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Fabrication of Nanostructures of GaN on Sapphire and Si Substrates by Dry Etching

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ABSTRACT

This research aims to fabricate GaN nanostructures such as nano-holes and nano-columns. GaN is firstly grown on Sapphire and Si (111) substrates by Metalorganic Chemical Vapor Deposition (MOCVD) followed by a top-down process technique by dry etching with the nano-mask on top. The first structure is nano-holes penetrated into a GaN layer on a sapphire substrate. These holes were created with the same pattern as the nano-mask called porous alumina with the thickness of about 400 nm. The geometry of the nano-holes was discovered by FESEM which showed that the average pore diameter and depth were about 70 nm and 530 nm, respectively. The second structure is GaN nano-columns formed on Sapphire and Si substrates with the pattern of nickel nano-dots on the top surface before etching back into the GaN layer. The FESEM images indicated that the lateral sizes were varied from 70 nm to 180 nm while the column heights were different due to performing GaN nano-columns with various etching times.

Key words: Nanostructures, Dry etching, MOCVD, GaN

INTRODUCTION

In recent year, there are many research groups developing various techniques to fabricate semiconductor devices on a low dimensional scale, in order to increase efficiency and obtain more potential applications [1-3] Fabrication of low dimensional semiconductors tends to be on a micro- or nano-metre scale. The general technique is to pattern the top layer of the structure and then etch the physical structures of the semiconductor materials or remove unwanted materials. Creating nanoscale materials is performed by etching techniques which are categorized into either wet etching or dry etching. Wet etching is a commonly used technique to remove the exposed area by chemical etchants. Since this technique does not require advanced equipment or a complicated process, it is a powerful method to etch various materials by choosing the right etchants. However, there are limitations to this method. Wet chemical etching is an isotopic process, which etches the materials both laterally and vertically in regions defined by the mask [4]. The etch rate depends on the material and the crystal planes [5]. Therefore, this technique may not be suitable for fabricating nanostructure. The alternative is dry etching [6]. This process uses plasma and is also known as plasma etching which has many advantages [7]. It has good controllability, uniformity and high reproducibility. In addition it is useful for creating nanostructures because the etch profile is anisotropic. Hence, it is an important process for fabrication of photonic and electronic devices [8].

This research presents the procedures how to fabricate nanostructures such as nano-holes and nano-columns of GaN materials on Sapphire and Si substrates by using the etch mask and dry etching system.

Materials And Methods

2.1 The template preparation on sapphire and Si substrates:

The samples used as templates in this research were prepared by growing GaN on (c-plane) Sapphire and Si (111) substrates in an Aixtron 200/4-HT RF-S MOCVD reactor, whilst being monitor using a LayTec Epi-Da TT spectroscopic reflectometer. Trimethylaluminum (TMAl), trimethylgallium (TMGa), trimethylindium (TMIn) and ammonia (NH_3) were used as aluminum, gallium, indium and nitrogen sources, respectively. After loading sapphire, a thermal cleaning procedure

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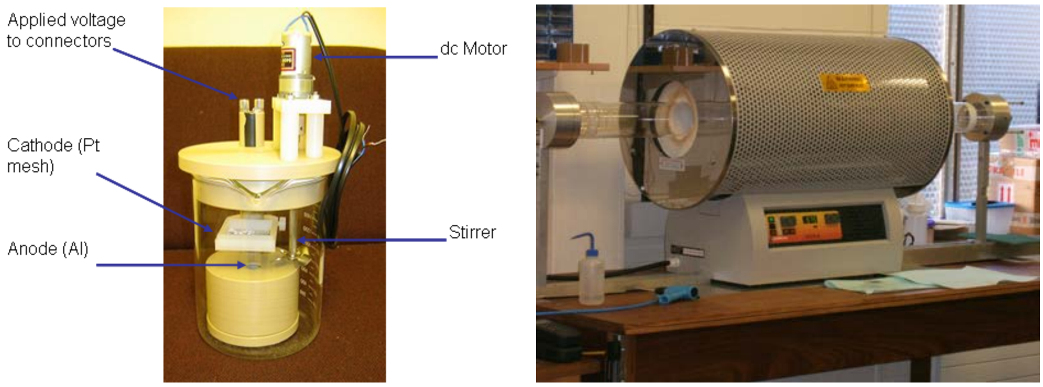
was employed to the substrates for 10 min under H_2 at 1090°C to get rid of native oxide from the surface. Prior to growing step, the substrate was cooled down and a GaN buffer layer of about 30 nm was deposited at 525°C. After that, the temperature was elevated to 1020°C to grow a 1µm thick GaN layer. In case of Si (111), the substrates were thermally desorbed for 10 min under H_2 at 1140°C and a reactor pressure of 100 mBar. Then a thin Al layer was deposited for a few seconds to prevent the surface from nitridation before switching in ammonia for a 40 nm AlN buffer layer growth. The growth temperature and chamber pressure were then increased to 1020°C and 200 mBar to grow a thick GaN layer.

2.2 The fabrication of the etch mask on the GaN templates:

Before the nanostructure created, the templates have to be masked either by a porous alumina membrane or a Ni nano-dot array as etch masks to consequently obtain nano-holes or nano-columns, respectively. The instruments to produce the etch masks are shown in Figure 1. Figure 1(a) is the anodization cell which the Al film located between 2 electrodes is exposed to the electrolyte. A positive electrode is connected to the sample while a negative electrode is a Pt mesh above the sample. This equipment is used to produce the alumina membrane. Figure 1 (b) is a commercial furnace from the Carbolite Company. The quartz worktube, wafer carrier, push rod, aluminum caps and supports and Nitrogen supply were designed and implemented. The furnace is designed to anneal the sample by pushing a long rod half way through the work tube to form Ni dot array.



(a) (b)

Fig. 1: The instruments to fabricate the etch masks: (a) the anodization cell and (b) the tube furnace

To create the alumina mask, high purity Ti (99.99%) and aluminum (99.999%) were deposited on the GaN template by electron beam evaporation with the thicknesses of 10 nm and 1000 nm, respectively. After that, the template with thin Al film was anodized in 0.3 M oxalic acid at 5°C with constant voltage of 40 V. To produce highly ordered alumina film, the anodization is performed two steps because high periodic undulating pattern on the Al surface after removing the first oxide layer is very helpful to quickly begin the pore penetrated nicely and orderly during the second step. The first and second steps are performed for 20 min and 9 min, respectively. Before using the alumina mask, the bottom layer at the interface between the mask and GaN surface was removed by the solution of 5% H_3PO_4 at 35°C for 15 min.

To create Ni nano-dot array, the GaN surface was firstly coated by SiO_2 using PECVD at 300°C to prevent the Ni to react with GaN material to be nickel-gallide at high temperature [9, 10]. After that, high purity Ni was deposited on the top surface by e-beam evaporation. 5 nm thick Ni film was subsequently annealed in the tube furnace at 845°C for sapphire and 800°C for Si.

2.3 The fabrication of the nano-holes and nano-columns by dry etching:

There are two etching system such as a Plasmalab 80 plus and a Plasmalab system 100 from Oxford Instrument Company. The second system has a higher potential due to the loadlock chamber, much higher RF and ICP powers influenced on the etch profile of the nanostructures

2.3.1 GaN nano-holes with the alumina mask:

Etching occurs through the nano-pore pattern to create air-hole within the GaN layer. Bare GaN templates as the test piece was firstly used to find out the etch rate before etching the real sample. Gases used to etch GaN are Cl_2 and Ar from the ICP system.

2.3.2 GaN nano-columns with Ni nano-dot array:

In this structure, Ni nano-dot pattern was firstly transferred into SiO_2 to obtain SiO_2 nano-columns used as an etch mask as well. The dielectric layer was etched by the RIE system with CHF_3 and SF_6. The GaN layer was consequently etched with the same gas mixture as to create GaN nano-holes by the ICP system.

Results And Discussion

3.1 The porous alumina mask on GaN/sapphire:

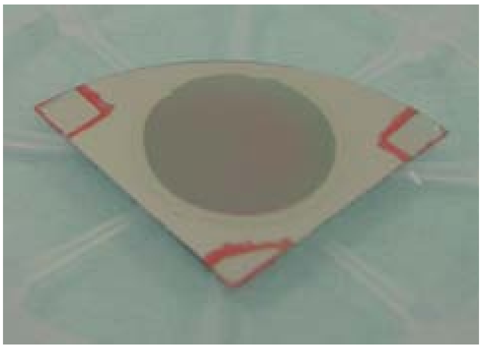


Fig. 2: The porous alumina mask on GaN/sapphire

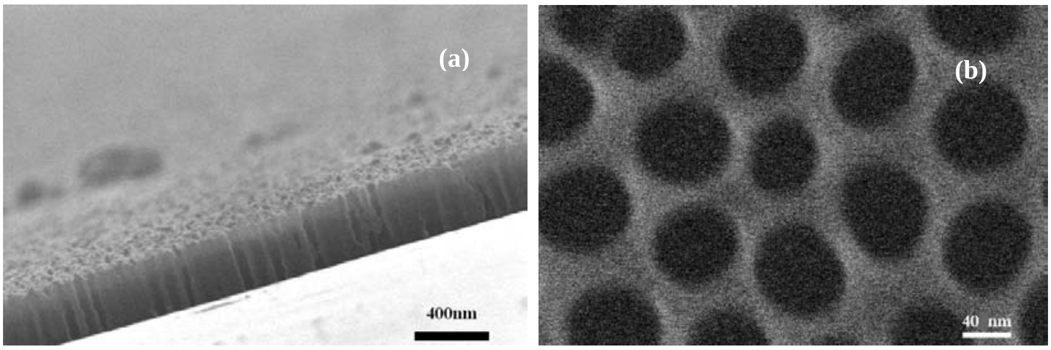


Fig. 3: FESEM images of the porous alumina mask : (a) cross section (b) plan-view

Figure 2 shows the translucent porous alumina membrane on the GaN/sapphire substrate after the second anodization. The sample was investigated by FESEM to observe the geometry of the membrane. The thickness of the mask is about 400 nm and the average diameter is about 70 nm after widening the pore and removing the bottom layer at the same time.

3.2 Ni nano-dot mask on GaN/sapphire and GaN/AlN/Si:

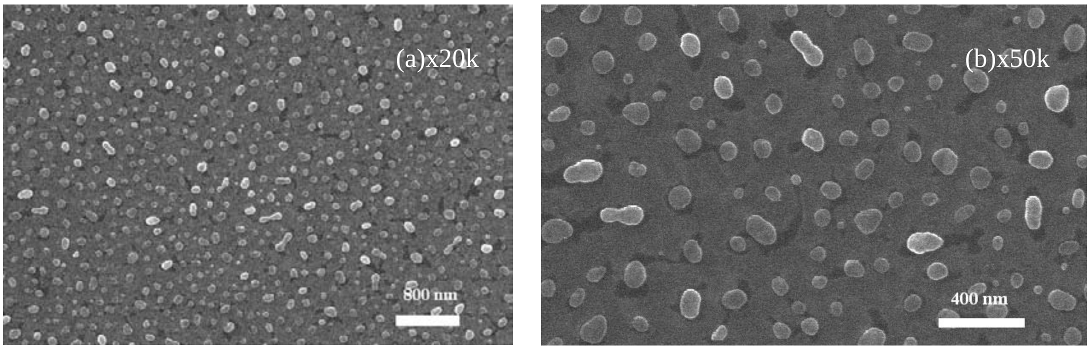


Fig. 4: Ni dots formed at 845ºC for 45 sec (sapphire)

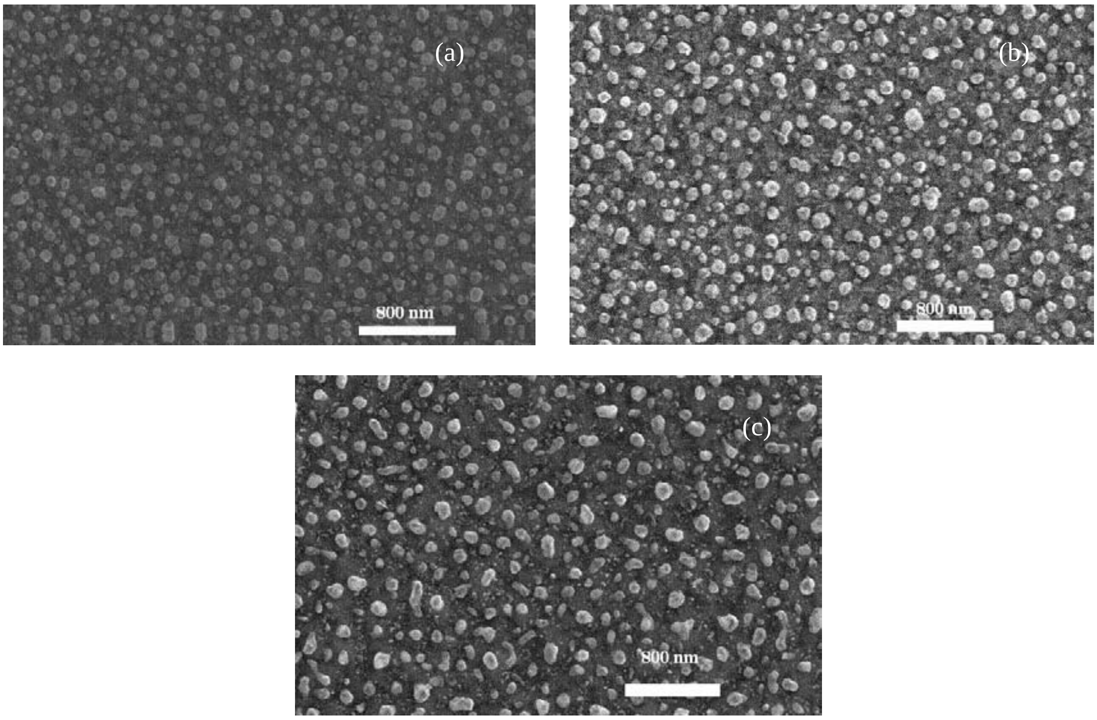


Fig. 5: Ni dots formed at 800ºC for (a) 30 sec (b) 31 sec and (c) 33sec (Si)

Figure 4 and 5 are Ni nano-dots used as the etch masks on GaN/sapphire and GaN/AlN/Si substrates, respectively. The sapphire substrate was annealed in the furnace at higher temperature and longer period of time, comparing to these parameters of performing Si substrate because these two substrates have different the thermal conductivities. The thermal conductivity of Si is 156 W/m.K which is much higher than that of sapphire (42 W/m.K). We found that Ni dot sizes and densities on Si substrate were slightly smaller and higher, respectively.

3.3 Etched Nano-holes and Nano-columns:

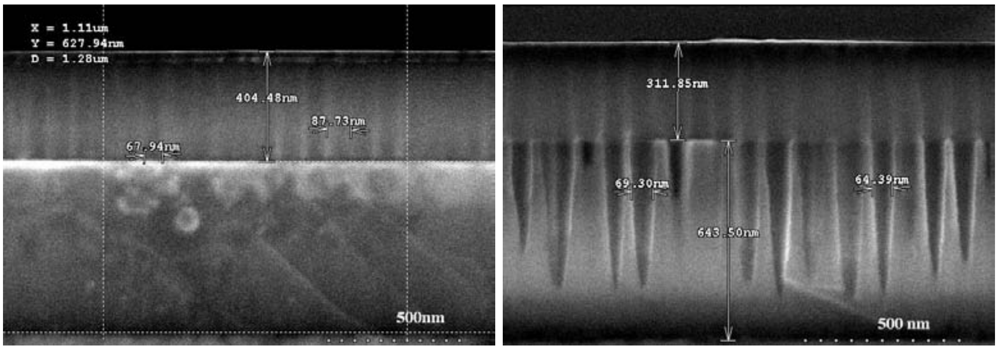


Fig. 6: FESEM cross-section views of the sample : (a) before and (b) after etching GaN

The thicknesses of the alumina film and GaN layer are around 404 nm and 627 nm, respectively, as shown the cross section in Figure 6 (a). The image shows straight holes down to the interface. Also the barrier layer was completely removed from the bottom of the film. Figure 6 (b) shows the GaN nano-holes which are etched for 4 min. The etch profile is still tapered for the internal walls. Modifications to the ICP recipe were considered to improve the etch profile. Firstly, using a lower RF power would slow down the plasma to allow wider holes to be etched in the GaN. Secondly, the etch profile definitely depends on the aspect ratio of the mask and the required etch depth of the GaN. Finally, results could be improved by using an ICP machine which could reach lower base pressures using a load lock.

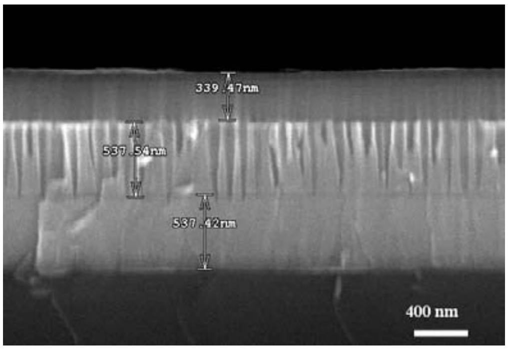


Fig. 7: FESEM image after improving etch profile

The cross sectional image of Figure 7 shows deeper etching of the GaN layer, compared to the results of the previous experiment. The etch depth is ~ 537 nm and the remaining alumina mask is~ 339 nm. The recipe of ICP (Plasmalab 80) which was set for etching GaN consisted of Cl_2 = 30 sccm, Ar = 7 sccm, RF power = 130 w, ICP power = 500 w, and base pressure = ~$3x10^{-6}$ torr.

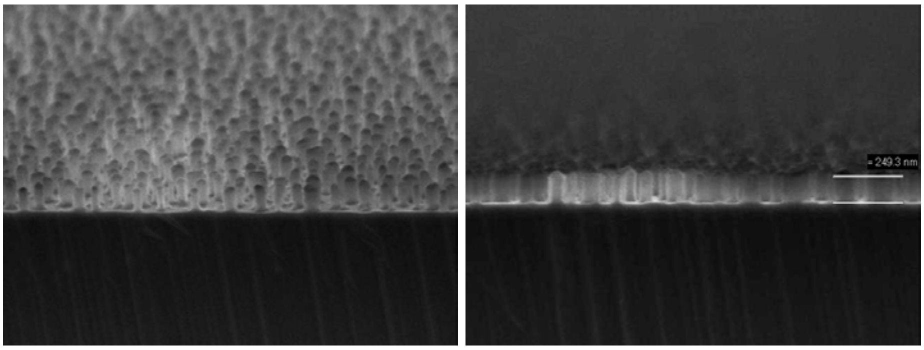


Fig. 8: FESEM images of SiO_2 nano-columns

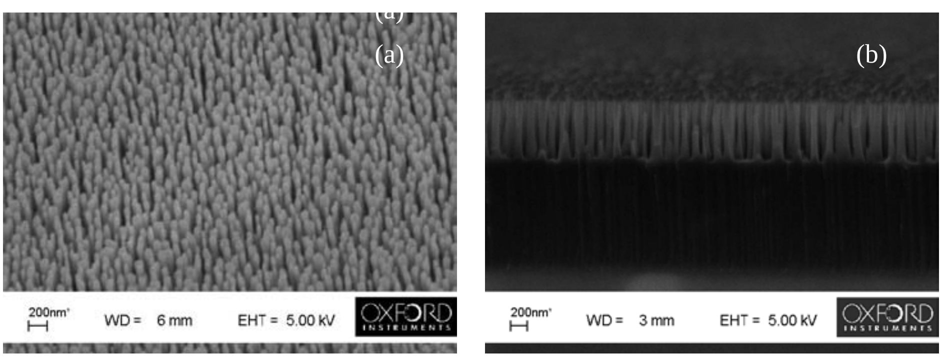


Fig. 9: FESEM image of GaN nano-columns

The SiO_2 layer on the GaN surface was etched down to the interface as shown in Figure 8. Image (a) shows an inclined view of the SiO_2 nano-columns, which were measured to be ~ 249.3 nm, as shown in Figure 8(b). SiO_2 was RIE etched with the parameters as the details below.

CHF_3 = 25 sccm, SF_6 = 5sccm, RF power = 200 watt, base pressure = 3 x 10^{-5} Torr. To further etch down to GaN as shown in Figure 9, the recipe consists of Cl_2 = 50 sccm, Ar = 10 sccm, RF power = 100W, ICP power = 1000w, and base pressure = 4 x 10^{-6} Torr. The material was etched for 2 min. Analysis showed that the GaN layer had been etched down ~ 650 nm, while the SiO_2 mask still remained with ~80 nm on top of the nano-columns. The sidewall angle is 90 degrees as presented in Figure 9 (b). The high density of GaN nano-columns can be seen from the tilted view in Figure 9(a).

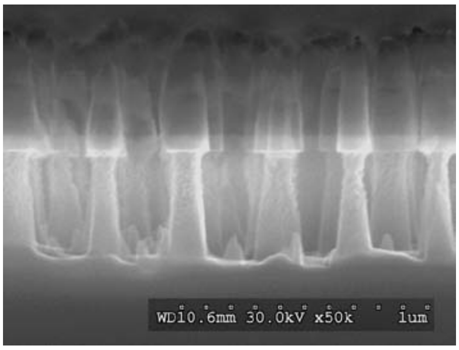


Fig. 10: FESEM image of GaN/AlN/Si nano-columns

The sample is GaN/AlN/Si which is etched for 1 min and 30 sec. The image shows that the SiO_2 mask still remained on top of the columns. The etch profile was slightly tapered at the bottom and produced a bottle neck shape at the interface between the nitride layer and the Si column. The recipe that we used was slightly different. This consists of Cl_2 = 40 sccm, Ar = 10 sccm, RF prower = 100 W and ICP power = 1200 W.

Conclusion:

In this study, porous alumina and Ni nano-dots by annealing process to fabricate nanostructures of GaN and GaN/AlN grown on sapphire and on Si substrates are very simple and a good technique. The first mask that we used to fabricate nano-holes was porous alumina with nearly 70 nm in pore diameter and ~ 400 nm in thickness. The template with the etch mask was etched through the mask. The etch profile was improved after slightly decrease the RF power. The etch depth of nano-holes is ~537 nm. The second mask that we used to create nano-columns of either SiO_2 or GaN is Ni nano-dots. The SiO_2 was etched by RIE system with the recipe above. To obtain GaN nano-columns, the ICP system was used with different gases. The results show high density GaN nano-columns with the sidewall angle of 90 degree. In case of etching Si, the recipe still kept the same gases such as Cl_2 and Ar with different set up values. The etch profile of nitride/Si nano-columns was slightly tapered.

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