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Microstructure of porous gallium nitride nanowall networks

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Abstract

Porous GaN films consisting of irregular nanowall arrays were heteroepitaxially grown on 6H–SiC(0001) substrates by ion-beam-assisted molecular beam epitaxy at different substrate temperatures. X-ray diffraction, Rutherford backscattering spectrometry, scanning electron microscopy as well as scanning transmission electron microscopy (STEM) were applied to investigate the porous GaN thin films. Special attention was focused on the characterization of the microstructure of the thin films using a Cs-corrected high-resolution STEM. A high crystalline quality of the formed hexagonal GaN nanowalls was demonstrated. Based on the results, a growth mechanism of porous GaN thin films is discussed.

Keywords: GaN; Porous; IBA-MBE; STEM; Cs-corrected

1. Introduction

Gallium nitride (GaN) is an academically interesting and commercially widely applied semiconductor material. Because of its wide bandgap of 3.4 eV and a direct bandgap transition, GaN is suitable for use in optoelectronic devices, e.g. lighting engineering, building high-brightness blue and white LEDs, laser applications (especially for information storage devices), high-mobility field effect transistors and sensor technology [1]. For industrial applications, GaN with hexagonal crystal structure (w-GaN) is usually produced in the form of thin films with different thicknesses and lattice orientations. These thin films are mainly deposited heteroepitaxially on various single crystalline substrate materials for which low lattice mismatch epitaxial relationships exist. Suitable substrate materials include *c*-plane sapphire (16% lattice mismatch), *r*-plane sapphire (16% lattice mismatch) and 6H-silicon carbide (3.5% lattice mismatch). Regarding the lattice mismatch, the 6H–SiC(0001) substrate is best suited for GaN thin film growth [2–4].

In the last years, an increasing number of GaN-based nanosized structures like nanowires or nanorods were prepared and investigated with the particular aim of adapting them for solid state lighting purposes (see e.g. the review in Ref. [5,6]). The expected superior crystalline and optical qualities of such nanosized structures and the reduced volume in comparison to compact thin films allow the design of new high-brightness optoelectronic devices.

In the present paper, the morphology of GaN thin films with a porous microstructure consisting of nanowalls is studied. It should be noted that the porous GaN films here were not obtained by any kind of etching process of pre-deposited GaN films (top-down process), but that the nanowall networks were created by a growth process (bottom-up process). The porous GaN films were grown directly on 6H–SiC(0001) without any buffer layers using ion-beam-assisted molecular-beam epitaxy (IBA-MBE) [7–10]. Surface topography, crystalline structure, microstructure and morphology of the thin films were studied in detail by scanning electron microscopy, X-ray diffraction, Rutherford backscattering spectrometry and Cs-corrected scanning transmission electron microscopy (STEM), respectively. In particular, the local structure of the nanowalls and the GaN–SiC interface was analyzed

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by advanced high-resolution transmission electron microscopy (TEM) techniques.

2. Experimental

The GaN thin films were produced in a self-designed ultra-high vacuum (UHV) system (base pressure 5×10^{-6} Pa) for IBA-MBE, as described in Ref. [10]. The 6H–SiC(0001) substrates were cleaned with isopropanol in an ultrasonic bath and, after drying under a N_2 stream, were directly transferred into the vacuum system in order to protect the substrates against contamination. After transfer into the deposition chamber the substrates were heated to 750 °C. This temperature was kept constant for ~10 min to remove residual water and solvents from the substrate surface. For the growth of GaN layers, the chamber was equipped with a conventional Ga effusion cell and a hollow anode N ion-beam source [7]. This ion-beam source is based on a constricted DC glow discharge that ionizes the N_2 gas flowing through the source, and thereby producing a flux of N^+ and N_2^+ ions directed towards the substrate. The maximum kinetic energy of the ions was 25 eV. Additionally, at the exit of the ion source a divergence-reducing, ring-shaped SmCo permanent magnet was placed that increases the ion beam current towards the sample position. The N_2 gas flow through the ion source was kept constant at 20 sccm, leading to a working pressure in the deposition chamber of 7.5×10^{-2} Pa. The resulting fixed N ion flux onto the sample was 6.3×10^{14} cm^{-2} s^{-1}. The Ga effusion cell was operated at temperatures between 970 °C and 1020 °C, corresponding to Ga fluxes onto the sample from 1.0×10^{14} cm^{-2} s^{-1} to 2.3×10^{14} cm^{-2} s^{-1}. At the beginning of the film deposition, a positive gradient of the Ga flux was established in order to reduce the nucleation of the cubic GaN polytype (z-GaN) and therefore to establish optimal initial conditions for the growth of a hexagonal GaN layer. For this purpose, an effusion cell temperature ramp over a period of 20 min was set in order to reduce the ratio of N ion to Ga atom (I/A ratio) gradually from 6.3 to 2.7. Consequently, the growth rate increased during the Ga flux ramping (for details see Ref. [12]). The substrate temperature was kept constant during the deposition and was in the range of 750–850 °C. Deposition times of up to 7 h were used, resulting in a maximum film thickness of 700 nm.

The surface topography of the films was investigated with a field emission scanning electron microscope (SEM, FEI Quanta 250) equipped with secondary electron (SE), backscatter electron (BSE) and energy dispersive X-ray (EDX) detectors. X-ray diffraction experiments (XRD) were performed on a high-resolution diffractometer (XRD 3003 PTS-HR, Rich. Seifert GmbH) using a collimated and monochromated Cu $K\alpha_1$ beam with a wavelength of 0.15406 nm. This diffractometer with a four-axis goniometer allows for tilt (polar angle χ, 0–88°) and rotation (azimuthal angle φ, 0–360°) of the sample with respect to the X-ray beam to perform texture goniometry measurements. For such measurements, angular step widths of 1° in both χ and φ were chosen. To accumulate information about stoichiometry and defect density, Rutherford backscattering spectrometry (RBS) and ion channeling (RBS/C) experiments were performed at the ion accelerator facility (High Voltage Engineering, Singletron Accelerator) of the University of Leipzig. A 2 MeV the He^+ ion beam was applied to detect the backscattered ions at a detector angle of 170°. The random measurement was performed with the sample normal tilted away from the beam axis by an angle of 7°. During the random measurement the sample was randomly rotated around its normal. For the aligned measurement the beam was aligned along the w-GaN(0001) direction, resulting in a sample tilt angle of less than 0.5° and a fixed sample rotation angle. TEM was performed with a Titan^3 G2 60-300 (FEI). This microscope is equipped with a probe Cs corrector and a high-brightness electron gun (X-FEG), bright-field (BF), dark-field (DF) and high-angle annular dark field (HAADF) STEM detectors as well as a post-column Gatan imaging filter (GIF Quantum 963/P with DualEELS and fast shutter). The TEM was operated at 80 kV and 300 kV acceleration voltages. EDX analysis was performed by using a SuperX detector. Cross-sectional samples for TEM analysis were prepared by the focused ion beam (FIB) technique (Auriga CrossBeam FIB-SEM, Carl Zeiss Microscopy GmbH) so that all investigated samples were oriented in the w-GaN[$2\bar{1}\bar{1}0$] zone axis. The TEM lamellae were cut with a Ga ion beam at an acceleration voltage of 30 kV and beam currents of 16, 4 and 1 nA. After the lift-out procedure, the lamellae were attached to TEM grids by Pt precursor deposition and afterwards thinned to electron transparency with Ga ion beam currents of 120 and 50 pA. To improve the quality of TEM specimens, a focused low-energy argon ion milling using NanoMill system (Model 1040, Fischione Instruments) was applied. Ion energies from 900 eV down to 200 eV were used to achieve final sample thicknesses between 10 and 30 nm as well as to remove Ga ion implanted and amorphized regions caused by the FIB process.

3. Results

Fig. 1a and b shows SEM images of GaN thin films grown on 6H–SiC(0001) substrates at substrate temperatures of 750 °C and 850 °C, respectively. The surface topography of the films presents a rough and porous structure. The pore size varies with changing substrate temperature. The diameter of the pores is 40 ± 10 nm for the sample grown at a substrate temperature of 750 °C (Fig. 1a) and ranges from 100 to 500 nm for the sample deposited at a substrate temperature of 850 °C (Fig. 1b). Fig. 1c gives a FIB cross-section of the sample shown in Fig. 1b. From Fig. 1c it is possible to determine that the pores penetrate the film down to the substrate without branching or crossing. It should be noted that similar