Journal of Crystal Growth 351 (2012) 155–160

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

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

Morphology control of gallium nitride grown on silicon nanoporous pillar array: From cone-strings to nanowires

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ARTICLE INFO

Article history:
Received 2 December 2011
Received in revised form
15 April 2012
Accepted 21 April 2012
Communicated by K. Deppert
Available online 4 May 2012

Keywords:
A1. Nanostructures
A3. Chemical vapor deposition
B1. Gallium nitride
B1. Silicon nanoporous pillar array (Si-NPA)

ABSTRACT

Fascicle arrays of gallium nitride (GaN) nanostructures were grown on silicon nanoporous pillar array (Si-NPA) by a reactive chemical vapor deposition method. Through adjusting the distance between the gallium source and Si-NPA substrate, the morphology of GaN nanostructures was tuned from cone-strings, cone-strings plus nanowires to nanowires, accompanied with the average diameter changed from ~800 nm to ~13 nm. Both the cone-strings and the nanowires were found growing along [0001] direction. These results indicate that Ga concentration is a key factor in determining both the morphology and the average diameter of GaN nanostructures. The growing process of the GaN nanostructures was explained under the frame of vapor–liquid–solid deposition mechanism. Our method might be expanded to the growth of other compound semiconductor nanostructures on patterned silicon substrates for constructing functional nanodevices.

1. Introduction

In the past two decades, semiconductor nanostructures have attracted considerable attention for their unique optical and electrical properties which might be of advantage in fabricating optoelectronic nanodevices [1–3]. As a compound semiconductor with wide and direct bandgap, gallium nitride (GaN) possesses the characteristics of high thermal conductivity, high electron mobility and good chemical stability [4,5], and thereby has been widely used for preparing chemical sensors [6,7], biosensors [8], field effect transistors [9], and short-wavelength light-emitting diodes [1,10]. Mainly aiming at obtaining novel physical properties, much effort has been made in recent years for preparing various GaN nanostructures, such as GaN nanoparticles [11], nanowires [12,13], nanocolumns [14], nanobelts [15], nanorings [16], and nanosized cone-strings [17], and the physical properties of these GaN nanostructures were found to be highly depended upon their structural and morphological characteristics. For clarifying the correlation between GaN nanostructures and their physical properties, the probe on controllable growing techniques and the study on the underlying growing mechanisms would be of key importance.

Among various GaN nanostructures, GaN cone-strings were found to be of unique morphology and might find potential applications in constructing GaN-based nanodevices. Nevertheless, GaN cone-strings were usually found to co-grow with nanowires [17–20]. This made the study on the basic properties of GaN cone-strings more difficult. Therefore, the research on the preparation conditions for obtaining pure GaN cone-strings as well as that for realizing the morphology conversion from cone-strings to nanowires, such as the deposition conditions and substrate choice, would be both necessary and meaningful.

Silicon nanoporous pillar array (Si-NPA) has been proven to be a micron-nanometer silicon hierarchical structure characterized by a regular array consisted of micron-sized, quasi-identical and nanoporous silicon pillars [21]. The structural characteristics together with the properties of large specific surface area, high and broadband light absorption, and efficient blue–red photoluminescence (PL) make Si-NPA a well-established functional substrate for constructing Si-based nanoheterostructures. The successful examples include the demonstration of a CdS/Si-NPA nanoheterostructure array with three-primary-color PL and excellent electrical rectification [22,23], a nest array of carbon nanotubes/Si-NPA with enhanced field emission [24], and a GaN/Si-NPA nanoheterostructure array with efficient near infrared light emission [18]. These experiments illustrated that Si-NPA was a promising substrate for fabricating patterned Si-based nanosystems with enhanced physical properties.

In this study, we report our research on the morphology and size control of GaN nanostructures grown on Si-NPA by a reactive chemical vapor deposition method. We will illustrate that just through adjusting the distance between Ga source and Si-NPA substrate, the morphology of the grown GaN nanostructures as well as their average diameters could be tuned effectively. The Ga

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http://dx.doi.org/10.1016/j.jcrysgro.2012.04.032

concentration was demonstrated to be crucial in determining both the morphology and the average diameter of the GaN nanostructures, and the growing process was analyzed under the frame of vapor–liquid–solid deposition mechanism.

2. Experimental details

Si-NPA used as substrates here was prepared by hydrothermally etching (111) oriented, boron doped ($\rho = 0.015\ \Omega$ cm) single crystal silicon (*sc*-Si) wafers in a solution of hydrofluoric acid containing ferric nitrate [21]. Before growing GaN nanostructures, a thin layer of platinum (Pt) ($\sim$3 nm), which would acts as catalyst in the subsequent CVD process, was pre-deposited on Si-NPA by a radio-frequency magnetron sputtering method. Here high-purity Ga metal (99.999%) and NH_3 gas (99.999%) were used as the Ga and N sources for growing GaN nanostructures, respectively. As shown by the schematic diagram given in Fig. 1, the Ga source and Si-NPA were placed at the center of the constant-temperature zone ($\sim$20 cm) of a tube furnace and were separated by a series of distances (source–substrate distance, SSD) of 1.3, 1.6, 1.9, 2.2, and 2.5 cm, for preparing samples with different morphologies. The furnace was evacuated to a pressure of $\sim 10^{-3}$ Torr to repel out the residual air and moisture. After the furnace was heated up to 1050 °C, NH_3 gas was introduced into the furnace. The gas flow rate was set as 20 sccm to maintain an inner pressure of 7.5 Torr. The inner temperature was kept at 1050 °C all through the CVD process. The growing time was optimized at 15 min.

The structure and the surface morphology of as-prepared GaN nanostructures on Si-NPA (GaN/Si-NPA) were characterized by an X-ray diffractometer (XRD, PANational X' Pert Pro), a field emission scanning electron microscope (FESEM, JSM 6700F), a transmission electron microscope (TEM) and a high resolution TEM (HRTEM, JEM 2100F).

3. Results and discussion

Fig. 2(a) shows the XRD patterns of the five samples prepared with different SSDs of 1.3, 1.6, 1.9, 2.2, and 2.5 cm. All the diffraction peaks that appeared in the five spectra were indexed to those of hexagonal wurtzite GaN with lattice constants of $a = 0.3189$ nm and $c = 0.5185$ nm [25]. This proved the formation of wurtzite GaN on Si-NPA through the CVD process. By analyzing the data of these XRD spectra, two evolution tendencies for every diffraction peak with SSD were found, i.e., a gradually decreasing intensity and a gradually increasing full width at half maximum (FWHM). The variation of the FWHM for the three strongest diffraction peaks, (100), (002) and (101), was depicted in Fig. 2(b). Considering synthetically the factors that might affect the XRD spectra, the decrease of the peak intensity and the broadening of the FWHM with SSD should be attributed to the reduction of the quantity, quality and average size of the deposited GaN nanostructures.

The surface morphologies of as-prepared GaN/Si-NPA with different SSDs were obtained by FESEM observation and are presented in Fig. 3. Obviously, as SSD increases, both the deposition

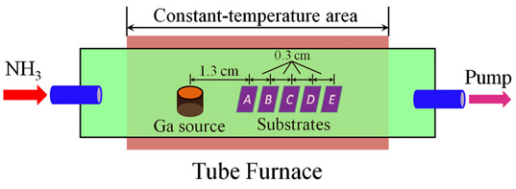

Fig. 1. Schematic diagram of Ga source and Si-NPA substrates with different SSDs in the tube furnace.

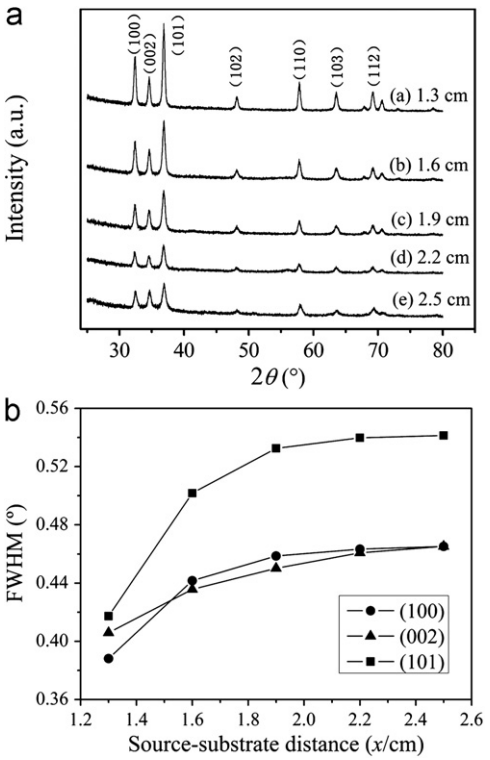

Fig. 2. (a) XRD patterns of GaN/Si-NPA with different SSDs. (b) Variation of the FWHM of the three strongest diffraction peaks with SSD.

quantity and morphology of the GaN nanostructures changed tremendously. An evident trend is that the larger the SSD adopted, the less the quantity deposited. This result could well explain the increment of the diffraction intensity with SSD observed from the XRD spectra (Fig. 2(a)). For the samples prepared with different SSDs, two typical morphologies were observed, GaN cone-strings and nanowires. With a SSD of 1.3 cm (Fig. 3(a)), a GaN thick film was grown on the substrate and the array of Si-NPA was almost covered up. The image taken with a bigger magnification (Fig. 3(b)) discloses that the deposited thick film was composed of large quantities of stacked GaN cones. When the SSD increased over 1.6 cm, three kinds of fascicle arrays of GaN nanostructures, cone-strings for 1.6 cm (Figs. 3(c) and (d)), cone-strings (major) plus nanowires (minor) for 1.9 cm (Figs. 3(e) and (f)), and nanowires for 2.2 cm and 2.5 cm (Fig. 3(g)–(j)), were obtained. A simple statistical result showed that the average diameters for the cone bottoms of the cone-strings presented in Figs. 3(b), (d), and (f) were $\sim$800 nm, $\sim$300 nm and $\sim$90 nm, and those for the nanowires shown in Figs. 3(h) and (j) were $\sim$15 nm and 13 nm, respectively. The variation of the average diameter (d) with SSD (x) as well as the fitting curve was illustrated in Fig. 4. The simulation result disclosed that the experimental data could be well fitted by an exponential function:

$$d(x) = d_0 \exp(-a_0 x). \quad (1)$$

with d_0 and a_0 being fitting constants. This result infers that SSD was an effective parameter for tuning both the diameter and the morphology of the deposited GaN building blocks.

The crystal structures of the deposited GaN cone-strings and nanowires were further determined by carrying out the experiments of TEM and HRTEM, and the obtained images were presented in Fig. 5.The sample prepared with a SSD of 1.9 cm was chosen as the observing object because of the co-presentation of the two typical morphologies in it. From the TEM image given in Fig. 5(a), the cone-strings were found to consist of GaN cones connected one by one with the apex of one cone being adhered to the center of the cone