Vacuum 86 (2011) 201–205

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Evolution of GaN nanoflowers from AlN–SiO_2 grains on a silicon substrate by chemical vapor reaction

Min Jeong Shin [a], Min Ji Kim [a], Hun Soo Jeon [a], Hyung Soo Ahn [a], Sam Nyung Yi [a,*], Dong Han Ha [b], Yoon Huh [c], Bong Hwan Kim [d], Seoung Hwan Park [d]

[a] Department of Applied Science, Korea Maritime University, Dongsam-dong, Busan 606-791, Republic of Korea
[b] Division of Convergence Technology, Korea Research Institute of Standards and Science, Daejeon 305-340, Republic of Korea
[c] Department of Analysis and Assessment, Research Institute of Industrial Science and Technology, Pohang 790-330, Republic of Korea
[d] Department of Electronics Engineering, Catholic University of Deagu, Hayang, Gyeongbuk 712-702, Republic of Korea

A R T I C L E I N F O

Article history:
Received 22 March 2011
Received in revised form
21 May 2011
Accepted 9 June 2011

Keywords:
Nanoflowers
GaN
HVPE
Nanostructure

A B S T R A C T

Gallium nitride (GaN) nanoflowers were synthesized on a silicon (Si) substrate at growth temperatures of 650 and 600 °C and under HCl:NH_3 flow ratios of 1:20, 1:30, and 1:40 by hydride vapor phase epitaxy. Numerous nanorod and nanoneedle burs were formed within each nanoflower. The nanoflower size increased with increasing NH_3 gas flow rate. The nanoflower formation mechanism is proposed based on cross-sectional scanning electron microscopy images and bright field image of scanning transmission electron microscopy. Nanoflowers were evolved from irregular regions with AlN–SiO_2 grains on a Si substrate, i.e., the roughness of substrate affects nanoflower formation by causing nanoburs to protrude, exposing them to higher gas concentrations.

1. Introduction

GaN is a III–V compound semiconductor with a wide direct bandgap, high strength, high melting point, high breakdown field, and an extremely high chemical stability [1]. Consequently, GaN has attracted considerable attention because of its great potential for use in visible and UV optoelectronic applications and in high-temperature, high-power electronic devices [2,3]. Recently, one-dimensional nanostructures have attracted much attention due to their wide potential applications, e.g. field effect transistors, polarization-sensitive nanoscale photodetectors, ultraviolet nanolasers and field emission devices. Since the novel properties and potential applications of nanomaterials depend sensitively on their shapes and sizes, many efforts have been made to synthesize various types of nanostructures including nanorods, nanowires, nanotubes, nanobelts, nanoneedles, nanorings, nanowhiskers, nanotetrapods, nanoribbons, and nanoparticles.

One-dimensional nanostructures have been produced by various techniques, including hydride vapor phase epitaxy (HVPE) [4], molecular beam epitaxy [5], metal organic chemical vapor deposition [6], arc discharge [7], catalytic growth based on a vapor–liquid–solid (VLS) mechanism [8], the reaction between Ga_2O_3 films and ammonia [9], and the sublimation of GaN powder in an ammonia atmosphere [10]. Of these methods, HVPE has both a high growth rate and a low cost. There are many variables associated with growing GaN nanostructures by HVPE, including substrate roughness, growth temperature, HCl:NH_3 flow ratio, choice of buffer layer and substrate, and carrier gas flow rate. Of these factors, growth temperature, HCl:NH_3 flow ratio, and carrier gas flow rate have great effect on nanostructure morphologies [11,12].

Up to now, there have been few reports on the syntheses of nanoflower materials, e.g., AlN [13], SnO_2 [14], CdS [15], InN [16,17], Cu_2O [18], MgO [19], GaP [20], ZnO [21–23], and MoS_2 [24]. However, no studies have been reported on the syntheses of GaN nanoflowers. Here we describe the direct observation and growth process of GaN nanorod and nanoneedle flowers. It is believed that GaN nanoflowers have a great deal of potential applications in optoelectronic devices and field emission based flat panel displays.

2. Experiments

Si(111) substrates were cleaned in an ultrasonic bath and etched in a buffered oxide etch solution to remove the oxidation layer. They were sequentially sonicated in acetone and methanol, and rinsed in deionized water for 5 min. An approximately 50 nm thick

* Corresponding author. Tel.: +82 51 410 4448; fax: +82 51 404 3986.
E-mail address: snyi@hhu.ac.kr (S.N. Yi).

0042-207X/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2011.06.006

AlN buffer layer was then deposited by radio frequency sputter for 25 min. On the other hand, SiO_2 grains were made on an AlN buffer layer through the partial co-sputtering method. At this time, the shutter of the AlN target was opened completely but that of the SiO_2 target was opened slightly. The pressure inside the sputtering chamber was 5×10^{-5} Torr. The plasma power was 200 W and an Ar gas flow rate was 50 sccm. As a result, the SiO_2 grains were placed randomly on the surface of AlN layer.

GaN nanoflowers were grown on an AlN/Si(111) substrate in an atmospheric, horizontal HVPE system. The HVPE furnace was divided into source, reaction, and growth regions, which were individually controlled at different temperatures. High purity NH_3 gas and a Ga ingot were employed as the nitrogen and the gallium sources, respectively. GaCl vapor was formed in the source region, which was maintained at 850 °C, by reacting Ga metal with HCl gas. At this time, HCl does not directly affect on the AlN/Si substrate [4,25]. GaCl and NH_3 gas reacted together to produce GaN in the reaction region, which was maintained at 1050 °C. GaN was then transported to the substrate in the growth region using N_2 as the carrier gas. The temperatures were controlled at 600 and 650 °C, and the employed HCl:NH_3 flow ratios were 1:20, 1:30, and 1:40. The carrier gas flow rate was maintained at 1340 sccm and the growth time was 2 h.

The morphologies and crystalline structures of the samples were investigated by field-emission scanning electron microscopy (FE-SEM), scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), cathodoluminescence (CL) spectroscopy, and energy-dispersive X-ray spectroscopy (EDS).

3. Results and discussion

The formation of GaN structures is strongly affected by the growth temperature, HCl:NH_3 flow ratio [11], and carrier gas [12]. In previous experiments, nanorod and nanoneedle structures were formed at 650 and 600 °C, respectively [11]. Fig. 1(a–c) and (d–f) shows FE-SEM images of GaN nanorod and nanoneedle flowers, respectively, that formed at various HCl:NH_3 flow ratios. The samples shown in Fig. 1(a) and (d), which were grown at a HCl:NH_3 flow ratio of 1:20, are in the initial stages of nanoflower development and consist of short nanorods or nanoneedles. More complete

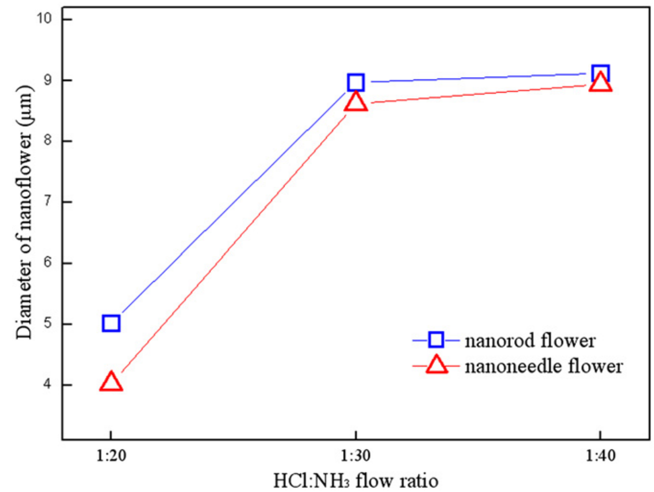

Fig. 2. Diameter of GaN nanorod (square) and nanoneedle flowers (triangle) as a function of the HCl:NH_3 flow ratio.

and hemispherical nanorod and nanoneedle flowers were obtained when the HCl:NH_3 flow ratios were increased to 1:30 and 1:40 (see Fig. 1(b) and (e), and (c) and (f), respectively). Fig. 2 shows that the maximum nanoflower diameter at each set of growth conditions increases with increasing gas flow ratio.

Several models are proposed to describe the growth mechanism of nanorods, which include VLS and VS (vapor–solid) [13,14,21]. At the same time, the formation of nanoflower or the tilted one-dimensional nanostructures are explained as position controlled growth with patterned mask [23], large liquid droplets [16], rough and three-dimensional surface mechanisms [26] and seed layer assisted solution route [27]. In our experiments, the GaN nanoflowers were prepared by direct chemical vapor reaction on a Si(111) substrate without the presence of any catalyst. Therefore, the VLS mechanism could be ruled out because no metal catalyst was used. It is more likely to be governed by a VS process. On the other hand, the position controlled growth implies the seed layer in the patterned holes and several one-dimensional nanostructures

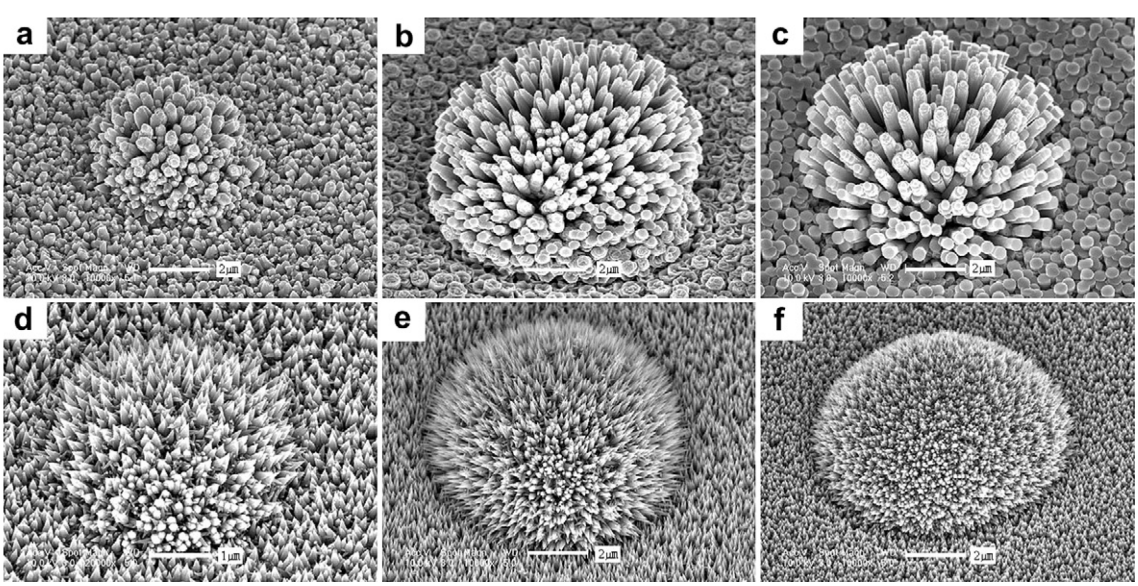

Fig. 1. FE-SEM images of GaN (a–c) nanorod and (d–f) nanoneedle flowers grown at HCl:NH_3 flow ratios of (a, d) 1:20, (b, e) 1:30, and (c, f) 1:40. The samples of GaN nanorod and nanoneedle flowers were formed at 650 and 600 °C, respectively.