

GaN Based Nanomaterials Fabrication with Anodic Aluminium Oxide by MOCVD

Yadong Wang¹, Melissa Sander², Chen Peng², Chua SooJin^{1,3*}, C.G.Fonstad, Jr⁴

1 Singapore-MIT Alliance, Advanced Materials for Micro- and Nano-Systems Programme, 4 Engineering Drive 3, Singapore 117576

2 Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602

3 Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576

4 Department of Electrical and Computer Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA 02139

Abstract— A highly self-ordered hexagonal array of cylindrical pores has been fabricated by anodizing a thin film of Al on substrate and subsequent growth of GaN and InGaN in these nanoholes has been performed. This AAO template-based synthesis method provides a low cost process to fabricate GaN-based nanomaterials fabrication.

I. INTRODUCTION

THIS GaN-based materials have been the subject of intensive research for blue and ultraviolet light emission and high temperature electronic devices^[1-4]. Due to the continual demand for reduction in device size, it is naturally of interest to fabricate nanodevices based on nanoscale materials with novel properties. Interest in the synthesis of GaN nanocrystals arises from the possibility to explore novel quantum confinement effect in a material with a well-recognized potential for device application.

A method which entails synthesizing the desired material within the pores of a nanoporous membrane is called “template synthesis”^[5]. In this case the size and shape of the nano-structures are controlled by the size and shape of the openings of the nanotemplates. One of the attractive templates is anodic aluminum oxide (AAO). Anodic aluminum oxide (AAO) film, which has ordered pores of dimensions ranging from the submicrometer to nanometer range, recently has attracted much attention because of the usage of applying a host or template for the fabrication of nanodevices such as electronic, optoelectronic, and micromechanical devices^[6-8]. AAO is known for more than 50 years but only in 1995, it was observed that ordered arrays of porous alumina could be obtained and could be used as a template for nanofabrication^[9]. The geometry of anodic porous alumina may be schematically represented as a honeycomb structure with a high aspect ratio (depth divided by width) of fine channels characterized by a close-packed array of columnar hexagonal cells, each containing a central pore, as shown in Fig.1^[9]

The template method has a number of interesting and useful features. First, it is very general; this method can be used to prepare conductive polymers, metals, semiconductors, carbon tube and other materials. Furthermore, nanostructures with extraordinarily small diameters can be prepared which too small to be made with the lithographic method. And the

diameters of the hole can be easily controlled through external conditions such as acid concentration and applied voltage.

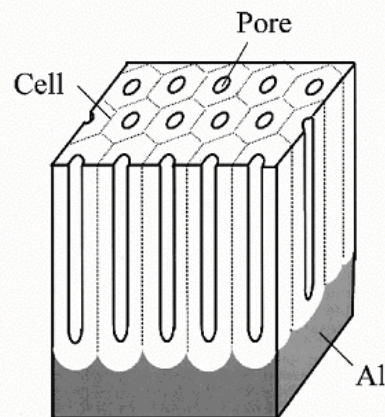


Fig 1 Schematic drawing of the structure of anodic porous alumina

Anodic aluminum oxide (AAO) films possess very regular and highly anisotropic porous structures with pore diameters ranging from below 10 to 200 nm, pore length from 1 to 50 μm , and pore densities in the range 10^9 - 10^{11} cm^{-2} . The pores have been found to be uniform and nearly parallel, making the AAO films ideal templates for the deposition of nanometer-scale particles. The AAO template also allows one to manipulate the nano-structure arrays and to incorporate them into a variety of potential designs of nano-devices. To our knowledge, there are few reports on the fabrication of nano-GaN based material using the AAO.

II. EXPERIMENTS AND RESULTS

A. Template Fabrication

Anodization was conducted under constant cell potential in aqueous solution as electrolyte. The sample with Al deposited on the substrate was mounted on a copper plate serving as anode and exposed to the acid in a thermally isolated electrochemical cell (See Fig 2). During anodization, the electrolyte was stirred.

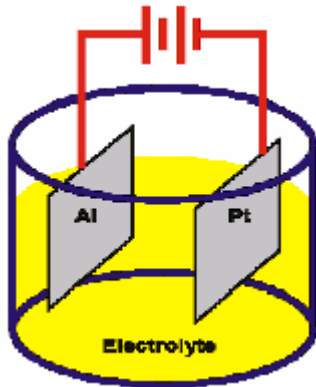


Fig 2 Schematic equipment of anodization

In this work, an evaporated film of Al about 1 μm thick on the substrate is used to fabricate the AAO template rather than by anodizing aluminum using bulk or thin sheets of aluminum. This method can avoid tedious procedures that limit their practicality^[11,12]. The process steps used in the fabrication of the AAO are described as follows. We use a two-step anodizing process reported by Masuda^[9]. The e-beam deposited Al film is first anodized at the voltage of 40V in 0.3 M oxalic acid solution at about 4 \square . Then the anodized layer, which covers the top part of the film is removed in a mixture of phosphoric acid and chromic acid. The textured Al plate was anodized again under the same condition as the first. The second anodization step lasted until the Al film has been completely converted to an AAO film. Subsequently, the samples were dipped in 5% H_3PO_4 at room temperature for 45 minutes to remove the thin barrier layer. The pore diameter can be increased by an additional pore widening etch.

Figure 3 shows the SEM image of the AAO. We confirm that nanoholes with relative uniform size are hexagonally arranged with high regularity. The mean diameter of the holes as measured from the SEM was about 65 nm. Figure 4 shows the AFM image of the AAO template. The cross-sectional view of SEM shows that the holes were non-intercepting and parallel cylinders. The thickness of the template is about 300 nm.

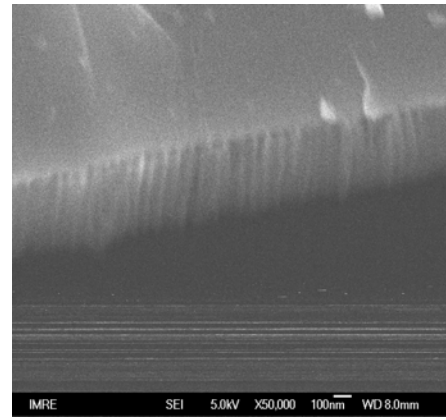
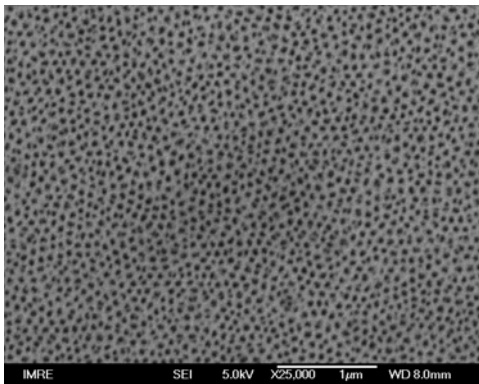


Fig 3 (a) Top view of a FE-SEM image of AAO template (b) a cross-sectional view FE-SEM image of AAO template

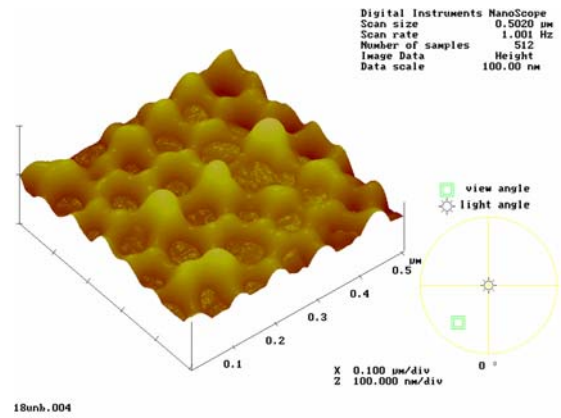


Fig 4 The 3D AFM image of AAO template

B. Samples Growth Using MOCVD

Table 1 presents the information of samples used in this study.

Samples	Growth Temperature	TMGa (sccm)	TMIn (sccm)	Growth Time (mins)
1# GaN/Si	960 \square	30	0	25
3# InGaN/A IN	760 \square	5	420	3

Fig 5 shows the SEM images of sample 1. We can see the AAO template can remain stable at the relatively high growth temperature (960 \square). The image reveals that some GaN nanowires have grown out of the uniform holes of the AAO. GaN maybe nucleate at the top of the surface and cover the surface. This may be due to the fast deposition rate during the growth. The surface of the holes becomes blocked before the chemical vapor can traverse the length of the holes.

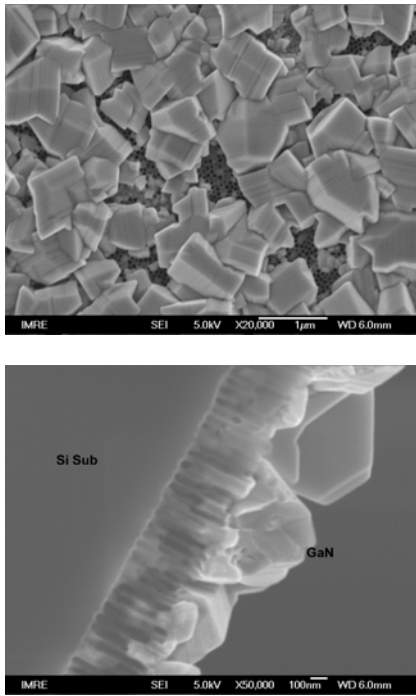


Fig 5 (a) Top view of a FE-SEM image of Sample 1 (b) a cross-sectional view FE-SEM image of Sample 1

Photoluminescence has been observed from the sample 1 using the He-Cd laser with 325 nm excitation wavelength at room temperature. The spectra are dominated by two very broad peaks centered at 3.36 eV and 2.25 eV which are common observed in GaN samples^[10]. We also note that there was no significant luminescence above the band gap (3.48eV), as might be expected if we were observing effects due to quantum confinement. Because the as-prepared GaN nanoparticles are too large for quantum confinement. It is also possible that we do not see the effects of quantum confinement. We thus identify the energies of the peaks with the energies reported for GaN thin films.

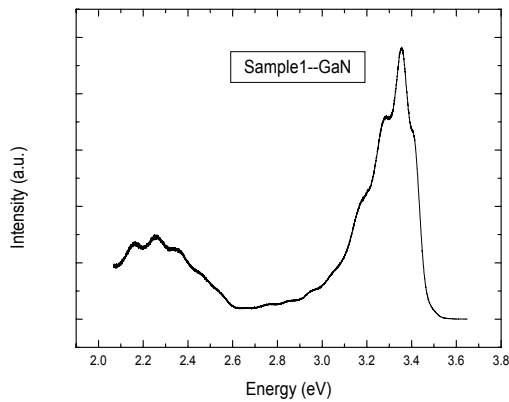


Fig 6 Photoluminescence spectra of GaN grown in the AAO template at room temperature

Fig 7 shows the SEM image of sample 3. The growth time is very short for sample 3 (3 minutes). From the SEM image, no InGaN nucleates and grows at the top surface of the template. However, from the cross-sectional view of SEM, we can not tell clearly that there is InGaN grown in the holes. The 3D AFM image of this sample is shown in Fig 8. Further experiments and characterizations are needed to investigate the details.

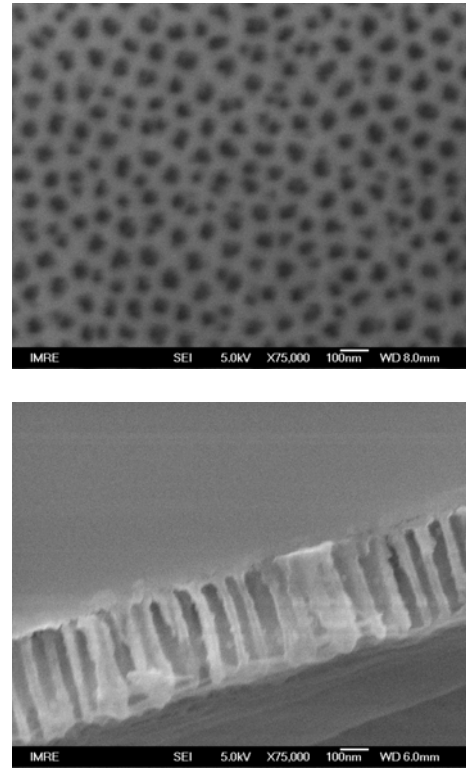


Fig 7 SEM image of the InGaN embedded in nanoholes of AAO (Top view and Cross-sectional view)

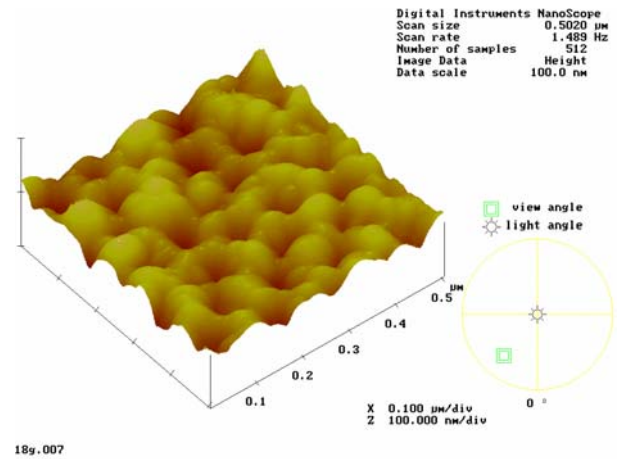


Fig 8 The 3D AFM image of InGaN embedded in nanoholes of AAO

III. CONCLUSION

A highly self-ordered hexagonal array of cylindrical pores has been fabricated by anodizing a thin film of Al on substrate and subsequent growth of GaN and InGaN in these nanoholes has been performed. The AAO template can stand the very high temperature at which GaN is grown. Using AAO as template, the nitride nanowire arrays can be grown which would have possible applications in nano-technological optoelectronic devices. Further experiments and considerations are needed to get the optimal condition for the growth.

REFERENCES

- [1] F.A.Ponce and D.P.Bour, *Nature (London)* 386, 351 (1997)
- [2] S.Nakamura, *Science* 281, 956 (1998)
- [3] H.Morkoc, S.Strite, G.B.Gao, M.E.Lin, *J. Appl. Phys.* 76, 1363 (1994)
- [4] J.C.Zolper, R.J.Shul, A.G.Baca, R.G.Wilson, S.J.Pearnton, *Appl. Phys. Lett.* 69, 794 (1996)
- [5] Martin CR (1996) *Chem Mater* 8: 1739
- [6] R.E.Ricker, A.E.Miller, D.F.Yue, and G.Ganejee, *J. Electron. Mater.* 25, 1585 (1996)
- [7] H.Masuda, M.Ohya, H.Asoh and K.Nishio, *Jpn. J. Appl. Phys.* 40, L1217 (2001)
- [8] M.Sun, G.Zangari, M.Shamsuzzoha and R.M.Metzger. *Appl. Phys. Lett.* 78, 2964 (2001)
- [9] H.Masuda and K.Fukuda, *Science*, 268, 1466 (1995)
- [10] J.A.Wolk, K.M.Yu, and E.D.Bourret-Courchesne, *Appl. Phys. Lett.* 70, 2268 (1997)
- [11] P.Hoyer, N.Baba, and H.Masuda, *Appl. Phys. Lett.* 66, 2700 (1995)
- [12] M.Nakao, S.Oku, T.Tamamura, K.Yasui, and H.Masuda, *Jpn. J. Appl. Phys. Part1* 38, 1052 (1999)