

Fabrication of GaN-based nanorod light emitting diodes using self-assemble nickel nano-mask and inductively coupled plasma reactive ion etching

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Abstract

We report a novel method to fabricate GaN-based nanorod light emitting diodes (LEDs) with controllable dimension and density using self-assemble nickel (Ni) and Ni/Si₃N₄ nano-masks and inductively coupled plasma reactive ion etching (ICP-RIE). Under the fixed Cl₂/Ar flow rate of 50/20 sccm, ICP/Bias power of 400/100 W and chamber pressure of 0.67 Pa, the GaN-based nanorod LEDs were fabricated with density of 2.2×10^9 to 3×10^{10} cm⁻² and dimension of 150–60 nm by self assemble Ni nano-masks with various size. The size of Ni/Si₃N₄ nano-mask was control by the thickness Ni film ranging 150–50 Å and rapid thermal annealing condition. The technique offers a controllable method of fabrication of GaN-based nanorod LEDs and should be applicable for fabrication of the others III–V nanoscale photonic and electronic devices.

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1. Introduction

Wide-bandgap gallium nitride (GaN) and other group III-nitrides based semiconductors have been successfully employed to realize short-wavelength light emitting diodes (LEDs) and laser diodes [1–3]. Additionally, due to quantum confinement effects, fabrication and studies of nano-structure have recently attracted a great deal of interest for potential application on electronic and optoelectronic devices. Potential applications for nanorod LEDs include quantum cryptography and information processing. With the recent progress in semiconductor process technology, various nano-structure fabrication methods have been investigated such as e-beam lithography, and metal-catalyzed nano-structure synthesis by vapour–liquid–solid growth process on different materials

[4–5]. For GaN-based materials, the fabrications and synthesizing of GaN nanowires and nanorods have been reported using various methods, for example, carbon nanotube-confined reaction, metal-catalyzed growth assisted by laser ablation, and the high temperature pyrolysis approach and so on [6–11]. Furthermore, using photoenhanced wet etching technique to produce GaN whiskers [12–14] were also reported recently. However, all these reported methods are relatively complicated and mostly using synthesis approach with catalysts assist, and had no mention about the control of dimension and density for these fabricated GaN-based LEDs. Since we was reported a method to fabricating controllable GaN-based structure dimension and density using no mask by ICP-RIE [3], but the method caused GaN-based structure top-surface was etching and formation high resistance, so unable to fabricating GaN-based light emitting devices. The study of the self-assemble nanometer-sized metal or semiconductor islands has become particularly important recently as

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it is an attractive method for producing intrinsic nanoscale devices without the need for expensive lithography. In this paper, we report a novel technique to fabricate GaN-based nanorod LEDs with controllable dimension and density using self-assemble nickel nano-mask and inductively coupled plasma reactive ion etching (ICP-RIE).

2. Experimental details

The GaN-based LED structures were grown by metal-organic chemical vapor deposition (MOCVD) on *c*-axis sapphire substrate. The GaN-based LED structure has a 3.0 μm n-type GaN:Si layer and 30 nm thick GaN buffer layer on a (000 1) sapphire substrate. This was followed by the growth of 0.1 μm thick InGaN/GaN multiple quantum well (MQW) layers, followed by the deposition of a 0.1 μm thick p-type

GaN:Mg layer on top. These LED samples were separated into two sets for different process procedures. As shown in Fig. 1(a), the first set of samples was deposited thin Ni layer with a thickness of 150 \AA directly on top of the GaN LED film using an electron-beam evaporation. As shown in Fig. 1(b), the second set of samples was deposited a 3000 \AA Si_3N_4 thin film layer on GaN-based LED film, followed by the deposition of a Ni layer with the thickness ranging from 50 to 150 \AA . All samples were subsequently rapid thermal annealing (RTA) under flowing N_2 at temperatures 800–900 $^\circ\text{C}$ for 1 min to form various nanometer-sized Ni clusters (nano-masks). Finally, all GaN-based LED samples (first and second sets of samples) with various Ni nano-masks were then etched using a planar type ICP-RIE system (SAMCO ICP-RIE 101iPH) at the ICP power and bias power source with RF frequency of 13.56 MHz. The ICP has a reactor chamber which is connected to a load-lock chamber. The etchant gases

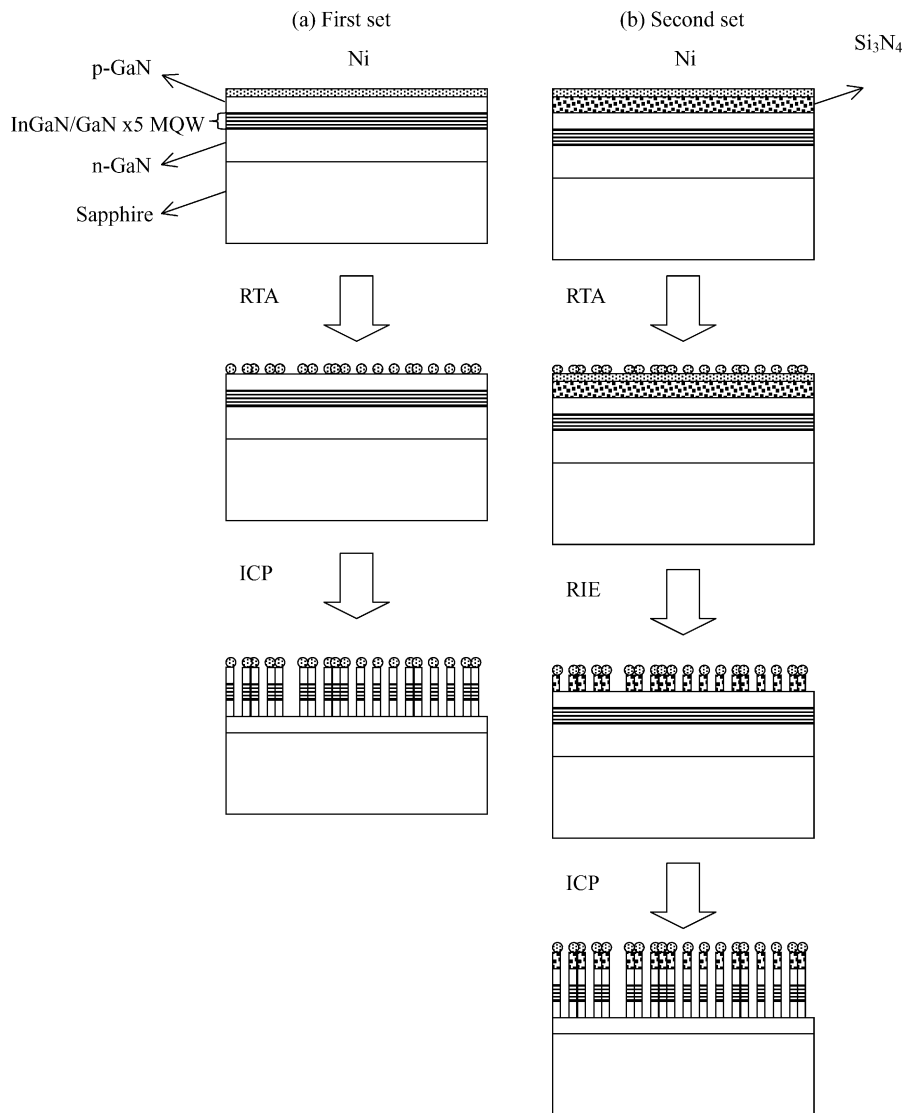


Fig. 1. Schematic illustration of GaN-based nanorod LEDs' process: using (a) Ni (first set) and (b) Ni/ Si_3N_4 (second set) as nano-masks formation. The reaction products after RTA and ICP-RIE etching, leading to the formation of GaN-based nanorod LEDs.

of Cl_2 and Ar gases were introduced into the reactor chamber through independent electronic mass flow controllers (MFCs) that can control the flow rate of each gas with an accuracy of about 1 standard cubic centimeter min (sccm). An automatic pressure controller (APC) is placed near the exhaust end of the chamber to control the chamber pressure. The etching rate is about $4000 \text{ \AA}/\text{min}$ under a gas mixture condition of $\text{Cl}_2/\text{Ar} = 50/20$ sccm with the ICP source power, bias power set at 400/100 W and chamber pressure of 0.67 Pa for 3 min of etching time. After the etching process, the dimension and density of the nanorods were estimated by the scanning electron microscope (SEM) (Hitachi FE-SEM S-5000).

3. Results and discussion

3.1. Effect of Si_3N_4 film under Ni layer

As shown in Fig. 2(a) is the SEM image of Ni/ Si_3N_4 nano-mask image, the Ni/ Si_3N_4 mask dimension size were about 200/150 nm and Ni clusters height was about 100 nm. Fig. 2(b) and (c) shows the first and second set SEM images with the same Ni thickness 150 Å, at the RTA condition of 850 °C for 1 min and ICP-RIE etching process to form the GaN-based nanorod LEDs. As shown in Fig. 2(b) and (c), the second set GaN-based nanorod LEDs with the dimension of about 130–190 nm was more uniform and narrower than that of the first set with the dimension of about 200–300 nm. This can be explained by the strain effect. The room temperature lattice constant of Ni was about 0.352 nm and that of the corresponding crystalline GaN (first set) surface to be 0.318 nm in a direction and 0.518 nm in c direction. This gives the room temperature strains were $\varepsilon_{a(\text{GaN}/\text{Ni})} = 10\%$ and $\varepsilon_{c(\text{GaN}/\text{Ni})} = -32\%$, however, Si_3N_4 (second set) surface to be 0.761 nm in the a direction and 0.291 nm in the c direction gives the room temperature strains as $\varepsilon_{a(\text{Si}_3\text{N}_4/\text{Ni})} = -53\%$ and $\varepsilon_{c(\text{Si}_3\text{N}_4/\text{Ni})} = 21\%$, respectively. This means that the deposition of Ni on Si_3N_4 result in a higher compressive strains in a direction, and resultant Ni nanoclusters size is smaller and more uniform than that of the first set of samples [15]. The dimension of the second set of nanorods shows more uniform and narrower than first set of nanorods due to the Ni nano-mask dimension was more uniform and smaller, and additionally undercut effect on nano-masks Si_3N_4 underlayer after RIE etching.

3.2. Effect of temperature

We estimate the mean dimension and density of the GaN-based nanorod LEDs as a function of the Ni nano-mask RTA temperature. The RTA temperature need to be chosen above 700 °C to form the Ni self assemble nano-masks. Fig. 3 shows the nanorods density can be estimated about $2\text{--}3 \times 10^9 \text{ cm}^{-2}$ as the Ni nano-mask RTA temperatures between 800 and 900 °C for 1 min at fixed Ni film thickness 150 Å on the first and second set samples. The dimension of the GaN-based

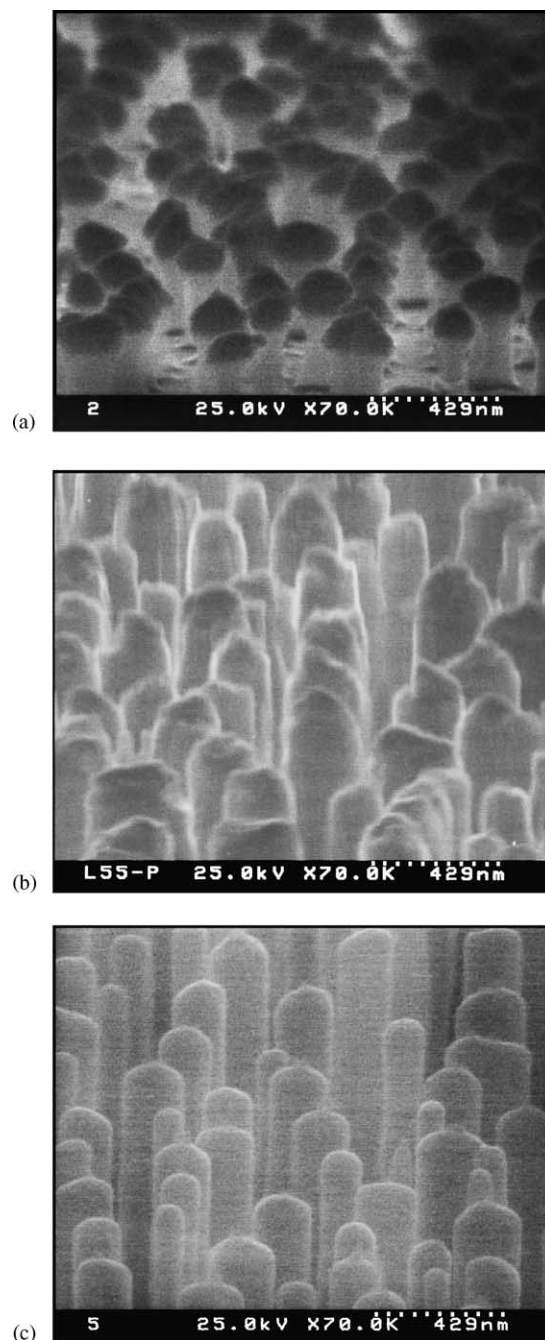


Fig. 2. The SEM images of GaN-based nanorod LEDs samples: (a) only Ni/ Si_3N_4 nano-masks; (b) etching first set sample; (c) etching second set sample at fixed the same RTA temperature 850 °C, annealing time 1 min, Cl_2/Ar flow rate of 50/20 sccm, ICP/Bias power of 400/100 W, and chamber pressure of 0.67 Pa for 3 min of etching time.

LED nanorods on the first set was about 160–380 nm as the RTA temperature from 800 to 900 °C for 1 min, while the second set was about 120–220 nm. The Ni nano-masks formed under RTA temperature condition at 850 °C for 1 min showed more uniform distributed dimension with smaller standard deviation error bar. Therefore, we performed RTA at 850 °C for 1 min on the later experiments.

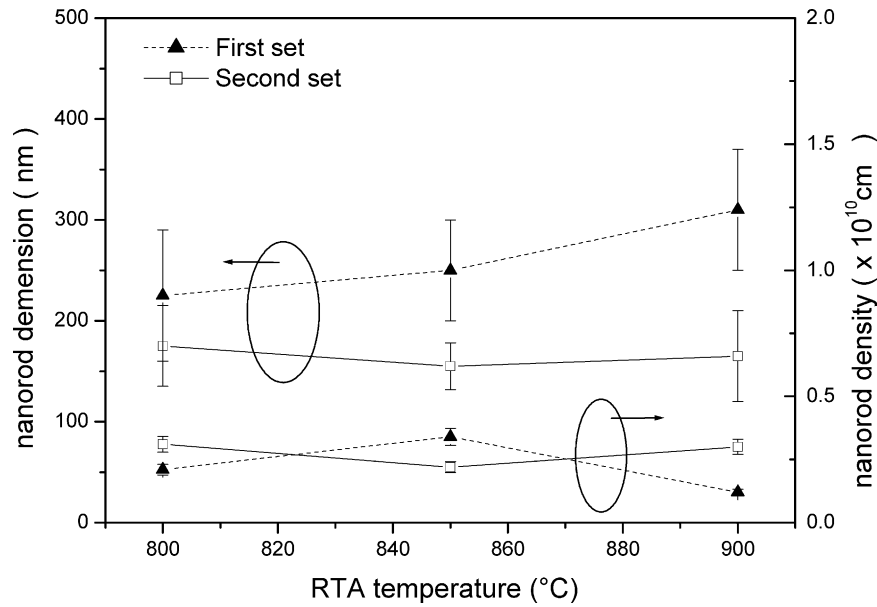


Fig. 3. The mean dimension and density of GaN-based nanorod LEDs on first and second set samples as a function of the RTA temperature varies from 800 to 900 °C for 1 min with Cl₂/Ar flow rate of 50/20 sccm, ICP/Bias power of 400/100 W, and chamber pressure of 0.67 Pa for 3 min of etching time.

3.3. Effect of thickness of the Ni film

It is known that the thickness of the Ni film can play an important role in determining Ni nanometer clusters at a given temperature. We have examined the influence of using various Ni initial layer thickness from 50 to 150 Å deposited on Si₃N₄/GaN LED film (second set) to investigate this effect at 850 °C RTA process for 1 min. The nanorod LEDs were then formed using various Ni/Si₃N₄ nano-masks and ICP-RIE. Fig. 4 shows the mean dimension and density of GaN-based nanorod LEDs as a function of Ni-mask initial layer thickness from 50 to 150 Å. The nanorod densities in-

crease from 2.2×10^9 to $3 \times 10^{10} \text{ cm}^{-2}$ and the dimension decrease from 150 to 60 nm as the Ni film thickness decrease from 150 to 50 Å. Under the same annealing condition, the Ni cluster get larger and dispersed resulting in bigger and dispersed nanorod LEDs. On the other hand, as the Ni initial thickness decrease, it is more easily for Ni migration and Ni clusters dimension size became smaller and denser at the same annealed condition [15].

The transmission electron microscopy (TEM) (JEOL, JEM-200CX) image of the InGaN/GaN MQW nanorod LEDs fabricated by Ni/Si₃N₄ nano-mask (50 Å Ni and 850 °C RTA) and ICP-RIE as illustrated in Fig. 5(a) shows that the diameter

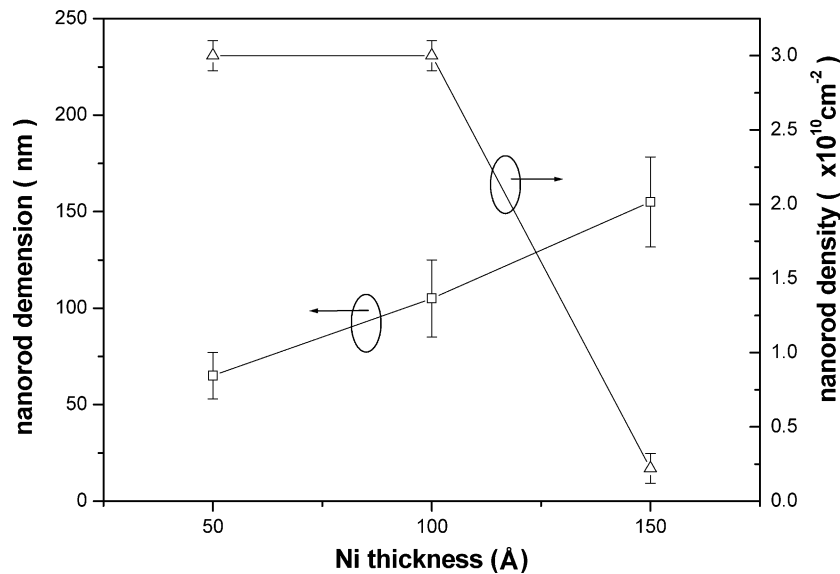


Fig. 4. The mean dimension and density of GaN-based nanorod LEDs on second set samples as a function of the Ni film thickness varies from 50 to 150 Å at the same RTA 850 °C for 1 min with Cl₂/Ar flow rate of 50/20 sccm, ICP/Bias power of 400/100 W, and chamber pressure of 0.67 Pa for 3 min of etching time.

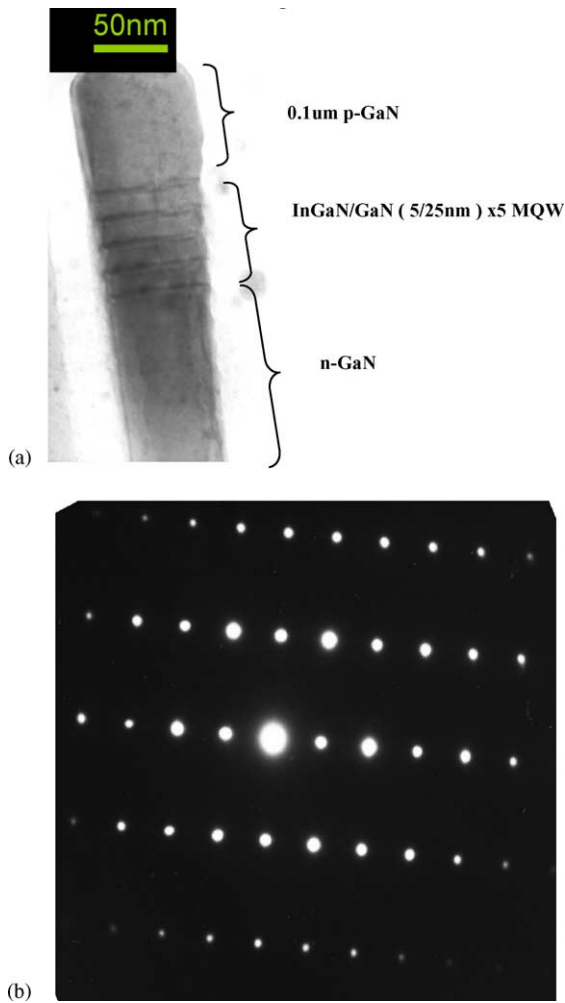


Fig. 5. (a) TEM image of a InGaN/GaN MQW nanorod LEDs with mean diameter of about 80 nm and etching depth of about 1 μm . (b) Selected-area electron diffraction patterns from the InGaN/GaN MQW nanorod.

of the GaN nanorods is approximately 80 nm and the etching depth is about 1 μm . and five pair InGaN/GaN MQWs embedded within the straight nanorod LEDs can be clearly observed. Many TEM images demonstrate that the diameter distribution of the GaN nanorods is average at 60–80 nm. The selected area electron diffraction pattern (SAED) is consistent with GaN single crystal indexed as wurtzite GaN (Fig. 5(b)).

4. Conclusion

In summary, we report a novel method to fabricate controllable dimension and density of GaN-based nanorod LEDs

by varying Ni-mask initial layer thickness using ICP-RIE etching. Under the fixed Cl_2/Ar flow rate of 50/20 sccm and ICP/Bias power of 400/100 W, the GaN-based nanorod LEDs were fabricated with density of 2.2×10^9 to $3 \times 10^{10} \text{ cm}^{-2}$ and dimension of 150–60 nm by self-assemble Ni nano-masks with various size. The size of Ni nano-mask was control by the thickness Ni film ranging 150–50 \AA and rapid thermal annealing condition. The technique offers a relatively simple method for fabrication of controllable mean dimension and density of GaN-based nanorod LEDs. It should be applicable for fabrication of other types of III–V based materials and structures including p–n junction, hetero-junction and laser devices.

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