Properties of GaN layers deposited on AlN/sapphire template substrates

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Abstract. Gallium nitride thick layers were deposited on template substrates which consisted of low temperature aluminium nitride (LT-AlN) buffer layer or AlN/Al0.2Ga0.8N double-layer buffer grown on (0001) oriented sapphire substrates. Buffers were deposited by using Metal Organic Vapor Phase Epitaxy (MOVPE) in various temperatures and thick GaN layers by Hydride Vapor Phase Epitaxy (HVPE) at 1050°C in two-step growth procedure. Morphology of samples was evaluated by AFM (Atomic Force Microscopy) and Scanning Electron Microscopy (SEM), crystalline quality by High-resolution X-Ray Diffractometry (HRXRD), optical quality by Photoluminescence (PL) spectra, and residual strain by micro-Raman scattering measurements.

1. Introduction

Group III nitrides are attractive materials because of their potential application in optoelectronic devices, emitters and detectors, operating over a wide range of wavelengths. Gallium nitride additionally exhibits thermal and chemical stability and could be applied as a material for fabrication of high-power and high-temperature electronic elements. However optoelectronic as well as electronic devices lifetime is limited by quality of epitaxial GaN layers. The large mismatch in lattice constants and thermal expansion coefficients between gallium nitride and substrate material causes generation of defects which results in insufficient optical and crystalline quality or surface morphology of fabricated layers. Commonly applied alternative substrate, sapphire, shows a slight thermal (0.01 10⁻⁶/K) and large lattice mismatch (14%) [1] to GaN. To overcome this problem various techniques such as: epitaxial lateral overgrowth (ELOG) or pendeo-epitaxial overgrowth (PEOG) [2, 3] or buffers are
applied e.g. AlN [4, 5] or ZnO [6, 7]. Lattice misfit of aluminium nitride mainly used as a buffer for GaN deposition on Si substrates [8, 9] is significantly lower (~2.4 %) than this for Al2O3. Recently reported results [5, 10, 11] indicate that application of AlN could reduce defects density and improve quality of subsequent GaN layer. Classical manufacturing techniques of bulk GaN require high pressure of nitrogen and high temperatures. Obtained crystals are rather of small sizes what limits their industrial application [12]. Application of the AlN buffer in connection with a fast growth, possible to be achieved in Hydride Vapor Phase Epitaxy (HVPE), could become an alternative technique to produce free-standing GaN substrates. In addition HVPE is a low cost technique in comparison with Metal Organic Vapor Phase Epitaxy (MOVPE) or Molecular Beam Epitaxy (MBE). Nevertheless, fast growth brings a lot of difficulties with cracks formation, sufficient crystalline quality and reproducibility of the growth parameters. Nouet et. al [11] reported that application of AlN layer promoted growth of relaxed HVPE GaN layer with the excellent crystalline quality. However, these layers contained screw dislocations and nanopipes what resulted in large amount of hillocks up to 1 mm in diameter. It is well known that first stages of growth are critical in epitaxial techniques. In this paper we have investigated particularly an influence of temperature of aluminium nitride buffer layer deposition in MOVPE on crystalline and optical properties of subsequent HVPE layers.

2. Experimental details
The GaN layers were grown on (0001) oriented sapphire substrates with buffer layers deposited in atmospheric pressure, single wafer, horizontal flow MOVPE system with low frequency (40 kHz) inductive heating. The source gases were trimethylgallium (TMGa), trimethylaluminium (TMAI) and ammonia (NH3). As a carrier gas H2 was used. Buffers were composed of single layer low temperature AlN (LT-AlN) – samples T28, T29, T30, and double layer LT-AlN/Al0.2Ga0.8N – sample T31. Temperatures of LT-AlN buffers growth were 500, 600, 700°C for samples T28, T29 and T30, respectively. The double-layer buffer was composed of AlN deposited at 600°C and followed by Al0.2Ga0.8N layer (grown at 1000°C). Before deposition substrates were pre-heated at 1120°C in the ambient of H2 for 10 min and nitridated in NH3:H2 atmosphere at graded temperature from 1120°C to the temperature of growth of each buffer. The AlN buffer of sample T31 was heated in MOVPE reactor for 10 min at graded temperature from 600 to 1000°C in NH3:H2 solution.

High temperature gallium nitride (HT-GaN) layers were grown in atmospheric pressure HVPE system. The templates before HT-GaN deposition were heated in NH3:N2 (1:10) solution for 10 min at 1050°C. Then the two-step growth was applied to grow HT-GaN layers, described elsewhere [13]. Durations of the steps were 20 and 180 min, respectively. The temperature of HT-GaN layer growth was 1050°C and their thicknesses of up to 50 μm.

LT-AlN layers morphology was investigated using Atomic Force Microscopy (AFM) technique. To evaluate morphology, crystalline quality and optical quality of HT-GaN layers Scanning Electron Microscopy (SEM) images, High-resolution X-Ray Diffraction (HRXRD) and Photoluminescence (PL) measurements were performed. XRD was made by using MRD-HR Philips Diffractometer with CuKα1 1.540597 Å irradiation source and two optics: Parallel Beam Optics and High Resolution Optics. For HT-GaN layers XRD Θ/2Θ-scans patterns were measured. The PL experiments were performed at room temperature using the 280 nm line of Xenon lamp as a pump beam with full width at half maximum (FWHM) of about 10 nm and the density of excitation power of 1 mW/cm². The PL spectra were not normalized to Xenon lamp spectra. Raman scattering spectra were measured using 632.8 nm line of He-Ne laser at room temperature. The laser beam diameter was of about 1 μm and power density of about 60 kW/cm².

3. Results and discussion
Morphologies of LT-AlN layers revealed by AFM measurement were nearly identical thus Fig. 1 presents only example maps for LT-AlN deposited at 500 (a) and 700°C (b). LT-AlN layers with increasing of temperature of deposition exhibit only a slight decrease of grain sizes.
Figure 1. AFM 3D images of AlN layers deposited in MOVPE technique at: a) 500°C and b) 700°C.

SEM images of HVPE HT-GaN layers revealed polycrystalline nature of samples (not shown) which was partially proved by XRD Θ/2Θ-scans patterns (Fig. 2).

Figure 2. XRD Θ/2Θ-scans patterns of HVPE HT-GaN layers deposited on MOVPE LT-AlN at: a) 500°C (T28), b) 600°C (T29), c) 700°C (T30) and MOVPE LT-AlN/Al0.2Ga0.8N deposited at 600/1000°C (T31).

Only samples T28 and T31 exhibited strong peaks that are attributed to GaN (00.2) at a 2Θ angle of 34.5°. There were no peaks for GaN (00.4) at an angle of 73°. This result suggested that these GaN
films had been grown with highly preferred orientation in the \( \langle 00.1 \rangle \) direction. Other remarkable peaks related to GaN were at \( 2\Theta \) angle of 32.25º (10.0) and 57.8º (11.0) – sample T29, and 70.5º (20.1) – samples T29, and T30. Reflection at \( 2\Theta \) of 36.7º attributed to GaN (01.1) had the smallest intensity for HT-GaN deposited on LT(500ºC)-AlN. The mentioned peak intensity was significantly greater as MOVPE buffer deposition temperature increased. Samples T29 and T31 which both contain LT(600ºC)-AlN layer exhibited peaks at \( 2\Theta \) angle of 70.5º related to GaN (20.1). There was also peak which was attributed to Al\(_2\)O\(_3\) (00.12). Results obtained using \( \Theta/2\Theta \)-scan which revealed large number of reflections confirm low quality of these layers what was suggested by microstructure morphology observed on SEM images.

Optical quality of HT-GaN layers was evaluated from PL spectra measurements at room temperature (Fig. 3). Samples which had the best crystalline quality – T28 and T30 – exhibited sharp peaks with the largest intensities. These samples had the best optical quality concluded from FWHM of peaks originating from band-to-band transition. Simultaneously main peaks were shifted of 0.07, 0.067 and 0.007 eV (reference band-gap energy after Pearnton et al. [14]) what indicates a stress of 2.6, 2.48 and 0.25 GPa for samples T28, T30 and T29, respectively, after [15]. Sample T31 layer seemed to be relaxed. In the case of T29 small value of stress could be related with its thickness. Thicknesses of HT-GaN layers of samples T28, T30 and T31 were comparable. Broadening of the main peak of the sample T28 could be a result of the main peak overlapping with 3.43 eV excitonic luminescence [16]. All samples exhibited typical for GaN large yellow defect emission peaking at 2.2 – 2.25 eV, observed also by [17-20]. PL spectra were not normalized to the pump beam spectra and could be only a material for comparison purposes between investigated samples.

![Figure 3. Photoluminescence spectra of HVPE HT-GaN layers.](image)

Raman scattering spectra were measured for \( z(x,x)z \) and \( x(z,y)x \) geometries (not shown). Shift of E2 mode of \( x(z,y)x \) maps measurements enabled biaxial stress evaluation near the surface and interface. Values were as follows: 1.34 and 1.58 (sample T28), 0.12 and 0.13 (sample T29), 0.38 (sample T30), 0.13 GPa (sample T31); formula after Kisielowski et al. [15]; 0.91 and 1.07 (sample T28), 0.08 and 0.09 (sample T29), 0.26 (sample T30), 0.13 GPa (sample T31); after Kozawa et al. [21]. Stress values obtained for samples T28 and T30 confirmed conclusions from PL spectra measurements; these samples had the largest stress. Stresses near the surface and interface of samples T30 and T31 were comparable. Bulk material Raman shift mode was taken as 568 cm\(^{-1}\) [22]. Assuming biaxial stress condition, Poisson ratio of \( \nu = 0.23 \) and a Young modulus of \( E = 290 \) GPa [15] also the strain within layers was calculated. The strain \( \varepsilon_a \) was: \( 3.82 \times 10^{-3} \) (sample T28), \( 0.32 \times 10^{-3} \) (sample T29), \( 1 \times 10^{-3} \) (sample T30), \( 0.34 \times 10^{-3} \) (sample T31) and strain \( \varepsilon_c \): \( -22.8 \times 10^{-4} \) (sample T28), -
1.9⋅10^{-4} (sample T29), -6⋅10^{-4} (sample T30), -2⋅10^{-4} (sample T31) where $\varepsilon_a$ is a strain which is induced in the basal plane and $\varepsilon_c$ - strain along the c-direction.

4. Conclusions
LT-AlN layers deposited at various temperatures in MOVPE system were used as buffer layers in HT-GaN growth on (0001) oriented sapphire substrates. Main GaN layers with thicknesses up to 50 µm were deposited by using HVPE technique. SEM images revealed polycrystalline structure of HT-GaN layers that was partially confirmed by HRD $\Theta/2\Theta$ patterns measurement. Only samples T28 and T31 exhibited GaN (00.2) reflections. Both layers which contained LT(600°C)-AlN showed (20.1) reflections. Photoluminescence spectra indicated good optical quality of T28 and T30 but also strong layer stress (2.6 and 2.48 GPa for T28 and T30, respectively). Samples T29 and T31 (with LT(600°C)-AlN) were relaxed. The stress occurrence in T28 and T30 was proved by Raman scattering shift of E2 mode. The performed experiments revealed that although hybrid of MOVPE and HVPE technologies is very promising for the fabrication of low cost thick GaN layers some additional steps of optimization are still required.

Acknowledgement
This work has been supported in a part by the grant of the Polish Ministry of Science and Higher Education under the grants no. R0201802, PBZ-MiEN-6/2/2006, NN 515 440633, Wroclaw University of Technology statutory grant and Slovak Grant Agency projects VEGA 1/3108/06, 1/3111/06, and bilateral Poland/Slovakia cooperation project.

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