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Effects of temperature and HCl:NH_3 flow ratio on the growth of GaN nanorods

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ABSTRACT

We studied the formation of GaN nanorods on AlN-covered Si(1 1 1) by the hydride vapor phase epitaxy method. The most well-formed GaN nanorods were obtained at an HCl:NH_3 gas flow ratio of 1:40 and a growth temperature of 650 °C. A high density of straight nanorods with diameters of about 350 nm formed uniformly over the entire substrate. The synthesis and structural properties of the nanorods were investigated by X-ray diffraction (XRD), scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDS). The obtained XRD patterns indicate that the GaN nanorods are preferentially oriented, with *c*-axes perpendicular to the substrate. EDS measurements of the nanorods indicate that they are composed of Ga and N with a ratio of 1.00:0.99.

1. Introduction

GaN, which has a wide and large direct band gap, is one of the most suitable materials for use in light-emitting diodes and high-temperature and high-power electronic devices [1]. With the recent surge in interest in nanotechnology, many studies have sought to synthesize one-dimensional nanostructures such as nanobelts, nanorings, nanowires, and nanorods [2–5]. Investigations into one-dimensional structure at the nanometer scale have the potential to enhance our understanding of the fundamental concepts that underlie the observed electronic, optical, and mechanical properties of materials. One-dimensional nanostructures have been synthesized by various techniques, including hydride vapor phase epitaxy (HVPE) [6], metal organic chemical vapor deposition (MOCVD) [7], molecular beam epitaxy (MBE) [8], an arc discharge method [9], catalytic growth based on the VLS (vapor–liquid–solid) mechanism [10], the sublimation of GaN powder under ammonia atmosphere [11], and the reaction between Ga_2O_3 films and ammonia [12]. Among these, lots of studies have been progressed by MOCVD and MBE. However the studies of nanostructures by HVPE have been just performed by few groups [13–15]. It is valuable to enhance the HVPE technique because of its promising advantages of higher growth rate and lower cost than MOCVD or MBE.

There are many variables in the formation of nanorods, including the choice of buffer layer and substrate, growth temperature, HCl:NH_3 flow ratio, and the amount and flow rate of carrier gas. Among these factors, the diameter and morphology of nanorods are strongly dependent on growth temperature, HCl:NH_3 flow ratio, and carrier gas. Thus, in the present experiment, we investigated the effects of growth temperature and HCl:NH_3 flow ratio on the formation of GaN nanorods. To study the growth mechanism of the nanorods, we analyzed their synthesis and structural properties by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDS).

2. Experiment

GaN nanorods were grown on Si(1 1 1) substrates with an AlN buffer layer using an atmospheric horizontal hydride vapor phase epitaxy (HVPE) system. Metallic gallium (Ga), ammonia (NH_3), and hydrogen chloride (HCl) were used as source materials, and N_2 gas was used as a carrier gas.

Si(1 1 1) substrates were etched using a buffered oxide etch (BOE; NH_4F:HF = 6:1) solution to remove the natural silicon oxide layer on the surface. They were then cleaned in an ultrasonic bath with a solution of acetone and methanol. AlN buffer layers were deposited on the substrates by RF sputtering for 25 min (~50 nm). The pressure in the sputtering chamber was 5×10^{-3} Torr, and the plasma power was 200 W. The argon (Ar) gas flow ratio was 50 sccm. We divided the furnace into source, reactor, and growth regions based on their contrasting temperatures.

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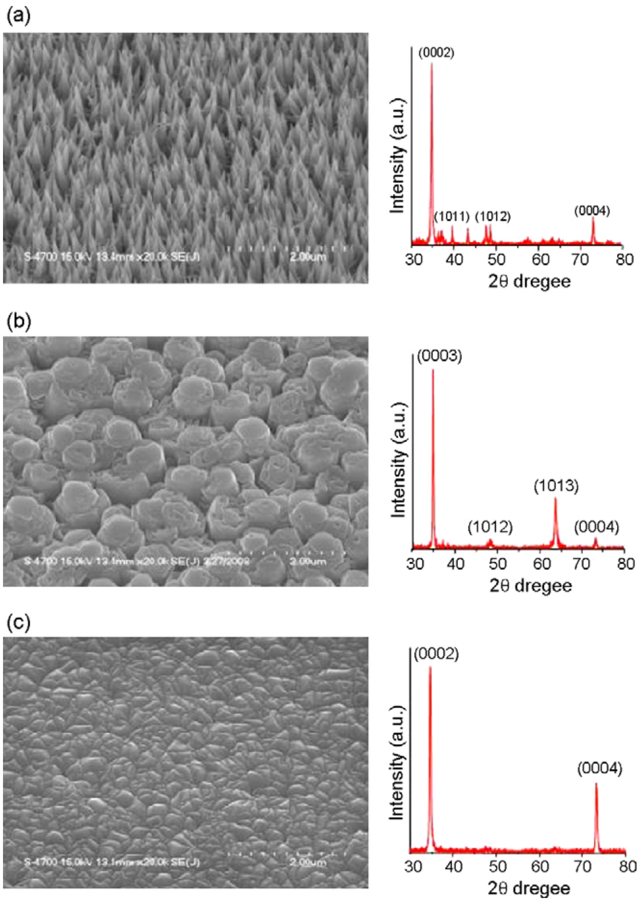

Fig. 1. FE-SEM images and XRD patterns of GaN nanostructures grown at temperatures of (a) 600 °C, (b) 650 °C, and (c) 700 °C.

Table 1
Gas flow rates employed in the different experiments.

	(a)	(b)	(b*)	(c)	(d)
HCl	29 sccm	29 sccm	29 sccm	29 sccm	29 sccm
NH_3	725 sccm	870 sccm	1015 sccm	1160 sccm	1305 sccm
Ratio	1:25	1:30	1:35	1:40	1:45

Sample b* is that shown in Fig. 1(b).

GaCl vapor species were formed by reacting HCl with liquid gallium in the source region at 850 °C. GaN species were made by reacting GaCl with NH_3 in the reaction region at 1050 °C; the samples were grown for 2 h. The HCl:NH_3 flow ratio was controlled to between 1:25 and 1:45, and growth temperature was maintained at 600–700 °C.

3. Results and discussion

Fig. 1 shows the samples grown at 600, 650, and 700 °C with an HCl:NH_3 flow ratio of 1:35. FE-SEM images of GaN nanostructures show a tip shape at 600 °C and a grain shape at 700 °C, as shown in Fig. 1(a) and (c), respectively. The sample shown in Fig. 1(b), which grew at 650 °C, has a rod-like shape. All samples show (0 0 0 2) and (0 0 0 4) peaks of wurtzite GaN in XRD patterns. For both tip-shaped and rod-shaped samples, we also observe additional peaks of $(1\,0\,\bar{1}\,1)$, $(1\,0\,\bar{1}\,2)$, and $(1\,0\,\bar{1}\,3)$, considered to correspond to inclined facets. FE-SEM images confirm that all samples grown at 600 and 700 °C are tip- or grain-shaped, as shown in Fig. 1(a) and (c), regardless of the gas flow ratio. Herein, we focus on the synthesis of the rod-shaped GaN nanostructures.

Fig. 2 shows FE-SEM images of GaN nanorods grown at 650 °C with HCl:NH_3 flow ratios of 1:25, 1:30, 1:40, and 1:45. Details of the gas flow ratio are summarized in Table 1. All of the prepared samples are rod-shaped crystals with hexagonal structure. The samples grown at a low NH_3 flux ratio have the structure of hexagonal inverted pyramids with $(1\,0\,\bar{1}\,1)$ facets. The development of rod-shaped crystallinity occurred by adsorption of GaN into the inverted pyramid hollow after hexagonal wall formation in regular sequence with increasing NH_3 amount. The smallest diameter of the nanorods is about 350 nm, as obtained with a 1:40 flow ratio.

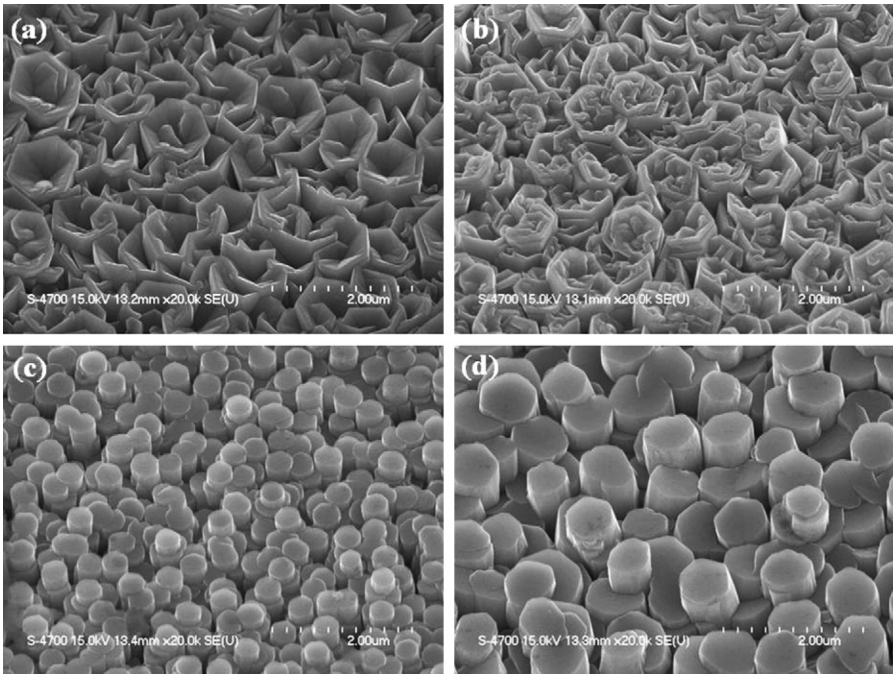

Fig. 2. FE-SEM images of GaN nanorods grown at HCl:NH_3 flow ratios of (a) 1:25, (b) 1:30, (c) 1:40, and (d) 1:45 on an AlN/Si(1 1 1) substrate.

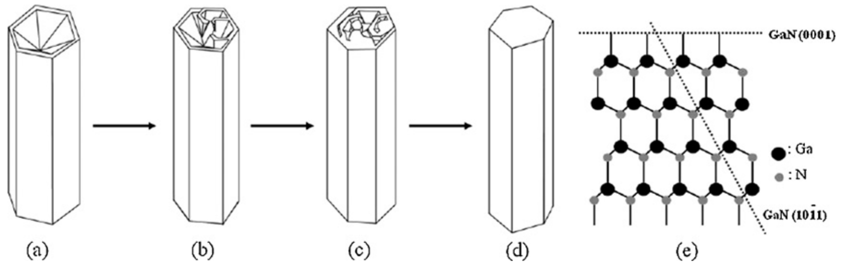

Fig. 3. Schematic development of GaN nanorods for HCl:NH_3 flow ratio of (a) 1:25, (b) 1:30, (c) 1:35, (d) 1:40, and (e) a representation of (0 0 0 1) and (1 0 $\bar{1}$ 1) planes.

Fig. 3 shows the schematic development of GaN nanorods in regular sequence of gas flow. The hollow hexagonal structure is infilled and gradually attains a complete nanorod shape with increasing HCl:NH_3 flow ratio.

We now consider the driving force for the evolution of the initial nanorod shape with hexagonal inverted pyramid structure to the complete nanorod. Previous studies report that the growth rate and direction of GaN nanostructures are affected by the gas flow ratio, differences in surface energy between each planes, and the anisotropic and polar nature of GaN itself [16–20]. The theoretical models for the GaN surface roughening transition state that under N-rich conditions, areas of the surface are covered with excess N [21]. In our experiments, the ratio of NH_3 flux played a crucial role in determining the shape of GaN nanorods. During the growth of GaN nanorods, the dissociated ammonia increase with the increase of NH_3 under high temperature, and then N be transported to the surface of substrate by carrier gas. When the dissociated ammonia arrives at these areas, we suggest that N atoms will be cause to the growth occurring through the more reactive polar (0 0 0 1) planes, which is due to the enclosure of the planes with the lowest surface energy [17,18,22]. Consequently the hexagonal inverted pyramid growth with {1 0 $\bar{1}$ 1} facet planes occurs at an early stage and then ⟨0 0 0 1⟩ direction develops by increasing N flow ratio. Therefore, the dependence of kinetics on the growth conditions and minimization of surface energy during crystallization is possibly responsible for the formation of GaN nanorods with a high aspect ratio. Further investigation is needed to determine the exact nature of the relevant reaction.

Fig. 4 shows the mean diameters of the obtained GaN nanorods as a function of HCl:NH_3 flow ratio. The mean diameter initially declined with increasing gas flow ratio, but increased after reaching a minimum diameter of 350 nm at a gas flow ratio of 1:40.

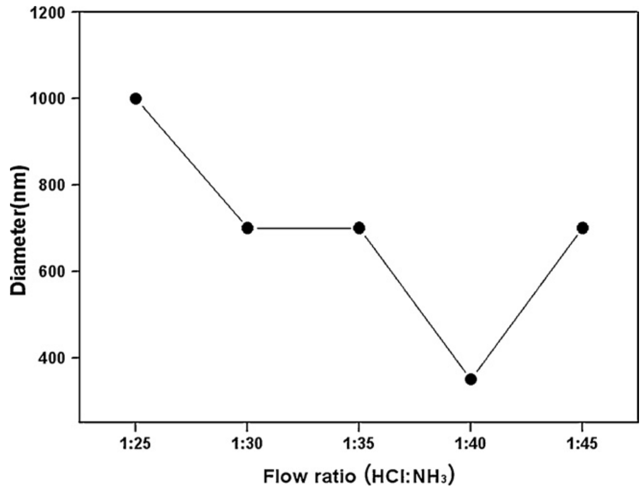

Fig. 4. Mean diameters of GaN nanorods grown at different HCl:NH_3 flow ratios.

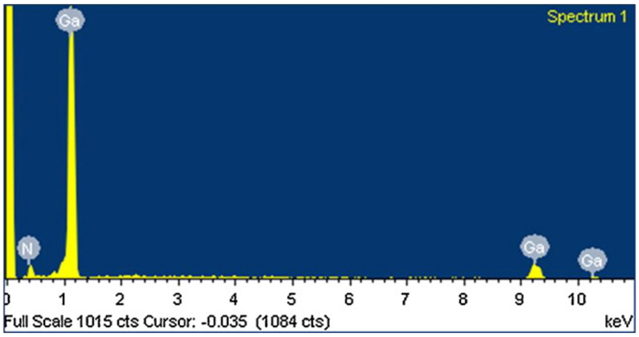

Fig. 5. EDS spectrum for the obtained GaN nanorods grown with an HCl:NH_3 gas flow ratio of 1:40.

The components of Ga and N in the sample shown in Fig. 2(c) were further analyzed using EDS. Fig. 5 reveals the presence of Ga and N with an approximate atomic ratio of 1.00:0.99 [23,24].

Fig. 6 shows the XRD patterns obtained for the sample shown in Fig. 2(c). The dominant diffraction peaks are 34.6° and 72.9°, corresponding to the GaN(0 0 0 2) and GaN(0 0 0 4) facets, respectively. Generally, well-grown GaN films show strong θ–2θ scan peaks that are attributed to GaN (0 0 0 2) and GaN (0 0 0 4), and these indicate that the films are single crystal because GaN grows only in the *c*-axis orientation [25]. Thus our result also indicates that the formed GaN nanorods are grown with a highly preferred orientation in the *c*-axes direction [26]. We note that the GaN nanorods have been purely grown on silicon substrate by HVPE method, while the other result of GaN nanorods grown using another mechanism reveals additional diffracted peaks [8].

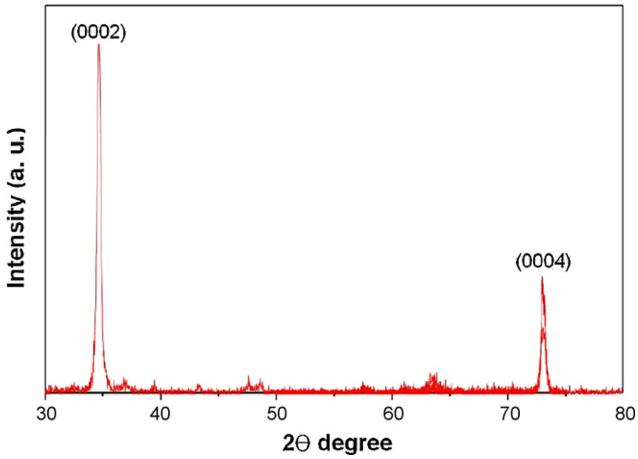

Fig. 6. XRD pattern for GaN nanorods grown with an HCl:NH_3 gas flow ratio of 1:40.

4. Conclusions

In summary, we formed GaN nanostructures under different temperatures and HCl:NH_3 flow ratios by the HVPE method. The morphologies of the samples show tip shapes, rod-like shapes, and grain shapes at growth temperatures of 600, 650, and 700 °C, respectively, with an HCl:NH_3 gas flow ratio of 1:35. The most well-formed nanorod crystals grew under an HCl:NH_3 flow ratio of 1:40 at 650 °C. The structural properties of the nanorods were characterized by FE-SEM, XRD, and EDS. A high density of straight nanorods with a diameter of about 350 nm formed uniformly over the entire substrate. The XRD results indicate that the formed GaN nanorods are preferentially oriented, with the *c*-axes perpendicular to the substrate, and are predominantly single crystalline hexagonal wurtzite GaN.

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