid–solid and vapor–solid mode with change of sample placement in the chamber. The morphology of the GaN nanorods was observed by field-emission scanning electron microscopy in secondary electron and back-scattered electron mode. High-resolution transmission electron microscopy, and X-ray scattering measurements revealed the GaN nanorods to have a single-crystalline wurtzite structure.

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## 1. Introduction

Gallium nitride (GaN) has a direct and wide bandgap of 3.4 eV at room temperature, and is a promising candidate material for short wavelength optoelectronic devices, such as light-emitting diodes (LEDs) and laser diodes (LDs), as well as high-power and high-temperature operation devices, on account of its high melting temperature, high breakdown field, and high-saturation drift velocity [1,2]. Recently, semiconductor nanostructures, such as nanowires, nanorods, nanobelts, nanotubes, have attracted considerable attention for future nanoscale devices. Semiconductor nanostructures have potential use as both interconnect and functional units for the fabrication of electronic, optoelectronic, electrochemical, and electro mechanical devices owing to their outstanding electrical, optical, thermal, and mechanical properties caused by their size effects [3–6]. Among the various semiconductor nanostructures reported, there have been extensive studies on low-dimensional GaN-based nanostructures because of their unique electronic and optical properties, which have allowed the fabrication of novel nano-electronic devices and quantum devices with high quantum efficiency [7]. For this reason, there has been considerable research carried out to synthesize several types of

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GaN nanostructures. Various methods for fabricating 1D nanostructures have been reported. These include catalyst-assisted growth mode, such as the vapor–liquid–solid (VLS) mechanism [8,9], and non-catalyst-assisted growth mode, such as the vapor–solid (VS) mechanism [10,11]. Metal catalysts, such as Au, Ni, and Fe, are commonly used to initiate the growth of GaN nanorods. From the view of GaN nanorod purity, Au is commonly used as a metal catalyst in the VLS growth mechanism because of its considerably smaller rate of diffusion into the GaN lattice than other metal catalysts, such as Ni and Fe metal catalysts even though the liquid metals have a better solubility for Ga and N [12–16].

In this study, GaN nanorods were synthesized on *c*-Al<sub>2</sub>O<sub>3</sub> substrates by a direct reaction between molten Ga, GaN powder and ammonia gas using an Au catalyst in a chemical vapor deposition (CVD) reactor. The tips of the GaN nanorods contained an Au catalyst particle depending on the location of substrates in the reaction chamber. It was possible to control the growth mode of VLS or VS mode for the GaN nanorods by changing the location on the samples, successfully.

## 2. Experimental procedure

The GaN nanorods were synthesized by thermal CVD. Fig. 1 shows a schematic diagram of the equipment used for GaN nanorods synthesis. The starting materials were a mixture of GaN powder (99.999%, high-purity chem.) and molten Ga (99.9999%, 9

Digit Co., Ltd.) at a 1:1 weight ratio [17]. The  $c\text{-Al}_2\text{O}_3$  substrate was cleaned by sonication in acetone, and a Au thin film as a catalyst was then coated to a thickness of 1 nm using a thermal evaporation system. The substrates for sample (a) were placed 2 cm away from the Ga sources in an alumina boat, which was located in the center of the quartz tube, horizontally. The other

substrates (sample (b)) were placed perpendicularly on the upper side of the alumina boat. Sample (b) was 1 cm away from the Ga source. High-purity Ar (99.999%) and  $\text{NH}_3$  (99.99%) were introduced into the reactor as carrier and reaction gases, respectively. All the other experimental parameters were of same condition with sample (a) and (b). The synthesis experiments were carried

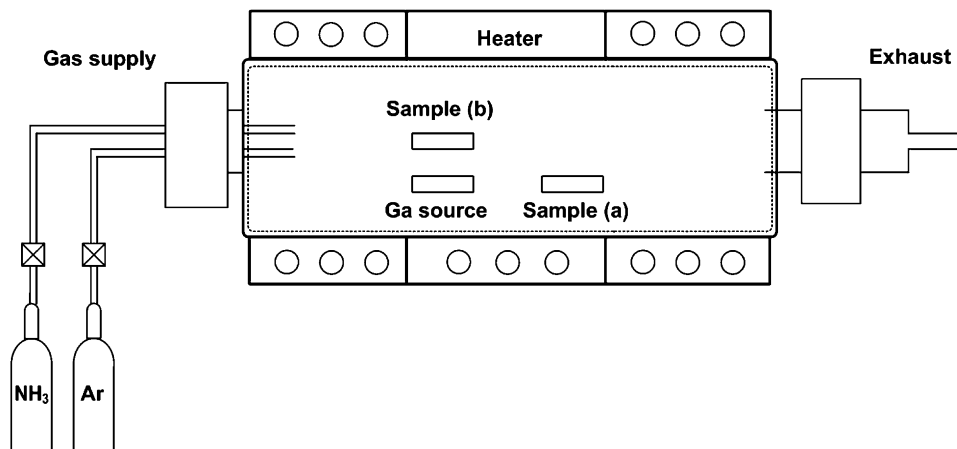


Fig. 1. Schematic diagram of the equipment used for GaN nanorod synthesis.

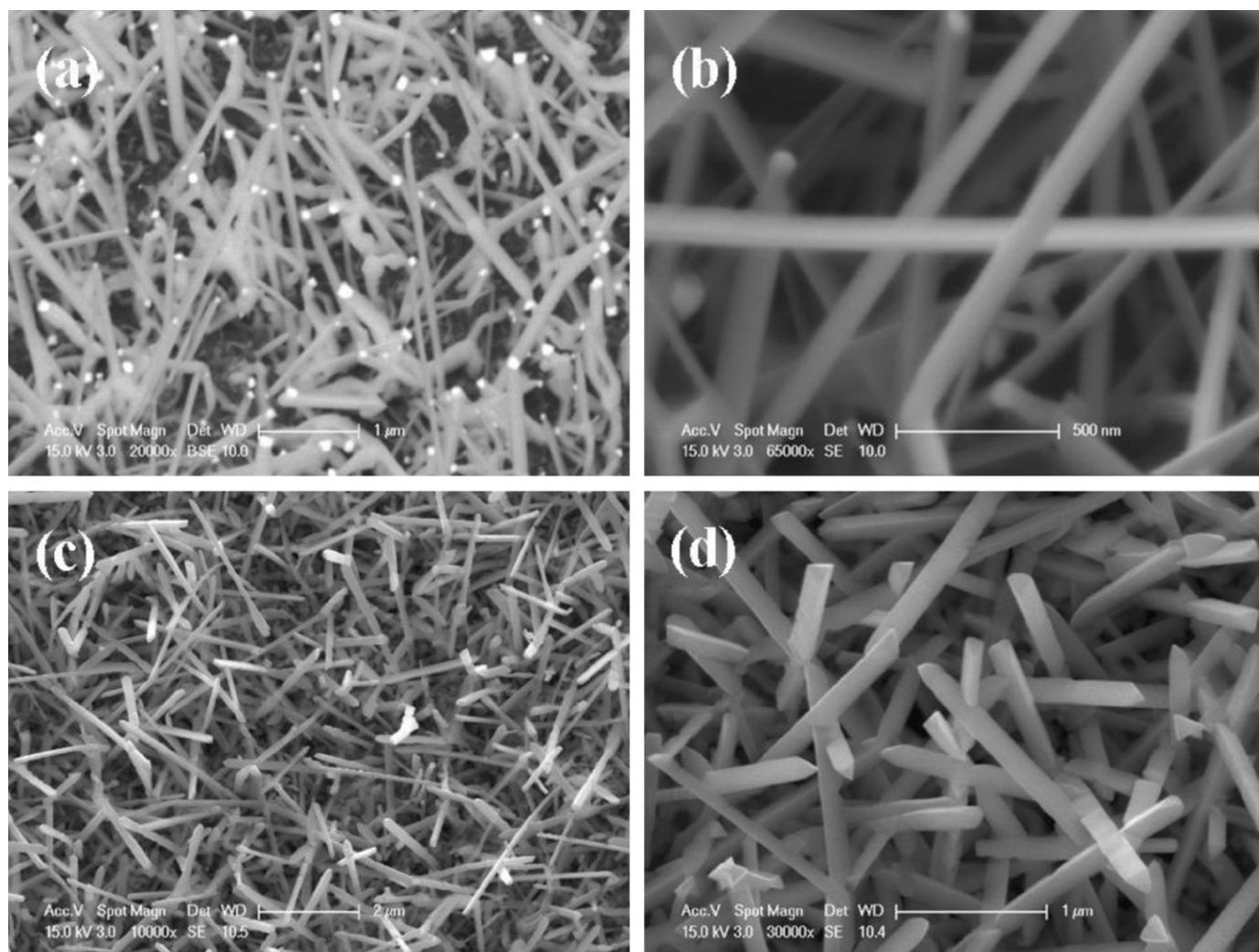
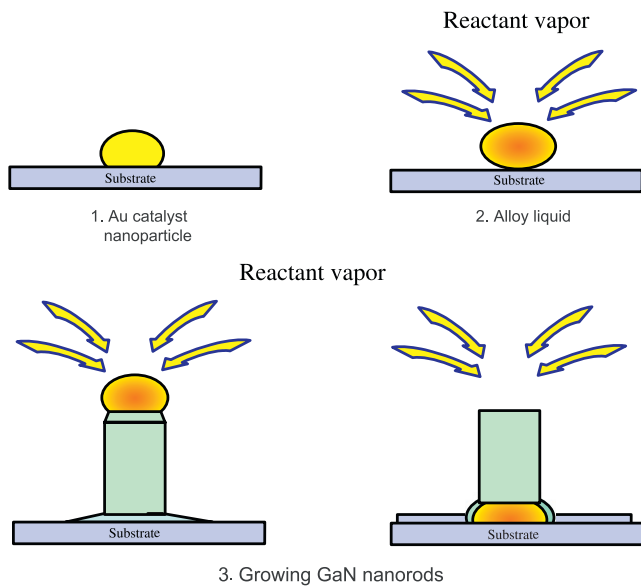


Fig. 2. FESEM images of GaN nanorods: (a) low-magnification BSE image of sample (a), (b) high-magnification SE image of sample (a), (c) low-magnification SE image of sample (b) and (d) high-magnification SE image of sample (b).

out for 1 h at 950°. During the main growth of the GaN nanostructure, Ar and NH<sub>3</sub> were introduced into the quartz tube at a flow rate of 1000 and 50 sccm, respectively. After the main growth phase, the samples were cooled naturally to room temperature.

The shape and morphology of the GaN nanostructures were observed by field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). The crystallinity and structure of the GaN nanostructures were examined by X-ray diffraction (XRD) using a Bruker D8 Discover system with CuK<sub>α</sub> radiation and selected area electron diffraction attached to the TEM. The chemical composition was investigated using energy-dispersive X-ray spectroscopy (EDX).

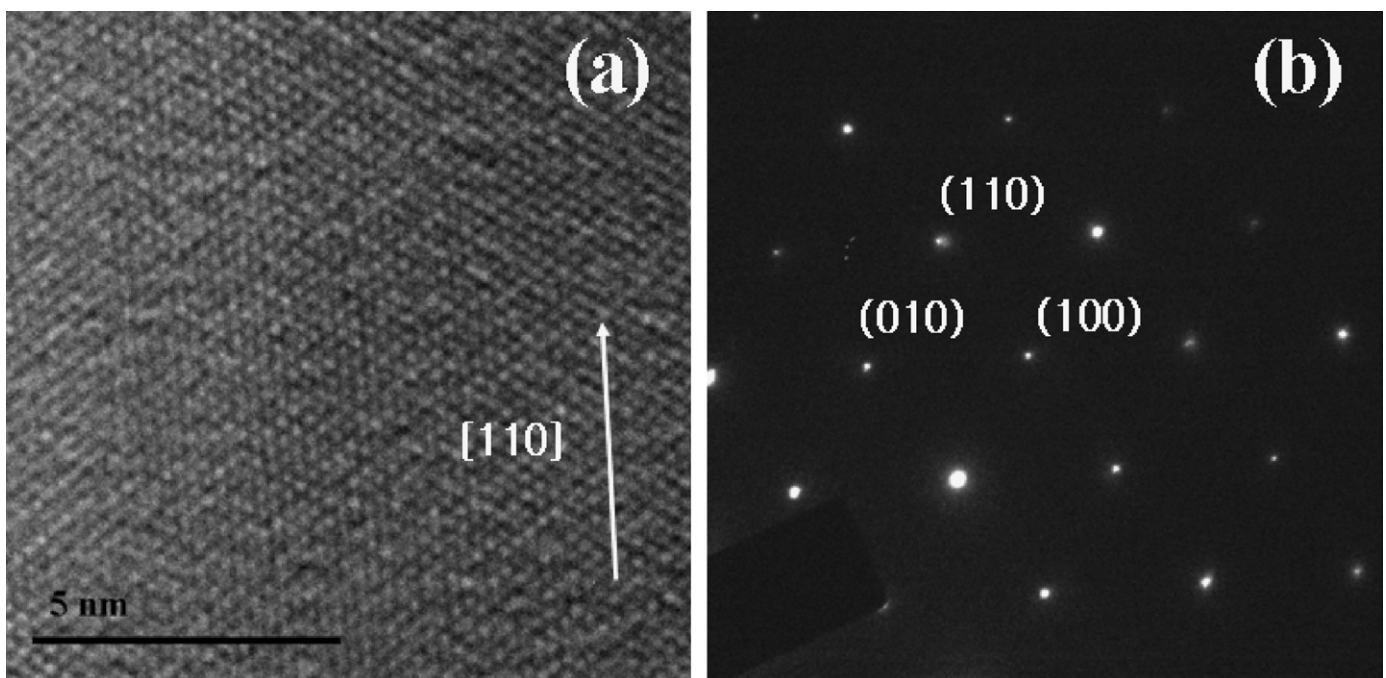


**Fig. 3.** Schematic diagram presenting each of the formation mechanism of GaN nanorods.

### 3. Results and discussion

The GaN nanorods were successfully synthesized by thermal CVD. Fig. 2(a) and (b) shows images of sample (a) grown on the *c*-Al<sub>2</sub>O<sub>3</sub> substrates, and Fig. 2(c) and (d) shows images of sample (b). Fig. 2 shows randomly oriented GaN nanostructures on the Al<sub>2</sub>O<sub>3</sub> substrate with an almost straight morphology and a smooth surface. The diameters of samples (a) and (b) ranged from 60 to 110 nm and from 120 to 160 nm, respectively. The difference in the diameter and length of the samples was attributed to their placement in the chamber, such as the direction and distance from the evaporated Ga source. Furthermore, it was found that the growth modes between samples (a) and (b) are different. As shown in Figs. 2(a) and (b), sample (a) contained a nano-sized Au catalyst particle at the end of the GaN nanorods. The back-scattered electron (BSE) image in Fig. 2(a) confirmed the presence of the Au catalyst. In case of sample (b), no Au catalyst was observed at the end of the GaN nanorods, as shown in Fig. 2(c) and (d). The secondary electron images and BSE images showed no other differences indicating the GaN nanorods are purely composed of Ga and N. It was concluded that GaN nanorods could be synthesized through the VLS and VS mechanism by changing the sample location in the chamber. In the first stage of growth, a GaN thin layer forms onto the Au catalytic layer because of the higher vapor pressure of the Ga source in sample (b) rather than the formation of Au–Ga eutectic liquid leads to the following growth of GaN nanorods via the VLS growth mode. Fig. 3 shows a schematic diagram presenting each mechanism for the formation of GaN nanorods. In addition, the synthesized GaN nanorods had a triangular-shaped cross-section, which was attributed to the triangular GaN nanorods not having a six-fold crystallographic symmetry axis as the growth direction, but instead a two-fold crystallographic axis [18].

The GaN nanorods crystallography was examined by HRTEM and electron diffraction. Fig. 4(a) shows the corresponding HRTEM image of sample (b), showing the (110) lattice plane perpendicular to the nanorod axis. The electron diffraction pattern was indexed to the hexagonal wurtzite structure with lattice constants



**Fig. 4.** TEM images of GaN nanorod: (a) high-magnification TEM image of GaN nanorod and (b) electron diffraction pattern taken along the [001] zone axis.

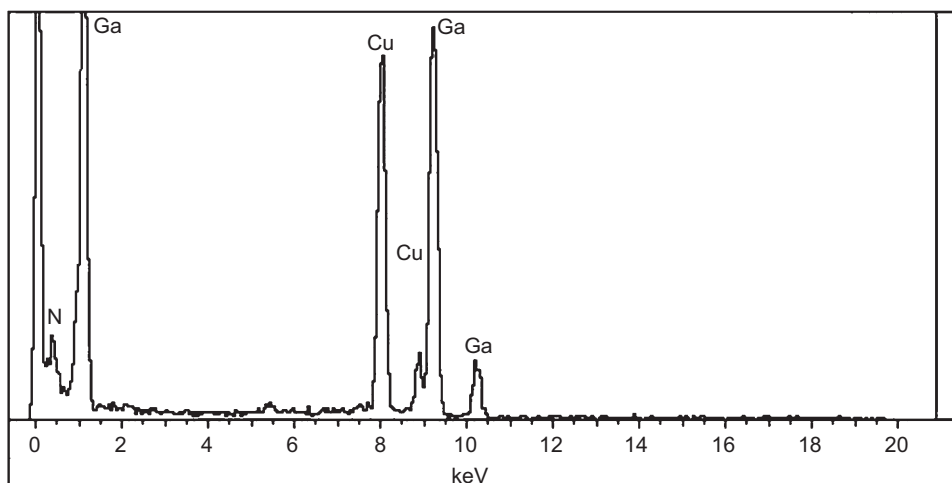


Fig. 5. The EDX spectrum taken from sample (b). The element of Cu peaks is originated from TEM grid.

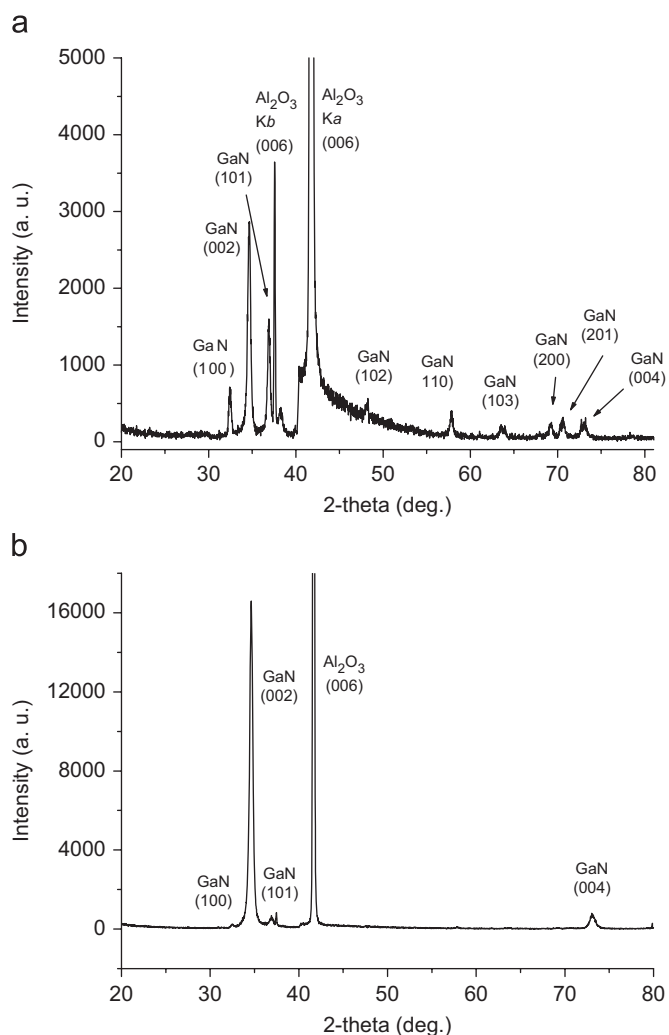


Fig. 6. X-ray diffraction pattern of synthesized GaN nanorods. (a) X-ray diffraction pattern of sample (a) and (b) X-ray diffraction pattern of sample (b).

of  $a = 0.319$  and  $c = 0.518$  nm (Fig. 4(b)), which agree well with the reported values of GaN bulk crystals. The electron diffraction pattern of the GaN nanorods, which demonstrates the nanorods to

be single crystalline with good crystallinity, could be indexed to the diffraction pattern of hexagonal GaN. The predominant growth direction of the nanorods was [110]. The electron diffraction taken along the [001] zone axis indicated a [110] growth direction, perpendicular to the (110)  $\alpha$ -plane of GaN, and revealed its triangular shape in a hexagonal structure. And, small fraction of the GaN nanorods of both samples (a) and (b) have a [100] growth direction.

We investigated the chemical composition of the GaN nanorods grown via VS mechanism using EDX measurements. The EDX spectrum is shown in Fig. 5 shows that the GaN nanorods were only composed of Ga and N elements without Au. This indicates that the grown nanorods correspond to GaN without any oxide phase, and the Au element supports VS mechanism, as shown in Fig. 3.

Fig. 6 shows the XRD pattern used for the structural characterization of GaN nanorods. All the diffraction patterns were indexed and identified by XRD to have the hexagonal wurtzite structure of GaN. Various diffraction peaks for GaN were observed in case of sample (a), such as those for the (100), (002), (101), (110), (103) and (201) planes. However, 2 intense peaks were observed at  $2\theta = 34.5^\circ$  and  $2\theta = 72.9^\circ$ , which were attributed to the GaN (002) and (004) plane reflections, respectively, with very small peaks observed in the case of the sample (b). It suggests that the intensity of the (002) and (004) peaks for GaN increased relative to those of the other peaks due to the contribution of thin layer formed via VS growth mode.

#### 4. Conclusion

GaN nanorods were synthesized by a direct reaction of molten Ga, GaN powder and  $\text{NH}_3$  gas using thermal CVD. The GaN nanorods were grown via the VLS or VS mechanism according to their location in the chamber. The FESEM images showed that the GaN nanorods grew via a VLS mechanism, which was influenced by the presence of a metal catalyst. In the case of a higher Ga vapor pressure, GaN nanorods with no metal tips were grown via the VS mechanism. The XRD and selected area electron diffraction results clearly showed that GaN nanorods grown via both VLS and VS modes are the single-crystalline wurtzite structure with a triangular shape. EDX showed that the grown GaN nanorods consisted purely of Ga and N without Au-related elements on the nanorod surface.

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