Electrochemical and Solid-State Letters, **14** (9) K51-K54 (2011)
1099-0062/2011/14(9)/K51/4/$28.00 © The Electrochemical Society

Nanoperforated and Continuous Ultra-Thin GaN Membranes

I. M. Tiginyanu,[a,b,*,z] V. Popa,[b] and M. A. Stevens-Kalceff[c]

[a]*Laboratory of Nanotechnology, Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, Chisinau 2028, Moldova*
[b]*National Center for Materials Study and Testing, Technical University of Moldova, Chisinau 2004, Moldova*
[c]*School of Physics, University of New South Wales, Sydney NSW 2052, Australia*

We report on fabrication of ultra-thin GaN membranes of nanometer scale thickness, by using the concept of surface charge lithography based on low-energy ion treatment of the sample surface with subsequent photoelectrochemical etching. Both nanoperforated and continuous membranes have been fabricated depending on the energy and dose of the ions. These membranes are transparent to UV radiation, emit mainly yellow cathodoluminescence and exhibit electrical conductivity. Successful fabrication of nanometer-thin membranes opens unique possibilities for exploration of two dimensional GaN-based structures predicted to be ferromagnetic with half-metallic or metallic configuration which is of peculiar importance for spintronics applications.
© 2011 The Electrochemical Society. [DOI: 10.1149/1.3603846] All rights reserved.

Manuscript submitted May 16, 2011; revised manuscript received June 3, 2011. Published June 21, 2011. This was Paper 1463 presented at the Montreal, QC, Canada, Meeting of the Society, May 1–6, 2011.

GaN is a wide band gap compound semiconductor ($E_g = 3.4$ eV at 300 K) exhibiting pronounced chemical and thermal stability with applications in high temperature and high power electronics, optoelectronics for light emitting diodes and lasers, etc. It is currently one of the most intensively studied semiconductor materials. Over the last decade many international research groups have been focused on developing and optimizing material nanostructuring. GaN nanorods,[1,2] nanowires,[3–5] nanotubes,[6] nanopyramids[7] etc, have been fabricated by various methods including molecular beam epitaxy, metalorganic chemical vapor deposition (MOCVD), hydride vapor phase epitaxy, photoelectrochemical etching (PEC) techniques etc. A few years ago[8] we demonstrated the possibility for controlled fabrication of GaN nanowalls and nanowires by using the so called surface charge lithography (SCL) proposed earlier.[9] SCL is a maskless approach based on direct writing on the surface of semiconductor by a focused ion beam of negative charge which shields the material against PEC etching. As shown recently,[10] the combination of low-energy ion beam treatment and photoelectrochemical etching of samples is feasible for the fabrication of GaN membranes. In this work, we demonstrate the fabrication of both nanoperforated and continuous GaN membranes with nanometer-scale thickness using the concept of the SCL.

The unintentionally doped wurtzite *n*-GaN layers used in our experiments were grown by low-pressure MOCVD on (0001) *c*-plane sapphire substrates. A buffer layer of about 25 nm-thick GaN was first grown at 510°C. Subsequently a 3 μm-thick *n*-GaN layer was grown at 1100°C. The concentration of free electrons was of the order of 10^{17} cm^{-3}, while the density of threading dislocations was in the range of 10^9–10^{10} cm^{-2}. Selected areas of the GaN epilayers were subjected to treatment by Ar^+ ions with energies of 0.4 or 1 keV, the fluence being equal to 10^{11} cm^{-2} for 0.4-keV ions, and to 10^{12} cm^{-2} for 1-keV ions. According to the concept of SCL,[8,9] the treatment of the sample surface by low-energy ions creates deep acceptors which trap electrons. The trapped electrons form a shield of negative charge that protects the material against PEC dissolution. Note that Monte Carlo SRIM-2008 simulations[11] predict the main projected range of the 0.4-keV Ar^+ ions in the GaN matrix to be 1.1 nm with a longitudinal straggling of 0.8 nm, while for 1-keV Ar^+ ions the projected range is 1.7 nm with a longitudinal straggling of 1.2 nm. Closed circuit PEC etching was carried out in a stirred 0.1 mol aqueous solution of KOH for 5 to 10 min under in-situ ultraviolet (UV) illumination provided by focusing the radiation of a 350 W Hg lamp to a spot of about 5 mm in diameter on the sample surface. In the particular case of pre-treatment by 1-keV Ar^+ ions, the duration of the etching process was up to 50 min. No bias was applied to the sample during etching. The morphology of samples was studied using a VEGA TESCAN TS 5130MM Scanning Electron Microscope (SEM) and a NANOSTATION Atomic Force Microscope (AFM). A JEOL 7001F Field Emission SEM equipped with a Gatan XiCLone cathodoluminescence (CL) microanalysis system was used for comparative morphological and CL characterization. The monochromatic CL images were collected using a Peltier cooled *Hamamatsu R943-02* High Sensitivity Photomultiplier Tube. The CL spectra have been excited with a 10 keV, 3.5 nA electron beam from ~350-nm diameter areas of typical regions of the specimen. The spectra have been collected with a Pixis 100 CCD camera with 300 l/mm grating blazed at 500 nm, and corrected for instrument response.

Figure 1a shows the morphology of a GaN sample subjected to PEC etching under weak stirring of the electrolyte. Note that, prior to the PEC etching, the left part of the sample shown in the image was pre-treated by 0.4-eV Ar^+ ions. According to the concept of SCL,[9] this led to the formation of deep acceptors trapping electrons with the excess negative charge then shielding the material against PEC dissolution. A nanometer-thick membrane was formed in the Ar-ion treated areas, while the material underneath the membrane was etched with the exception of whiskers representing threading dislocations. The extra-thin membrane has been found to be transparent to both keV-energy electrons and UV radiation, with good transparency to UV radiation providing conditions for PEC etching to occur underneath the membrane. As a result after etching the architecture of GaN consists of top ion-treated area in the form of nm-thin membrane and threading dislocations that survive due to their negative charge (see the left part of Fig. 1a). Exploring the morphology of many samples subjected to PEC etching allowed us to observe perforation of the suspended membranes by tiny holes (see e.g., Fig. 1b) which seem to be responsible for the membrane permeability to electrolyte species during etching.

We found that the topography of the membrane depends upon the electrolyte stirring intensity during PEC etching. Under relatively intense stirring conditions we evidenced the formation of undulating membranes resembling waves (see left part of Figs. 1c and 1d). In this case the membranes exhibit ruptures although the percolation of the material is often preserved. Note that even under relatively intense stirring it is possible to identify small areas where the membranes are continuous. This was demonstrated by atomic force microscopy (see the AFM topography image presented in Fig. 2). The analysis of many images typified by those in Figs. 1c, 1d and 2 shows that the "wave" crests are determined by networks of dislocations which in many cases exhibit well defined rows.

The top membrane is sometimes fragmented into micrometer-sized nanomembranes especially under intense stirring of the electrolyte. This gives rise to an island-like morphology (see Figs. 3a and 3b). In this case the network of dislocation-related whiskers appears clustered and covered by thin transparent films (Fig. 3a).

* Electrochemical Society Active Member.
z E-mail: tiginyanu@asm.md