GaN nanowires on Si (111) substrates via molecular beam epitaxy: growth, electronic and optical properties

A.D. Bolshakov¹, V.V. Fedorov³, G.A. Sapunov¹, A.M. Mozharov¹, L.N. Dvoreckaia¹, K. Shugurov¹, V. Shkoldin¹, I.V. Shtrom³, M.S. Mukhin², G.E. Cirlin¹-³, I.S. Mukhin¹,²

1. St. Petersburg Academic University, Khlopina 8/3, 194021, St. Petersburg, Russia
2. ITMO University, Kronverkskij 49, 197101, St. Petersburg, Russia
3. Ioffe Institute, Politekhnicheskaya 29, 194021, Saint Petersburg, Russia
4. Institute for Analytical Instrumentation RAS, Rizhsky Pr., 26, 190103, St. Petersburg, Russia

bolshakov@live.com

Abstract. In this report, we study influence of the Si (111) substrate surface preparation on the growth, electronic and optical properties of the GaN nanowires (NWs) obtained via plasma-assisted molecular beam epitaxy. The substrate preparation varied from bare Si (111) surface and its deliberately nitridated counterpart to growth on AlN and Ga₂O₃ buffer layers and Ga droplets seeding layers. Statistical data on the morphology of the synthesized arrays was obtained and analyzed. The most homogeneous NW array in terms of length distribution was obtained on AlN buffer layer. It was demonstrated that the NWs surface density drastically depends on the surface preparation method. Electrical properties of the arrays were studied via analysis of volt-ampere characteristics and optical properties were investigated with photoluminescence. The highest conductivity and optical response were obtained with AlN buffer layer.

1. Introduction

Attention to the nitride semiconductor nanostructures is evoked by the possibility of their use in photovoltaic and optoelectronic devices operating in the ultraviolet range [1]. As it was shown in our previous work, one of the promising practical applications of the GaN NWs/Si heterostructure is a solar cell, where NWs array can act as an effective light harvesting and antireflection coating [2]. An ability to control the NW aspect ratio and tapering allows the fabrication of the functional structures with strong light confinement and given distribution of electric field, promising for future laser devices [3], or for use as nanoscale terahertz emitters and detectors [4], [5] based on Gunn effect.

The high cost of GaN substrates promotes researchers to develop the nitride compounds growth techniques on more accessible wafers and find new technological solutions in order to reduce the effect of lattice mismatch [6]. Geometric confinement of the nanostructures can significantly affect physical properties and high surface area to volume ratio leads to the effective strain relaxation compare to...
epitaxial films even on highly mismatched substrates. As an example of the nanostructure advantages in the field of epitaxial growth - it was demonstrated that GaN nanowires (NWs) grown on Si substrate can have nearly defect-free crystal structure [7].

Instead of the most III-Vs the growth of GaN NWs by plasma-assisted molecular beam epitaxy (PAMBE) can be performed without use of a catalyst which role is usually played by golden droplets. This technique eliminates the inclusion of the catalyst material in the NW structure which can negatively affect the device characteristics.

Typically, Si (111) and (100) substrates are used for GaN NWs growth. In both cases, GaN NWs represent high quality wurtzite (hexagonal) crystal structure with the growth direction parallel to the [0 0 0 1] crystallographic direction and perpendicular to the substrate surface [8]. It was demonstrated that growth on the Si (100) leads to a less regular morphology of the NWs array compare to the Si (111), while the optoelectronic properties of the nanostructures are similar according to the photoluminescence spectra analysis [6]. One of the main drawbacks of GaN NWs synthesis on Si substrate in terms of further device application is virtually inevitable formation of the 1-2.5 nm thick amorphous silicon nitride layer at the heterointerface due to a large difference between the bond energies of Si-N (4.5 eV) and Ga-N (2.2 eV) [9].

Despite crystalline structure of the NWs it was demonstrated experimentally that their growth can be obtained on non-crystalline surfaces. To this end in [9] Si (100) substrate was thermally oxidized to form an amorphous ~ 320 nm SiO2 layer prior to deposition of GaN. The resulting NWs had an insufficient diameter dispersion, good crystal structure and a growth direction along the c-axis perpendicular to the substrate surface. Furthermore, 2 nm of silicon nitride was formed on the oxide.

Growth of GaN NWs can also be obtained via deposition of the Ga wetting layer prior to the NWs synthesis [2, 10]. As was demonstrated the presence of Ga puddles with a diameter up to 340 nm lead to the NWs formation at the surface free of Ga and the puddles serve as reservoirs of Ga adatoms [2].

In order to prevent reaction between metallic Ga and Si, a thin AlN buffer layer (few nm) can be used to increase the homogeneity of the nucleation and orientation of the NWs [6, 11]. The growth of GaN NWs on 15 nm thick amorphous AlxO layer on Si (111) substrate was also demonstrated [12].

Despite vast experimental data on synthesis and investigation of the GaN NWs properties discrepancy of the results takes place due to difference in experimental setups used for the nanostructures synthesis. In this report we study mutual influence of the substrate preparation of Si(111) substrate on geometrical, electronic and optical properties of GaN NWs.

2. Experimental

GaN nanostructures were grown by plasma-assisted molecular beam epitaxy (PAMBE). The experimental setup can be found elsewhere [13]. Silicon (111) p-type wafers with a 4° miscut oriented towards <1-1 0>, cleaned with Shiraki method were used as substrates. After thermal annealing (20 min @ 950 °C) atomically clean Si surface was obtained as confirmed by observation of a 7x7 reflection high energy electron diffraction (RHEED) reconstruction pattern and smooth surface morphology on AFM images.

Typical nitrogen molecular beam flux equivalent pressure (BEP) was in the range of 2·10⁻⁷ to 3·10⁻⁷ Torr. The Ga source BEP was kept sufficiently small 1·10⁻⁸ Torr in all of the experiments.

In our experiments after the oxide removal we carried out different substrate surface treatment procedures. In the first growth experiment (sample 1) we deposited GaN immediately after the oxide removal. The second sample was subjected under activated nitrogen plasma and annealed for 20 minutes with a temperature rising from 630°C to 810°C for formation of a thin SiNx amorphous layer which is commonly used to obtain GaN NWs growth. The third substrate was covered with a thin AlN buffer layer. In order to do that the substrate was heated to 650°C and deposition of Al for 1 min was carried out. After 1 minute growth interruption the nitridation of the metal layer was carried out. All of the GaN deposition experiments were carried out at 810°C. Prior to placement into the MBE growth chamber the fourth sample was covered with Ga2O3 layer with atomic-layer deposition (ALD).
The rest of the samples (5th-7th) were covered with Ga droplet seeding layer performed prior to the ignition of the RF-plasma. Ga droplets were formed after Ga deposition on the reconstructed Si (111)-(7x7) substrate surface at 630°C. All of the samples were doped with Si for the last few hours for further investigation of the NWs and heterointerface electrical properties.

Morphology of the synthesized nanoheterostructures was studied with scanning electron microscopy (SEM) (Zeiss SUPRA 25-30-63). The back electrical contact was made via Al thermal vacuum deposition with the following thermal annealing. At the next stage a dielectric layer was deposited on the top surface of the substrate. The latter was then etched with oxygen plasma to unsheathe the NW top parts. Later the samples were covered through metal mask with ITO transparent conducting layer in the shape of 2.5mm disk mesa to provide top contact to the NWs.

To study device application potential of the synthesized nanostructures volt-ampere characteristics (VACs) were measured. The VACs were measured on the thermo-stabilized table at 25°C with the use of Keithley 2400 SourceMeter multimeter.

3. Results

All of the used growth techniques provided good verticality of the synthesized NWs. The best vertical orientation homogeneity is demonstrated with 0.3ML and 0.6ML thick Ga seeding layers. Slight inclination of the grown nanostructures is observed on both clean and nitridated Si (111) substrates and on Ga:Ox buffer layer. Further increase of the inclination is registered with AlN buffer, while for the last sample with a relatively thick Ga seeding layer presence of randomly inclined NWs is observed. The third sample grown with the use of a thin AlN buffer layer is the only one that possess a 3D GaN layer. NWs demonstrate hexagonal cross-section which is an indication of their high crystal quality. All of the synthesized NWs exhibit vertical sidewalls – no sufficient anisotropic lateral extension along the NW length was observed.

The most homogeneous is the array of GaN nanowires synthesized on AlN buffer layer with a mean length distribution of only 5%. At the same time these NWs are the less sparsely distributed with the corresponding surface density of 69 mkm\(^2\). Such a phenomenon demonstrates crucial influence of the substrate preparation on the NWs nucleation and adatoms diffusion leading to the highest NWs elongation rate (40.3 nm\(\text{h}^{-1}\)) in case of AlN buffer layer. All of the mentioned geometrical properties of the latter array together with its good verticality demonstrate its device application potential.

After post-processing of the synthesized arrays explained in details in the experimental section the VACs were measured. Analysis of the transport properties of the synthesized arrays necessitates consideration of different current channels. In the case of n-GaN/p-Si heterostructure there is no sufficient contribution from the hot holes due to high value of the potential barrier for these carriers. At the same time, in this case exists a contribution of electrons and holes recombination at the heterointerface due to presence of the surface states. This current in the first approximation is proportional to concentration of electrons and holes at the interface. Thus properties of the interface affect both quantity of the surface states and material properties in the region close to it, e.g. doping and presence of deep levels in the band gap.

Analysis of the experimental data demonstrates strong influence of the buffer and seeding layers on transport properties of the heterointerface. AlN buffer layer provides the best electrical properties in our experimental series. Aluminum is a p-type dopant for Si having close value of covalent radius with the latter providing good incorporation of this material in Si. That is why in sample 3 Si surface layer has high doping level. At the same time Al induces formation of the deep levels in Si enhancing the recombination current through the diode. According to the VAC analysis recombination current plays the main role in this particular case. The latter fact most probably corresponds to high electron concentration at the heterointerface due to doping effect of Si during initial stages of the NWs growth.

Compare to AlN buffer 2 ML thick Ga seeding layer provides worse conductivity than in the first case due to lower capabilities of Ga compare to Al in terms of Si doping. Thus recombination contribution is lower in case of Ga presence but it still plays the main role. Decrease of Ga layer
equivalent thickness leads to drop of the recombination and total currents. When the seeding layer thickness is only 0.3ML Si-Ga chemical bond adopts sp3 hybridization equivalent to native Si leading to decrease of Ga bulk diffusion into Si with the corresponding drop of the doping level.

In case of G2O3 buffer layer formation of n-GaN/Ga2O3/p-Si heterostructure takes place with a negligible barrier for electrons in the conduction band and high barrier for holes in the valence band. The aim of this layer deposition was to spatially separate free electrons in GaN and holes in Si to decrease the interface recombination. Nevertheless, current through this structure at high bias is lower compare to the other samples due to high resistance of Ga2O3 layer. Improvement of the layer conductivity can be realized via doping during the PECVD deposition.

Analysis of the photoluminescence spectra taken at 10K demonstrates strong influence of the surface preparation on optical properties of the synthesized nanostructures. Spectra shows that no yellow luminescence occurs in our samples, indicating high crystal quality of the synthesized GaN nanostructure arrays. Three PL lines corresponding to free excitons of light XA, heavy XB holes are observed as well as two PL lines corresponding to D0XA and D0XB excitons bound to neutral donors. The highest intensity excitation was obtained again with AlN buffer layer.

Conclusions
In this letter we study effects of the Si (111) substrate preparation on the growth and physical properties of GaN NWs. It is demonstrated that geometry and surface density of the nanostructures can be tailored via the surface preparation. AlN buffer layer is considered to be the most appropriate option in terms of potential semiconductor device application due to several reasons. First is the length homogeneity of the array and its sparse surface density together with a good verticality of the nanostructures. Second is the good electronic properties with the highest achieved conductivity of the heterostructure. The optical response from the discussed heterostructure was the highest among all of the synthesized nanoheterostructures most likely due to highest crystalline quality of the array.

Acknowledgements
This work was carried out with the support of the Russian Federation President grants (MK-6492.2018.2 and MK-3632.2017.2), the Russian Foundation for Basic Research (16-32-60094 mol_a_dk and 18-32-00899 mol_a), the leading universities of the Russian Federation (grant 074-U01), grant of government of the Russian Federation (3.9796.2017/8.9, 16.2593.2017/4.6 and 16.2483.2017/4.6).

References
[1] Nakamura, S. (1998). Science, 281(5379), 956-961.
[2] Ristić, J., Calleja, E., Fernández-Garrido, S., Cerutti, L., Trampert, A., Jahn, U., & Ploog, K. H. (2008). Journal of crystal growth, 310(18), 4035-4045.
[3] Fernández-Garrido, S., Kong, X., Gotschke, T., Calarco, R., Geelhaar, L., Trampert, A., & Brandt, O. (2012). Nano letters, 12(12), 6119-6125.
[4] Reznik, R., Kotlyar, K., Ilkiv, I., Soshnikov, I., Kukushkin, S., Osipov, A., ... & Cirlin, G. (2016, June). In AIP Conference Proceedings (Vol. 1748, No. 1, p. 040003). AIP Publishing.
[5] Calabrese, G. et al. (2016). Applied Physics Letters, 108(20), 202101.
[6] Bertness, K. A. et al. (2011). IEEE Journal of selected topics in quantum electronics, 17(4), 847-858.
[7] Bertness, K. et al. (2011). (No. SPIE Newsroom).
[8] Reznik, R. et al. (2016, June). In AIP Conference Proceedings (Vol. 1748, No. 1, p. 040003). AIP Publishing.
[9] Stoica, T., et al. (2008). Small, 4(6), 751-754.
[10] Guo, W. et al. (2010). Nano letters, 10(9), 3355-3359.
[11] Songmuang, R. et al. Applied Physics Letters, 91(25), 251902.
[12] Sobanska, M. et al. (2016). Nanotechnology, 27(32), 325601.
[13] Bolshakov, A. D. et al. (2018). Beilstein Journal of Nanotechnology, 9(1), 146-154.