Dense GaN nanocolumn arrays by hybrid top-down–regrow approach using nanosphere lithography

V. Z. Zubialevich[1,*], P. Pampili[1,2], M. McLaren[3], M. Arredondo-Arechavala[3], G. Sabui[4], Z. J. Shen[4] and P. J. Parbrook[1,2]
[1]Tyndall National Institute, University College Cork, T12 R5CP Cork, Ireland, *email: vitaly.zubialevich@tyndall.ie
[2] School of Engineering, University College Cork, Cork, Ireland
[3]School of Mathematics and Physics, Queen's University Belfast, BT7 1NN Belfast, Northern Ireland, UK
[4]Electrical and Computer Engineering Department, Illinois Institute of Technology, IL-60616 Chicago, USA

***Abstract*—** A comprehensive description of a procedure to form dense locally ordered 2D arrays of vertically aligned hexagonal in section GaN nanocolumns (NCs) without height deviations will be presented. Particular focus will be given for the preparation of silica nanosphere hard masks, dry etching to form GaN NCs, wet etching to modify NC shape, thermal annealing and regrowth to recover non-polar *m*-plane facets, improve NC crystal quality and array fill factor.

I. Introduction

In many applications materials structured in 3D on a nanoscale are more advanced in comparison to their 2D (flat) analogues due to a much higher surface/volume ratio and the exposure of different facets, other than the basal facet of a flat template. Particularly useful examples are arrays of nanocoulumns (NCs). In the case of GaN such arrays have been previously successfully formed by different variations of a so-called "bottom-up" approach both by molecular beam epitaxy and metal-organic chemical vapour deposition (MOCVD) [1, 2]. While the bottom-up approach has its advantages, it is rather complex (particularly, as in the case of MOCVD it requires pulsed epitaxy for best results) and less compatible with mass production. At the same time very similar results can be achieved by "top-down" processing. In this study we combined all previously implemented elements of the top-down approach (silica nanosphere (SNS) lithography followed by inductively coupled plasma (ICP) dry etch [3-5], wet etch in a KOH solution [6-8], annealing [9] and regrow [5, 10]) to develop a hybrid top-down–regrow procedure of formation of locally ordered high filling factor arrays of GaN NCs with variable aspect ratio and diameters and with minimal height variation.

II. MOCVD of initial GaN layers

Initial GaN/sapphire templates were prepared by MOCVD in a showerhead-type 3x2" AIXTRON reactor using trimethylgallium and ammonia as Ga and N precursors, disilane (50 ppm in helium) as a silicon dopant source and hydrogen as the carrier gas. GaN growth was on AlN/sapphire wafers (Kyma Technologies) at 1060°C (surface temperature measured by LayTec pyrometer), 150 mbar and V/III ratio of 1000. The first 200 nm-thick layer was undoped (no disilane was supplied), next ~2 µm of material were doped at ~5×10^{18} cm^{-3} and the final ~3 µm layer was deposited with 50 times reduced disilane flow to create a typical *n*+/*n*- Schottky diode structure.

III. SNS lithography

SNSs were first floated on the water surface, using a small volume fraction of heptane in a 1 : 2-3 ethanol : chloroform mixture to promote surface hydrophobicity of SNSs suspended in it. Spheres of up to at least 1 µm in diameter can be floated by slow dispensing of the suspension onto the water surface. The resulting self-assembled colloidal SNS monolayers were then transferred to the target semiconductor wafers by scooping [11] or conventional Langmiur-Blodgett method (Fig. 1, *a*). To form arrays of spaced out SNS a fluorine-based ICP dry etch is typically used [9]. This however results in a much more significant reduction of the vertical dimension of SNSs in comparison to their lateral shrinkage so that they take the form of "nanolenses" or "nanolentils" due to the directional nature of the dry etch. Here we apply a novel method of an isotropic HF-based wet etch of SNSs to prevent this issue and have a conformal size reduction instead (Fig. 1, *b*). This method also reduces occurrences of the monolayer defects in the form of second layer SNSs (above the desired monolayer).

IV. Forming of GaN NCs

To form initial GaN NCs, a chlorine-based dry etch is used over the SNS hard mask. As a result, tapered NCs with damage due to exposure to ion bombardment during the ICP etch can only be achieved (Fig. 1, *c*). It is therefore desirable to apply an additional wet etch to improve NC shape [8] by removing the damaged material. Here we investigate the effect of the wet etch from the point of view of NCs shape thus assuming that all defects introduced by the ICP etch are removed at early stage of the wet etch. For the purpose of the wet etch we used 10% (by weight) KOH solution in DI water and the commercial KOH-based developer AZ® 400K (referred as AZ). Better results from NC shape point of view have been achieved using AZ and the particular results as well as the wet etch mechanism will be reported in the presentation.

V. Annealing

Although the above described wet etch procedure does produce well shaped GaN NCs with nearly perfectly vertical sidewalls (Fig. 1, *d*), they are of no particular crystallographic orientation (nearly circular in section), which may be a disadvantage for some applications. Previously we showed that nearly perfect *m*-plane facets can be recovered from initially circular in section GaN NCs by applying high temperature annealing in N_2+NH_3 atmosphere [9]. Here we investigated the

effect of annealing at different temperatures in more detail and compared the corresponding results for uncapped and still capped (with SiO_2) GaN NCs (Fig. 1, *e*). The material redistribution mechanism responsible for the observed behaviour is considered and will be reported.

VI. Re-growth

Based on the annealing experiments as described above, a fine-tuned re-growth procedure has been developed allowing without additional masks a good selectivity of GaN epitaxy. As a result of higher probability (at the chosen optimised conditions) of Ga adatom adsorption to the non-polar *m*-planes of GaN, NCs can be grown laterally while almost no growth in between NCs happens (Fig. 1, *f*). This allows for further improvement of our dense NC arrays fill factors. Additionally, this leads to a decrease in the effective dislocation density in the NCs as no new dislocations (in addition to those remained in them after the dry and wet etches applied) are introduced when the NCs expand laterally during the re-growth. Moreover, in the case of the capped NCs, no vertical growth on top *c*-plane facets occurs. This provides the same level of top parts of NCs throughout the arrays, which is beneficial for any future processing steps that might be necessary for particular device fabrication.

VII. Conclusions

A brief description of hybrid top-down–regrow procedure of nonofabrication of uniform GaN nanocolumn arrays with high fill factors is given. Different stages of our approach can be summarised in Fig. 1 below.

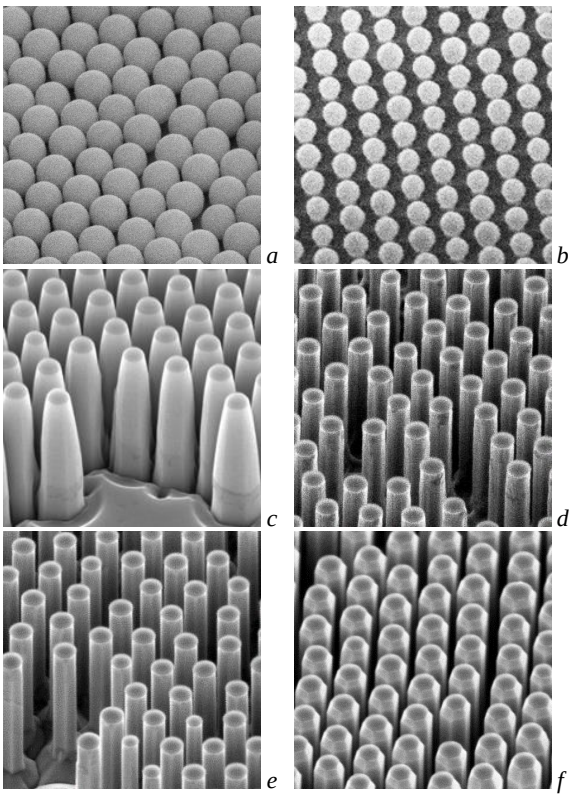

Fig. 1. Nanofabrication steps: *a* – SNS (here 760 nm) array formation, *b* – HF-based wet etch of SNSs, *c* – dry ICP etch through the array, *d* – AZ-based wet etch, *e* – annealing, *f* – regrowth.

The high density and uniformity of such arrays makes them ideal templates for various device applications in opto- and power electronics and photonics. The presented technique can easily be applied to various other material systems after the particular procedures of dry and wet etches as well as epitaxial regrowth are modified accordingly to match corresponding requirements and properties of the new material systems.

Acknowledgment

This study was carried out with financial support from Science Foundation Ireland (Grant no. SFI"13/US/I2860), Northern Ireland Department of Employment and Learning (Grant no. USI 058) and U.S. National Science Foundation (Grant no. EECS-1407540). One author (PJP) acknowledges funding from SFI Engineering Professorship scheme (SFI/07/EN/ E001A).

References

[1] T. Kouno, K. Kishino, K. Yamano, and A. Kikuchi, "Two-dimensional light confinement in periodic InGaN/GaN nanocolumn arrays and optically pumped blue stimulated emission," *Optics Express*, vol. 17, pp. 20440-20447, 2009/10/26 2009.

[2] L. Yen-Ting, Y. Ting-Wei, and P. D. Dapkus, "Mechanism of selective area growth of GaN nanorods by pulsed mode metalorganic chemical vapor deposition," *Nanotechnology*, vol. 23, p. 465601, 2012.

[3] C.-Y. Wang, L.-Y. Chen, C.-P. Chen, Y.-W. Cheng, M.-Y. Ke, M.-Y. Hsieh, *et al.*, "GaN nanorod light emitting diode arrays with a nearly constant electroluminescent peak wavelength," *Optics Express*, vol. 16, pp. 10549-10556, 2008/07/07 2008.

[4] M. A. Tsai, P. Yu, C. L. Chao, C. H. Chiu, H. C. Kuo, S. H. Lin, *et al.*, "Efficiency Enhancement and Beam Shaping of GaN–InGaN Vertical-Injection Light-Emitting Diodes via High-Aspect-Ratio Nanorod Arrays," *IEEE Photonics Technology Letters*, vol. 21, pp. 257-259, 2009.

[5] E. D. L. Boulbar, I. Gîrgel, C. J. Lewins, P. R. Edwards, R. W. Martin, A. Šatka, *et al.*, "Facet recovery and light emission from GaN/InGaN/GaN core-shell structures grown by metal organic vapour phase epitaxy on etched GaN nanorod arrays," *Journal of Applied Physics*, vol. 114, p. 094302, 2013.

[6] I. Morimichi, K. Toru, K. Choshiro, T. Misaichi, K. Koji, and A. Yoshinobu, "Straight and Smooth Etching of GaN (1100) Plane by Combination of Reactive Ion Etching and KOH Wet Etching Techniques," *Japanese Journal of Applied Physics*, vol. 45, p. 3988, 2006.

[7] Q. Li, K. R. Westlake, M. H. Crawford, S. R. Lee, D. D. Koleske, J. J. Figiel, *et al.*, "Optical performance of top-down fabricated InGaN/GaN nanorod light emitting diode arrays," *Optics Express*, vol. 19, pp. 25528-25534, 2011/12/05 2011.

[8] Q. Li, J. B. Wright, W. W. Chow, T. S. Luk, I. Brener, L. F. Lester, *et al.*, "Single-mode GaN nanowire lasers," *Optics Express*, vol. 20, pp. 17873-17879, 2012/07/30 2012.

[9] M. Conroy, H. N. Li, V. Z. Zubialevich, G. Kusch, M. Schmidt, T. Collins, *et al.*, "Self-Healing Thermal Annealing: Surface Morphological Restructuring Control of GaN Nanorods," *Crystal Growth & Design*, vol. 16, pp. 6769-6775, Dec 2016.

[10] N. A. Fichtenbaum, C. J. Neufeld, C. Schaake, Y. Wu, M. H. Wong, M. Grundmann, *et al.*, "MOCVD regrowth of InGaN on N-polar and Ga-polar pillar and stripe nanostructures," *physica status solidi (b)*, vol. 244, pp. 1802-1805, 2007.

[11] M. Conroy, V. Z. Zubialevich, H. Li, N. Petkov, J. D. Holmes, and P. J. Parbrook, "Epitaxial lateral overgrowth of AlN on self-assembled patterned nanorods," *Journal of Materials Chemistry C*, vol. 3, pp. 431-437, 2016.