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Liquid-target reactive magnetron sputter epitaxy of High quality GaN(000$\bar{1}$) nanorods on Si(111)

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ABSTRACT

Direct current magnetron sputter epitaxy with a liquid Ga sputtering target has been used to grow single-crystal GaN(000$\bar{1}$) nanorods directly on Si(111) substrates at different working pressures ranging from 5 to 20 mTorr of pure N_2. The as-grown GaN nanorods exhibit very good crystal quality from bottom to top without stacking faults, as determined by transmission electron microscopy. The crystal quality is found to increase with increasing working pressure. X-ray diffraction results show that the rods are highly (0001)-oriented. The nanorods exhibit an N-polarity, as determined by convergent beam electron diffraction methods. Sharp and well-resolved 4 K photoluminescence peaks at ~3.474 eV with a FWHM ranging from 1.7 meV to 35 meV are attributed to the intrinsic GaN band edge emission and corroborate the superior structural properties of the material. Texture measurements reveal that the rods have random in-plane orientation when grown on Si(111) with native oxide, while they have an in-plane epitaxial relationship of GaN[11$\bar{2}$0]//Si[1$\bar{1}$0] when grown on substrates without surface oxide.

1. Introduction

GaN is, thanks to its large direct band gap of 3.4 eV at room temperature, one of today's most important semiconductors used, for e.g., blue and ultraviolet light emitting diodes and laser diodes [1–3]. GaN nanostructures, such as nanorods, nanowires [4,5], nanobelts [6], and nanowalls [7] have drawn an interest due to their great prospects in novel nanotechnology applications as well as in fundamental physics. A few nanoelectronic and optoelectronic devices, based on GaN nanorods, have been reported [5,8,9]. Due to the high cost and low availability of native substrates, GaN is commonly grown hetroepitaxially on Al_2O_3, SiC, and Si substrates [10,11]. This, however, generally yields high threading dislocation densities because of the lattice mismatch and difference in thermal expansion coefficients between the materials. A benefit with nanorods is that very high crystal quality material, essentially free from extended crystal defects such as stacking faults and threading dislocations, can be grown even on Si substrates [12], which opens the possibility of integration with Si device technology.

The most common techniques to fabricate GaN nanowires and nanorods are chemical vapor deposition (CVD) and molecular beam epitaxy (MBE), [4,13] while growth of GaN-based nanostructures by direct-current magnetron sputter epitaxy (DC-MSE) has not yet been explored. Successful growth of high quality epitaxial GaN continuous films on sapphire substrates [14], core-shell $In_xAl_{1-x}N$ nanorods [15,16], and $In_xAl_{1-x}N$ nanospirals [17] have recently been demonstrated by DC-MSE. In DC-MSE, growth conditions are as pure as in the case of MBE,

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which means utilizing an ultra-high vacuum (UHV) base pressure and ultra-high purity gases during the growth. The magnetron configuration makes it possible to enhance the ionization of the sputter gas and to extend the process plasma towards the substrate vicinity where the ions can be utilized to stimulate the nucleation and growth. The relatively high amount of reactive nitrogen species that are produced in the N_2-containing plasma is sufficient to act as the sole nitrogen source in DC-MSE, thus eliminating the need of other nitrogen sources such as NH_3 or atomic nitrogen as needed in CVD and MBE. Sputtering from a liquid Ga target gives process advantages, such as high growth rate, elimination of target erosion effects, and a possibility of continuous supply of the source material. As magnetron sputter deposition is an industrially mature technology, DC-MSE can also easily be scaled up for deposition over large areas while maintaining excellent control over impurity incorporation.

Here, we report the growth of very high-quality, single-crystal GaN(0001) nanorods onto Si(111) at 1000 °C by a single-step DC-MSE growth process using a liquid Ga-target and N_2 gas as sources. The as-grown nanorods are characterized by scanning electron microscopy (SEM), cross-sectional high-resolution transmission electron microscopy (HRTEM), electron diffraction methods, X-ray diffraction (XRD), and micro-photoluminescence (μ-PL) spectroscopy.

2. Experimental

GaN nanorods were grown by reactive DC-MSE on (111) oriented Si substrates kept at 1000 °C and floating potential in a UHV chamber with a base pressure of $< 10^{-9}$ Torr. Liquid Ga (99.99999%) contained in a horizontal stainless steel tray of 50 mm diameter, was used as sputtering target. Each growth was carried out for 120 min in a reactive environment of pure N_2 (99.999999%) at pressures ranging from 5 to 20 mTorr, using a constant magnetron power of 10 W. Prior to the growth, the Si(111) substrates were cleaned in ultrasonic baths of trichloroethylene, acetone and 2-propanol for 5 min at each step, and were blown dry with N_2 just prior to inserting them into the chamber via a load-lock system. To investigate the effect of removing the native oxide layer prior to the growth of the nanorods, a control experiment was made, in which the native oxide was etched away by dipping the substrate into 5% HF solution for 60 s, after the normal cleaning process as described above.

To characterize the crystal structure, overview θ–2θ XRD scans were performed with a Philips 1820 Bragg-Brentano diffractometer. A PANalytical Empyrean system equipped with a 4-axis cradle, a capillary X-ray lens as the primary optics, and a parallel plate collimator as the secondary optics was used for pole-figure measurements. Pole-figure measurements were performed for the GaN $(10\bar{1}5)$-plane spacing with the fixed 2θ angle of $\sim 105.3°$, $0° \leq \varphi \leq 360°$ and $0° \leq \psi \leq 85°$ with step sizes of 5°.

Optical properties were characterized by μ-PL at 4 K in a backscattering geometry. A continuous-wave (CW) Coherent Verdi/MBD-266 laser system (λ_{exc}=266 nm) was used as the excitation source. The setup details can be found in Ref. [18]

The microstructure and elemental composition of the as deposited GaN films were investigated by HRTEM and energy-dispersive X-ray spectroscopy (EDX) in scanning transmission electron microscopy (STEM), mapping elemental distributions with nanometer resolution. The measurements were done at the Linköping double-corrected and monochromated FEI Titan^3 60–300 microscope equipped with a Gatan Quantum ERS GIF, high brightness XFEG source, and Super-X EDX detector, operated at 300 kV. In GaN the tetrahedron formed by nitrogen atoms in the unit cell defines the *c*-axis absolute direction of the crystal, i.e. the polarity. Hence, convergent beam electron diffraction (CBED) was employed to directly determine the polarity from intensity variations in certain reflection discs that arise due to dynamical electron scattering in crystals lacking a symmetry center when examined from a zone axis containing reflections not related to a mirror plane of the crystal [19]. The violation of Friedel's law in the non-systematic many-beam case was used to determine the absolute orientation of the crystal by comparing the experimental CBED patterns to computed results employing the multislice-approach method [20]. The cross-sectional TEM samples were prepared by mechanical polishing followed by Ar ion milling at 5 keV. Final polishing was done using low energy ions at 2 keV.

A Zeiss-Leo 1550 field emission SEM was used to study the morphology of the nanostructures. The average lengths and diameters of the nanorods were determined from histograms of size data obtained by measuring in cross-sectional overview SEM micrographs of the samples.

3. Results and discussion

Fig. 1(a)–(h) is SEM images of self-assembled GaN nanorods grown at different working pressures in a 100% N_2 environment onto ultrasonically cleaned Si(111) substrates. Fig. 1(a) and (b) presents the cross-sectional overview and top-view morphology of the rods, respectively, grown at 5 mTorr pressure. The cross-sectional image shows that all the rods have a uniform length of $\sim$550 nm with an average diameter of $\sim$74 nm. The top-view morphology image shows that the rods exhibit highly irregular cross-sections. Fig. 1(c) reveals that by increasing the total pressure to 10 mTorr, the average diameter of the rods shrinks to $\sim$60 nm and the average length increases to $\sim$900 nm. The top-view morphology image in Fig. 1(d) shows that the irregularity of the cross-section of rods has decreased and that the number of well-separated rods has increased. A further increase in the N_2 pressure caused the rods to further shrink in diameter, with the average values of 50 nm and 43 nm for pressures of 15 and 20 mTorr, respectively (Fig. 1(f) and (h)), and the rods became very well separated in both cases. The length of the rods is seen to vary from 45 nm to 1200 nm for 15 mTorr (see Fig. 1(e)). The average nanorod length for the 20 mTorr sample is nearly 1500 nm with an absolute variation in length ranging from 1200 nm to 1800 nm (see Fig. 1(g)). Fig. 1(i) and (j) shows the rods grown on Si(111) substrates dipped in HF, these results are discussed below.