High density single crystalline GaN nanodot arrays fabricated using template-assisted selective growth

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Abstract— High density, uniform GaN nanodot arrays with controllable size have been synthesized by using template-assisted selective growth. The GaN nanodots with average diameter 40nm, 80nm and 120nm were selectively grown by metalorganic chemical vapor deposition (MOCVD) on a nano-patterned SiO2/GaN template. The nanoporous SiO2 on GaN surface was created by inductively coupled plasma etching (ICP) using anodic aluminum oxide (AAO) template as a mask. This selective regrowth results in highly crystalline GaN nanodots confirmed by high resolution transmission electron microscopy. The narrow size distribution and uniform spatial position of the nanoscale dots offer potential advantages over self-assembled dots grown by the Stranski–Krastanow mode.

I   INTRODUCTION

Recently, self-assembled nanocrystals or quantum dots of wide-band-gap GaN and related group-III nitride semiconductors have received considerable attention because of their increasing applications in light-emitting and electronic devices, as well as potential applications in quantum information processing. [1-5] Self-organized Stranski-Kranstanov (SK) growth mode, which relies on partially release of strain energy by the formation of islands through elastic strain in the large lattice-mismatch system, has been widely applied to grow III-Nitride nanodots. In addition, growth of GaN nanodots on AlGaN has been achieved by using a so-called 'anti-surfactant' method, which changes the surface energy of AlGaN to prefer islands growth.[6] However; these growth processes result in a random size distribution of the nanodots. The randomness of nucleation and size variation cause a large spread in the electronic state energies. Moreover, these growth processes are only applicable to lattice-mismatched heteroepitaxial system. A precise control of the position and spacing of the nanodots has a great importance for future applications in numerous electronic and optoelectronic devices. In GaN based material system, fabrication of ordered nanodots with uniform size, high-density remains a great challenge.

In this letter we report a method to fabricate uniform, high density and size-controllable GaN nanodot arrays by selectively grown in the nanopatterned SiO2/GaN substrate. Selective growth in the patterned substrates has been recently used to fabricate the nanostructures.[7-9] This approach not only can realize highly ordered nanostructure arrays of narrow dot-size distribution, but also overcomes the limitation of self-assembled SK mode growth. The nanopatterns are usually created by lithography, which is limited by high cost and low throughput, especially for large-scale fabrication. And also it is very difficult to get pattern beyond 100nm. In our experiments the nano-scale windows in the silicon dioxide are created by the ICP etching using the nanoporous anodic aluminium oxide (AAO) as masks. Nanoporous anodic aluminum oxide provides an efficient and low cost alternative approach for realizing ordered nanostructures.[10-13] Self-organization during the pore growth, leading to a densely packed hexagonal pore structure, has been reported in oxalic, sulfuric, and phosphoric acid based solution. The interpore distances of the ordered pore arrangement can be varied in the range 50 – 420 nm. The structural properties of the ordered AAO make it a perfect template material for the nanofabrication.

II.   EXPERIMENTAL DETAILS

The experimental procedure is as followings. The first step is to grow a conventional low-temperature GaN nucleation layer on sapphire (0001) followed by the deposition of 1.5 μm of GaN at high temperature using an MOCVD setup. A thin layer of SiO$_2$ (60 nm) was deposited on the top of GaN by plasma enhanced chemical vapor deposition (PECVD) using SiH$_4$ and N$_2$O as gas source followed by 1 μm aluminum deposited by e-beam evaporation. The Alumina anodization was conducted by using a two-step anodization process reported by Masuda and Satoh. 0.2 M sulfuric acid, 0.3M oxalic acid and 0.3M phosphoric acid have been used as electrolytes. The corresponding applied voltages are 25V, 40V and 150V. This procedure allows fabrication with high reproducibility

and uniformity due to good adhesion of the template to the substrate. CF$_4$ based inductively coupled plasma (ICP) etching conditions are employed to transfer the nanopores in the AAO template onto the SiO$_2$ film. The etching conditions has been optimized to precisely control the etch depth and to etch the SiO$_2$ till the underlying GaN surface is exposed. Under our etching conditions, several seconds (60s-80s) are enough to etch through 60 nm SiO$_2$. Such etching will not affect the underling GaN surface although CF$_4$ plasma will etch GaN very slowly.[14]   Then the AAO templates are etched away in the chemical solution. After samples cleaning process, GaN growth was then carried out through the nanoporous SiO$_2$ template by MOCVD. Trimethylgallium (TMGa) was used as group III sources and NH$_3$ as the group V source. H$_2$ was used as a carrier gas. The samples are annealed in N$_2$ ambient for 2 minutes at the 1020℃ in the MOCVD reactor before GaN nanodots growth. This will recover he surface damage possibly caused by the ICP etching. After GaN growth, the SiO$_2$ template was removed using dilute HF revealing the well-ordered GaN nanodot arrays. The samples are characterized by scanning electron microscopy (JEOL 6700FESEM), and cross sectional transmission electron microscopy (Phillips EM 300 TEM). Cross-sectional samples for TEM have been prepared using standard procedures involving the sequence of grinding, polishing, and ion millings.

III.   RESULTS AND DISCUSSION

The as-grown GaN epilayers prior to SiO$_2$ deposition show step-like morphology and the surface roughness of the epilayers are about 0.4 nm, indicating a good surface morphology. A relatively smooth surface of the starting epilayer is a prerequisite, since at a later stage the sample has to undergo PECVD, anodization, and chemical cleaning. Also the presence of surface inhomogeneities will affect the timing during the ICP etching and chemical cleaning of SiO$_2$. Figure 1 shows the FESEM images of the hole patterns in the dioxide masks on the GaN surface after AAO template removal. The pattern is same with the original AAO template. Figure 2 shows three different pore periods with pore distances of 70, 110, and 400 nm which are corresponding to the template anodized in sulfuric, oxalic, and phosphoric acid solutions under voltages of 25, 40, and 150 V, respectively. The average diameter of the pores in the mask is 40, 80, and 120 nm, which can be tuned by the anodization conditions and pore widening times. This also gives a freedom to fabricate different density and different diameter of the nitride nanodots. Because the aluminum films in this experiment were only ~ 1μm, the pores were not hexagonally ordered, especially for the anodization in the phosphoric acid. It may be possible to obtain more ordered pores with a narrower size distribution by starting thicker films or by prepatterning the initial aluminum film using a mold .[15, 16]
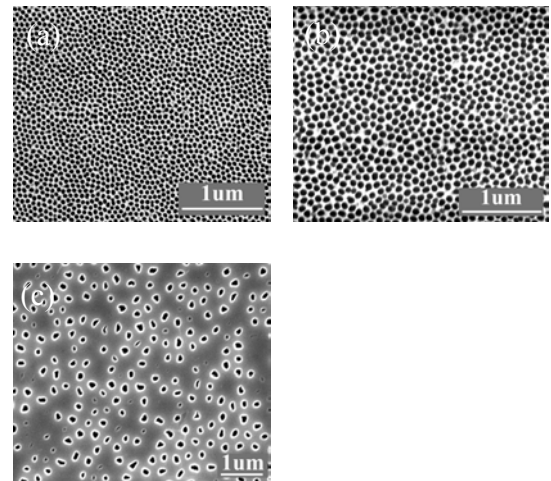

FIG. 1. SEM images of hole pattern in the SiO2 mask on GaN surface corresponding to the different anodization process and pore widening time. (a) 0.2 M sulfuric acid, 40 minutes pore widening; (b) 0.3 M oxalic acid, 80 minutes pore widening; (c) 0.3M phosphoric acid, 105 minutes pore widening.

Figure 2 show a top-view FESEM image of GaN nanodot arrays with average diameter of 40, 80, and 120nm after removing the SiO$_2$ mask. The diameter and the periodicity of the GaN nanodot arrays are similar to that of nanoholes in SiO$_2$. It is as we expect since the GaN dots growth is confined by the nanoholes in the SiO$_2$. Under the optimized growth conditions, GaN selectively grows inside the nano-windows of the silicon dioxides. The mechanism is similar to the initial stage of the ELO growth.[17] For the group III adatoms on the GaN surface, s = 1 whereas for the SiO$_2$ mask, s = 0. This is expected as the SiO$_2$ bond strength is much higher than that of other bonds. Thus, it would be unlikely for Ga, or N adatoms to form bonds with SiO$_2$ surface and no immediate GaN nucleation can be initiated on the SiO$_2$ surface. The Ga adatoms arriving at the surface of SiO$_2$ can not adhere to the surface and they would either evaporate or migrate and diffuse along the surface to the nanopores of SiO$_2$. Thus, such a process during GaN growth can create an additional supply of active species that can be transported via diffusion to the nano-window areas. This will further lead to growth rate enhancement on the nano-window regions. Besides having the properties transferred from the AAO template such as well ordered arrays of nanoholes with pore sizes from 10 nm to 300 nm which can be easily controlled, nanoporous oxide, as a template, has big advantages over the AAO template in nitrides nanostructure fabrication. It provides selective growth during GaN deposition. Also the thickness of the nanoporous oxide template can be controlled by PECVD process. It is very easy to grow oxide with the thickness under 100 nm.
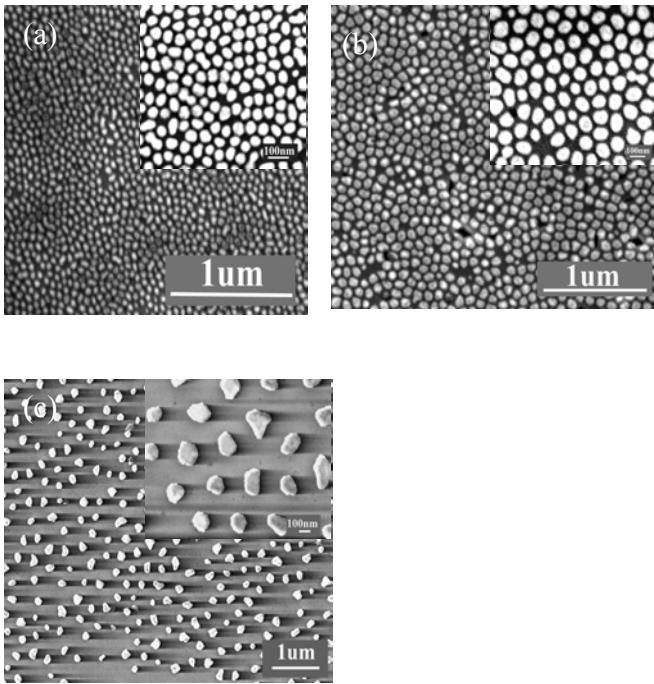
FIG. 2. Figure 2 SEM images of GaN nanodot arrays with different diameter and density. (a) 40 nm (b) 80 nm (c) 120 nm. Inset shows the larger magnitude.

Cross-sectional HRTEM micrograph of the GaN nanodot taken from [1120] (corresponding to 40 nm diameter) is shown in Figure 3 (a). No defects such as dislocations or stacking faults are observed in the GaN dots. There is no damage to the underlying GaN surface under our optimized etching conditions. The interface between the underlying GaN substrate and GaN dots is very continuous as shown in Fig. 3 (b). It is completely defect free and exhibit the wurtzite stacking structure exactly same with the underlying GaN.
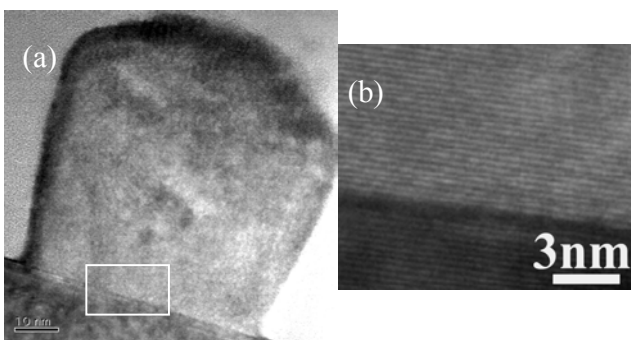

FIG. 3. (a) Cross-sectional TEM of the individual GaN nanodot; (b) enlarged TEM image of the interface between dots and underlying GaN layer

IV   SUMMARY

In conclusion, we have demonstrated an effective method to fabricate large scale, high density, uniform and size-controllable single crystalline GaN nanodot arrays using the template-assisted selective growth technique. GaN nanodots are selectively grown inside the nanowindows of dioxide, which are created by ICP etching using AAO template as masks. TEM results show that the GaN nanodots are single crystalline and the interface between dots and underlying GaN is very smooth. This method has the potential applications in the Nitrides nanofabrication.

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