Investigation of the influence of the initial step of deposition on the properties of gallium nitride layer

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Abstract. Gallium nitride layers were deposited in Hydride Vapor Phase Epitaxy (HVPE) system on nitridated in various intervals sapphire substrates in order to evaluate the influence of time of ammonia surface treatment on the properties of the GaN layer. Applied intervals were 5, 10 and 15 minutes. Series of samples were investigated and results exhibit well recurrence. Morphology, crystalline properties, and optical quality were estimated by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) imaging, High-Resolution X-ray Diffractmetry (HRXRD), and Photoluminescence (PL), transmission (T), and reflectance (R) measurements.

1. Introduction
Gallium nitride is a semiconductor material widely applied for fabrication of electronic and optoelectronic devices, as well as chemical sensors. Despite of the devices commercial availability the problem of good quality layers and substrates fabrication is still topical. Difficulties are caused by mismatch of thermal extension coefficients and lattice constants between GaN and applied alternative substrate. The most critical step of deposition is its initial stage. The nitridation mechanism of sapphire substrates and its influence on the growth and properties were investigated in Helicon wave plasma assisted technique [1]. GaN main layer properties are also dependent on buffer layer preparation. The decomposition of GaN nucleation layer [2] and influence of nitridation and buffer design on polarity were evaluated [3]. GaN properties are influenced also by temperature ramping of buffer layer annealing [4].

Decrease of defects amount and decay of background doping except a suitable design of nitridation and buffer could be also assured by growth of sufficiently thick layer. Application of Hydride Vapor Phase Epitaxy (HVPE) should be a promising technology in this case because it allows epitaxial layer growth with high rates. The thick layers could be also delaminated and used as free-standing substrates.

Most of investigations according to the optimization of the initial step of deposition of GaN were carried out in Metal Organic Vapor Phase Epitaxy [2, 4-7]. Because of the differences between these two technologies optimization of initial growth step conditions for HVPE is unavoidable. The series of
high-temperature gallium nitride (HT-GaN) layers were deposited in HVPE at substrates nitridated for various time. The purpose was the investigation of the influence on the properties of subsequent HT-GaN layer.

2. Experimental details
High-temperature gallium nitride layers were deposited on chemically cleaned (0001) sapphire substrates in HVPE system described elsewhere [8]. Ammonia and liquid gallium were used as a precursors. First, samples were nitridated in the solution of ammonia and nitrogen in the proportions of NH$_3$:N$_2$ (1:10) at 1050°C. Various times of nitridation were applied, for comparison purposes. Samples treated for 5, 10 and 15 minutes were chosen and named as sample #1, #2 and #3, respectively. Then layers were placed in 450°C and the nucleation layer (NL) was deposited. The duration of NL epitaxy was equal for all samples (6 min). HCl diluted in nitrogen (400 sccm/min) and ammonia flows were 8 and 400 sccm/min, respectively. Further coalescence of deposited NLs was performed at 1050°C for 10 min. Afterwards samples were cooled down and Atomic Force Microscopy (AFM) imaging was carried out.

AFM investigation was followed by chemical cleaning and growth of HT-GaN layers. After loading into the HVPE system chamber samples were pre-heated in the solution of NH$_3$:N$_2$ (1:10) at 1050°C for 10 min. Then two step growth was performed; first the epitaxy with slow and further high growth rate. Applied flows of gases and intervals ($t_p$) of each step of deposition process are presented in Table 1. NH$_3$ and carrier gas N$_2$ flows were unchanged during all stages of process, 400 and 4000 sccm/min, respectively.

| step of epitaxy | HCl/N$_2$ flow | $t_p$ (min) |
|-----------------|----------------|------------|
| nitridation     | 0/0            | 5, 10, 15  |
| nucleation      | 8/250          | 6          |
| coalescence     | 0/0            | 10         |
| pre-heating     | 0/0            | 10         |
| slow rate epitaxy | 10/250      | 20         |
| high rate epitaxy | 30/250      | 60         |

The morphology, crystalline quality and optical quality of HT-GaN layers were evaluated by application of Scanning Electron Microscopy (SEM) imaging, High-Resolution X-Ray Diffractometry (HRXRD) and Photoluminescence (PL), transmission (T), and reflectance (R) measurements. HRXRD was made by using MRD-HR Philips Diffractometer with CuK$_{α1}$ 1.540597 Å irradiation source. For HT-GaN layers XRD $θ$/2$θ$-scans patterns were measured. The optical properties measurements were performed at room temperature using the 300 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.

3. Results and discussion
The morphologies of NLs were investigated by AFM (Fig. 1). The smallest in diameter grains but simultaneously the highest were remarkable for the sample #1. NLs of the samples #1 and #2 were not continuous. Extension of surface nitridation time influenced the size of islands. The largest grains were observed for the sample #2. Islands on the sample #3 surface of comparable sizes to that of the sample #2 were overgrown by smaller grains and formed continuous NL. Observation of samples surfaces just after nitridation (not shown) revealed that nitridation time of 5 min was too short to assure uniform surface preparation.
SEM images of HT-GaN layers revealed poor morphology of the sample #3 (Fig. 2) what also indicated on its poor crystalline quality. On the surface of sample #1 terraces were remarkable while on the surface of sample #2 only small artifacts were present.

XRD Θ/2Θ-scans in parallel beam optics mode revealed that the samples #1 and #2 exhibited only strong peaks that were attributed to GaN (00.2) at a 2Θ angle of 34.5° and GaN (00.4) at an angle of 73° what suggested that these films had been grown with preferred orientation in the 〈00.1〉 direction. Other peaks were related to (00.12) and (00.6) Al₂O₃. Only polycrystalline layer pattern (sample #3) contained additional peak from (10.1) GaN, also intensity of (00.4) peak was considerably smaller.

For further estimation of crystalline quality Ω- and Θ/2Θ-scans for (00.2) peak were measured and FWHMs were evaluated. The smallest value of Ω-scan FWHM was observed for the sample #1 (367 arcsec). Samples #2 and #3 had similar FWHMs (~600 arcsec). Θ/2Θ-scans FWHMs for all samples were comparable (~50 arcsec). The smallest one was observed for the sample #3 what is in dissonance with SEM results and XRD Θ/2Θ-scans in the parallel beam optics mode.

Photoluminescence measurements for all HT-GaN layers were conducted at room temperature using 300 nm excitation wavelength of Xenon lamp and presented in Fig. 4. All PL spectra have been normalized at ~2.2 eV to observe a relative changes of the emission at ~3.4 eV comparing to the emission band centered at ~2.2 eV. Emission band at ~3.4 eV has been related to band-to-band recombination in GaN layer. Small exciton dissociation energy in GaN (~25 meV) comparing to
thermal energy at room temperature (~26 meV) suggested that the excitonic nature of this band should not be rather considered. However, its asymmetric shape indicated that this emission could be related also to donor-acceptor pairs (DAP) [9]. Band centered at 2.2 eV was caused by deep defect states, most probably N [10] or/and Ga [11-13] vacancies. This band could be also related to GaN surface defect states [14, 15], especially, since we examined samples with high surface area.

Obtained PL signal was not corrected by the setup characteristic which had a maximum of sensitivity almost exactly at 2.2 eV, what overestimated a high intensity of observed defect related emission, which should be much smaller in absolute scale. Additionally, scattering effects could also influenced this broad emission band since Xenon light was used for PL excitation. Nevertheless, relative comparison between the emission from an investigated samples still gave a valuable information.

Thus, as it could be seen in Fig. 4, for 5 min nitridation time there was no emission related to GaN band-to-band recombination and only deep defect related emission appeared. However, for 10 min nitridation time, a strong emission band at 3.43 eV was observed, the intensity of which decreased when the nitridation time increased further up to 15 min. The highest intensity for the samples #2 corresponded well with the crystalline quality concluded from the intensities relation of GaN (00.2) and (00.4) peaks from the XRD.

![Figure 4. PL spectra of HT-GaN layers.](image)

Additionally, for all samples reflectance and transmission spectra were measured (Fig. 5). As it could be observed transmission spectra were almost the same for all structures and exhibited a sharp edge close to the GaN energy band gap at ~3.42 eV (Fig. 5 (a)). Furthermore, PL spectrum obtained for the sample #2 was plotted in Fig. 5 (a). The PL peak position almost overlapped with the transmission edge. Thus, this suggested a very small Stokes shift, reflecting a small contamination of the shallow defect states in the samples. Fig. 5 (b) shows reflectance spectra which exhibited interference pattern, indicating a good surface quality of the investigated samples. Moreover, an evident feature could be observed similarly like in the case of the transmission edge at ~3.4 eV which overlapped with the emission peak position at 3.43 eV.

To analyse the optical properties in the details, absorption spectra were calculated by using the well known formula

\[
\alpha(E) = -\frac{1}{d} \ln \left( \frac{T(E)}{(1-R(E))^2} \right)
\]

where: \( \alpha \) – absorption, \( E \) – energy of photons, \( d \) – thickness of GaN layer.
For the absorption data *Tauc* [16] model was used to estimate the energy of the band gap for the obtained GaN layers. For this purpose, an absorption data were transformed by using the following expression

\[(\alpha h\omega)^m = A(h\omega - E_G)\] (2)

with \(m = 2\) which is typical for the direct band gap materials, \(h\omega\) – photon energy, \(E_G\) – band gap of GaN. By a linear approximation of the obtained data, the energy band gap was estimated for samples #1, #2 and #3 as 3.41, 3.42, and 3.41 eV, respectively. Taking into account a complicated shape of the analyzed R and T spectra and scattering effects, which were not taken into consideration during the absorption estimation, it could be concluded that the band gap for all investigated samples was the same and equal to about 3.41 eV which corresponded very well with the literature data. This gave the value of \(\sim 20\) meV for the Stokes.

Moreover, in Fig. 5 (c) it could be seen, that the absorption edge shown an exponential behaviour indicating that some number of shallow defect states were present in the samples. This, together with the small Stokes shift, could result in the asymmetric shape of the PL emission shown in Fig. 5 (a). Additionally, in Fig. 5 (c) an absorption band between \(\sim 2\) and \(3\) eV can be observed for all samples. This band was related to absorption via the deep defect states. This result corresponded very well with the broad PL emission band centered at around \(2.2\) eV (\(\sim 560\) nm).

**Figure 5.** Optical measurements of HT-GaN layers, a) transmission spectra together with PL spectrum for sample 2, b) reflectance spectra, c) absorption spectra. Inset: \((\alpha E)^2\) vs. energy together with the linear fits.

**Conclusions**

Sapphire substrates were nitridated in various intervals in order to evaluate the influence of ammonia surface treatment duration on the properties of the gallium nitride layers in HVPE system. Applied intervals were 5, 10 and 15 minutes.

Time of sapphire substrate surface nitridation influenced the size of NL islands. The highest and smallest in diameter grains were remarkable for the sample #1 but nitridation time of 5 min did not assure uniform preparation of the sample surface. NLs of samples #1 and #2 were not continuous. The
largest grains were observed for the sample #2, islands of the sample #3 NL had comparable sizes to that of the sample #2 but were overgrown by smaller grains and formed continuous NL. Nitridation time of 15 min did not provide proper NL structure to obtain good quality of HT-GaN what could be observed in SEM images. Sample #3 exhibited extended surface morphology what indicated its poor crystalline quality. SEM images of HT-GaN revealed terraces and artifacts on surfaces of sample #1 and #2, respectively.

XRD Θ/2Θ-patterns revealed preferred orientation in the (00.1) growth direction of HT-GaN (samples #1 and #2). Θ/2Θ-pattern of polycrystalline sample #3 consisted of additional peak from (10.1) GaN, additionally (00.4) peak was substantially weaker compared to patterns of other samples.

The highest intensity of PL band-to-band transition peak for the sample #2 corresponded well with its good crystalline quality. Calculated band-gap for all investigated samples is the same and equal to about 3.41 eV which accorded very well with reference data.

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