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Influence of the deposition parameters of nucleation layer on the properties of thick gallium nitride layers

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Gallium nitride layers were grown on sapphire (0001) substrates on low temperature (LT)-GaN layer deposited by the HVPE method. HCl flow rates and deposition times of the nucleation layer were varied in the range of 8–10 cm^3/min and 5–9 min (with the step of 2 min), respectively. Morphologies of LT-GaN buffer layers and subsequent high temperature (HT)-GaN layers were examined by scanning electron microscopy. Photoluminescence spectra of HT-GaN layers were recorded which allowed us to evaluate the optical quality of thick HVPE HT-GaN layers.

Key words: *HVPE method; thick GaN layer; HT-GaN; LT-GaN*

1. Introduction

Gallium nitride and other AIII-N compounds are promising semiconductor materials for variety of applications including optoelectronic devices such as light-emitting diodes (LEDs), laser diodes (LDs) [1] and high-power electronic devices such as high electron mobility transistors (HEMTs) [2].

Heteroepitaxial growth of GaN by vapour phase transport has been developed for about 35 years [3]. Nakamura et. al. [4] reported that application of thin buffer layer could significantly improve quality of GaN layers grown by metalorganic vapour phase epitaxy (MOVPE). It is well known that application of low temperature (LT) -GaN or AlN layer could reduce misfit dislocations also in other technologies [5]. Actually, various materials are applied as buffer layers: LT-GaN [5–7], high temperature (HT)-GaN [8], AlN [8, 9, 10,], ZnO [11, 12]. Additionally, many complicated

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techniques were developed allowing one to reduce the density of threading dislocations in heteroepitaxial GaN layers. The most common techniques applied for this purpose are epitaxial lateral overgrowth (ELOG) or pendeo-epitaxial overgrowth (PEOG) techniques [8, 13]. These techniques require dielectric layer deposition and lithography processes what complicates the growth of the layers and generates additional costs. Application of LT-GaN buffer layer allows reduction of the costs and simplifies the growth procedure by eliminating some technological steps. Though, the substrate nitridation and the growth of LT-GaN and subsequent HT-GaN layers could be performed in one-chamber multi-step technological process. It was found that conditions of deposition of buffer layers strongly influence the quality of thick HT-GaN layer. As a result, the reduction of the density of threading dislocations [14] could be obtained depending on the growth conditions of LT-GaN layers. Also the type of applied buffer layer influences the polarity and crystal quality of GaN layer [15, 7] and its morphology [6].

2. Experimental

Thick HT-GaN layers were deposited on sapphire (0001) substrates (10×10 mm^2) by atmospheric pressure hydride vapour phase epitaxy (HVPE) at a hot wall horizontal quartz reactor heated by a three-temperature section resistance furnace [16]. Nitrogen (6N) was the carrier gas and ammonia (NH_3, 7N) – the source gas. Flows of the gases were 4000 cm^3/min and 400 cm^3/min, respectively. GaCl was formed by the reaction of gaseous HCl (6N) and metallic liquid Ga (6N) at 920 °C. HCl was diluted by nitrogen (250 cm^3/min).

Multi-step growth process was adapted to grow thick GaN layers (Fig. 1). Before the growth process, sapphire substrates were degreased in organic solvents and etched in solutions of HF:H_2O (1:10). After cleaning, the sapphire substrates were rinsed in deionized water and dried in N_2 flow.

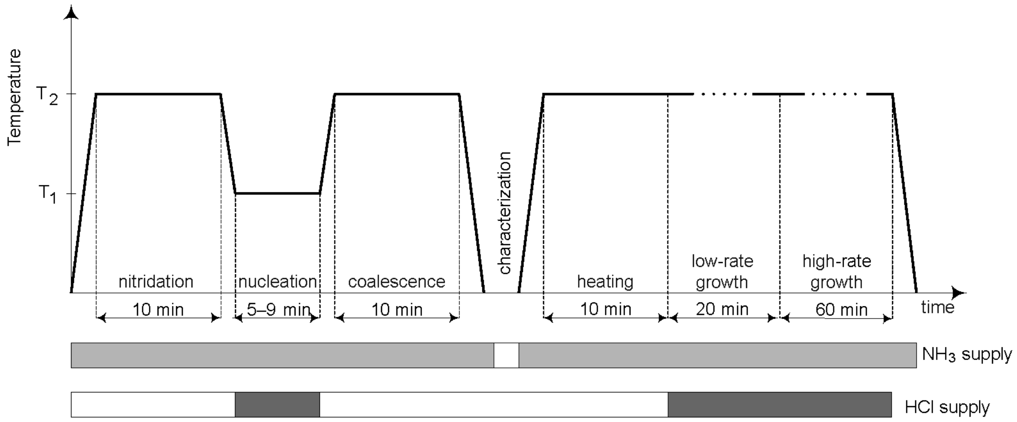

Fig. 1. Scheme of multi-step growth of GaN layers

First, sapphire substrates nitridation was performed in the atmosphere of the mixture of N_2:NH_3 (10:1) gases during 10 min, then nucleation layers were deposited at various HCl flows and times of deposition (t_n). Temperature was kept constant at 450 °C, HCl flows 8 and 10 cm^3/min and time intervals 5, 7 and 9 min were applied (Table 1).

Table 1. Flow rates of HCl and times of LT-GaN deposition

Sample	HCl flow rate [cm^3/min]	Time [min]
G87	8	5
G89	8	7
G91	8	9
G93	10	5
G95	10	7
G96	10	9

After LT-GaN epitaxy, the samples were heated for 10 min at 1050 °C in order to perform the migration of species and recrystallization. Further, the same samples were cooled down and SEM images were taken.

After characterization of LT-GaN layers, the samples were prepared as previously described and loaded to the epitaxial reactor. Heating of template substrates at 1050 °C in the mixture of N_2:NH_3 gases was performed to remove oxygen species and prevent the LT-GaN layer decomposition. Next, the HT-GaN (1050 °C) thick layers were deposited in a two-step growth process, first with a slow growth rate (about 6 μm/h), then with a high growth rate (> 20 μm/h). HCl flows were 10 and 30 cm^3/min per 20 and 60 min, respectively. Ammonia flow was 400 cm^3/min, N_2 carrier gas flow was 4000 cm^3/min and they remained unchanged during all steps of the growth process.

3. Results

Scanning electron microscopy images of LT-GaN layers are shown in Fig. 2. Samples G87, G89 and G91 were prepared with HCl flow rate 8 cm^3/min, other samples with HCl flow rate 10 cm^3/min. Depending on the deposition time of buffer layers and the flow rate of HCl, various densities of nucleation islands were observed. For the sample G87 (Fig. 2a) deposited for 5 min in the HCl flow 5 cm^3/min, the lowest density of nucleation layer was observed. The increase of the time interval of the buffer layer deposition caused the increase of the densities of nucleation sites and enlargement of the islands sizes (Fig. 2c). Apart from large crystallites (white points, about 1 μm in diameter) small crystallites (about 250 nm in diameter; density 80 per 100 μm^2) were also observed on the surface of sample G87. Islands on the surface of the sample G91 had, on average, about 4 μm in diameter. For the samples G93, G95 and G96 (HCl flow = 10 cm^3/min), the increase of the deposition time of the buffer layer had no significant influence. Sizes and densities of crystallites on the surfaces of

G93 and G96 samples were comparable. A comparison of surfaces of the samples G87 and G93 could lead to the conclusion that enhancement of deposition time caused the increase of density and size of nucleation islands what was not observed for other samples.

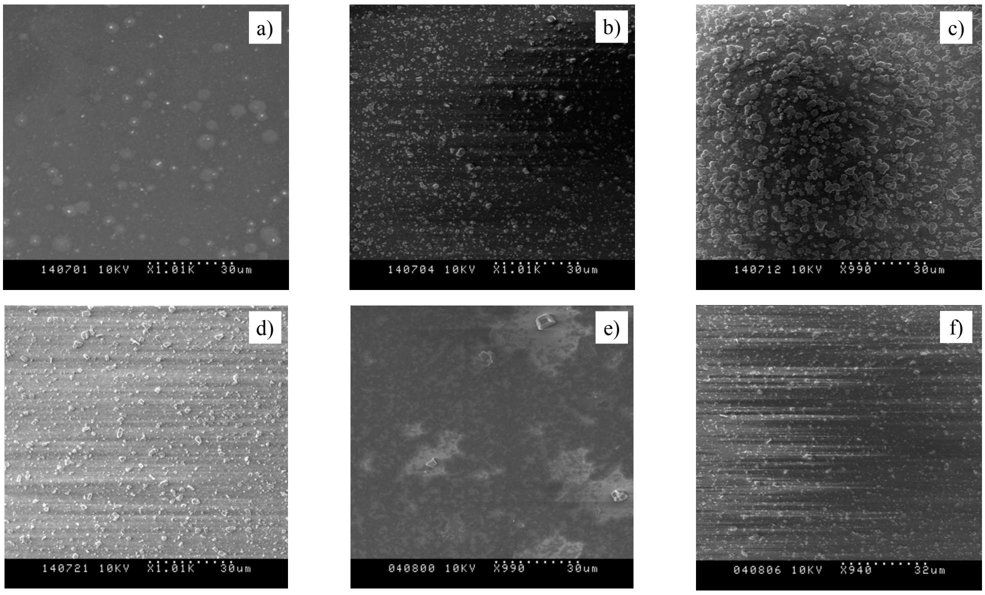

Fig. 2. SEM images of LT-GaN layers : a) G87, b) G89, c) G91, d) G93, e) G95, f) G96

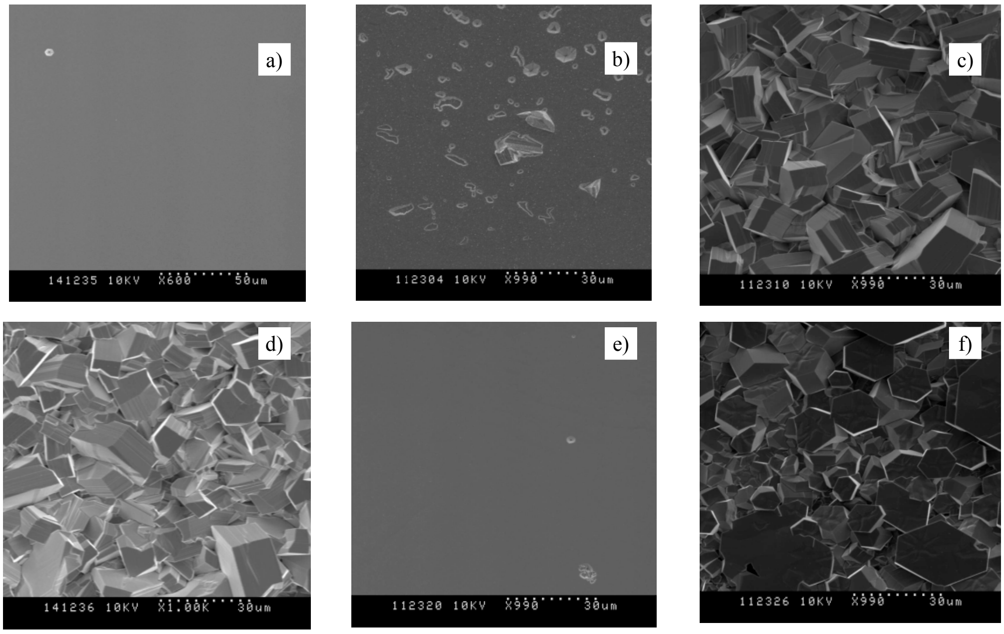

Fig. 3. SEM images of thick GaN layers: a) G87, b) G89, c) G91, d) G93, e) G95, f) G96

Next, thick HT-GaN layers were deposited on Al_2O_3/LT-GaN templates by the HVPE method. Thicknesses of these layers ranged from 10 to 20 μ. Scanning electron microscopy was used to determine the surface morphologies (Fig. 3), photoluminescence spectra were measured to evaluate the optical quality of the layers.

Morphologies of samples deposited on LT-GaN grown with HCl flow 8 cm^3/min were found to deteriorate on increasing the deposition times. The surface of the sample G87 was very smooth, whereas some irregularities could be observed on the surface of G89. On the surface of sample G91, polycrystalline growth was observed. No visible effect of the nucleation time of the layer on HT-GaN surface morphologies of other samples has been observed. The smoothest surface was obtained for the sample G95, the other ones were polycrystalline.

The sample G95 surface morphology could be closely related with growth rate (v_g) (Table 2). Low velocity of growth assured flat surface of the mentioned G95 and G87 samples. Table 2 contains also average thicknesses (t) of grown HT-GaN layers.

Table 2. Thicknesses and growth rates of GaN layers

Sample	t [μm]	v_g [μm/min]
G87	12.4	0.19
G89	21	0.31
G91	19.2	0.29
G93	17.3	0.26
G95	9.6	0.14
G96	14.8	0.22

Photoluminescence experiments were performed at room temperature by using the 330 nm line of a Xenon lamp as a pump beam. Full width at half maximum (FWHM) of the beam was of about 10 nm. The density of excitation power was 10 mW/cm^2. Silicon photodiode was applied as a detector for the emission signal collection. The PL spectra were not normalized to Xenon lamp spectra. Figure 4 shows PL for samples with the strongest emission.

The highest intensity of emission was observed for the sample G87. Two emission peaks were observed at 3.44 eV and 3.362 eV. The former one could be related to the band to band transition. The 3.362 eV peak was associated with an excitonic transition bound to dislocations or cubic inclusions in hexagonal GaN layers [17]. The samples G93 and G96 in spite of their crystalline surfaces have emission peaks near 3.4 eV. The maximum peak for the sample G93 was observed at 3.34 eV, the blue shift could be explained by residual tensile strain [18]. It has been identified as a defect-related donor–acceptor pair (DAP) transition by Trager-Cowan et al. [17]. Broad-band yellow emission was related to the presence of point defects in the GaN layer. A strong signal of the PL spectra observed in the range of 1.8 to 2.8 eV may be due to the lack of normalization of PL spectra to the pump beam spectra and this region will not be extensively analyzed in this paper. The measured FWHMs of PL spectra of samples were as follows: G87 – 0.34 eV, G93 – 0.32 eV, G96 – 0.42 eV. FWHM of the PL spectra of the sample G95 was about 0.21 eV. The samples G89, G91 and G93 exhibit a surprisingly weak emission.

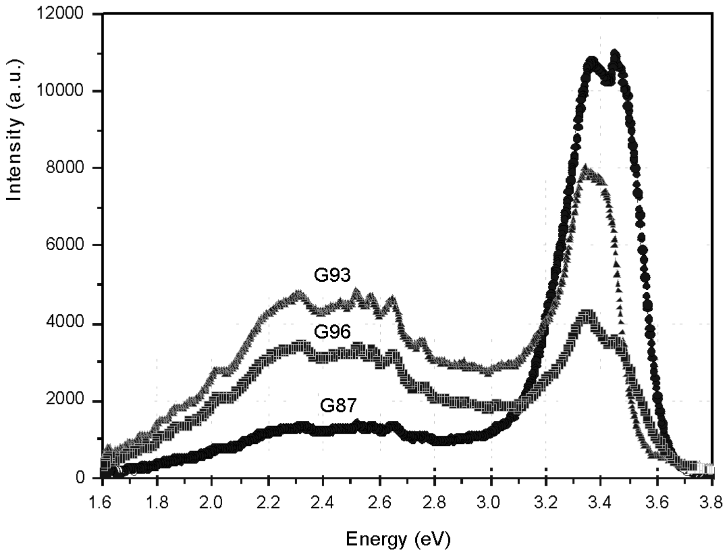

Fig. 4. PL spectra of GaN layers: G87, G93, G96

4. Conclusions

Layers of GaN were deposited by HVPE on Al_2O_3 (0001) substrates. LT-GaN layer grown in various process conditions was applied. The smoothest surface was obtained for the sample with LT-GaN deposited for 5 min in HCl flow rate 8 cm^3/min. Morphologies of samples deposited on LT-GaN obtained with HCl flow 8 cm^3/min were deteriorated on increasing deposition time. Three samples exhibited very strong emission related to near band to band transition. FWHM of main PL peaks of the samples spectra was very small what proved good optical qualities of the layers. A relatively weak yellow emission was also observed. The performed experiments showed that the optimal growth process parameters which allowed us to obtained GaN layers with good morphology were not sufficient to obtained layers with good optical properties. Earlier, we have observed a similar dependence for GaN layers grown by the MOVPE technique.

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