MOCVD growth GaN on sapphire

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Abstract. The n-type and p-type a-GaN films were successfully grown on a r-sapphire substrate, according to X-ray diffractometer and SEM results parameters measurement. The growth rate versus the growth temperature was investigated. The holes concentration (8x10¹⁷ cm⁻³) was achieved by the Cp₂Mg flow optimization and the parameters of thermal annealing in nitrogen. The GaN film growth rate dependence versus temperature at a constant hydrogen flow through a TEG source was investigated. The results indicate that defects density is reduced up to 10⁴ cm⁻², the surface morphology uniformity was improved. During growth the influence from V/III flows ratio was detected.

1. Introduction

InGaN/GaN films growth in nonpolar a-orientation is an important scientific and technological goal. It is known that the polarization effect leads to GaN bulk and surface changes in the band structure. The built-in polarization electric field leads to the LEDs efficiency reduce due to the quantum-dimensional Stark effect [1-7]. In quantum wells, carrier current separation occurs, the degree of wave functions overlapping reduces and the injection efficiency decreases. The built-in polarization field magnitude increases with indium concentration rise in the InGaN/GaN. This leads to a decrease in injection efficiency with a wavelength increase for LEDs and lasers. The proper solution is the semi-polar and non-polar substrates usage, for which the polarization field in the growth direction is minimal or completely absent. The grown films will reduce the effect of the built-in field on the injected charge carriers distribution, will reduce the nonradiative recombination rate and improve the efficiency of the emitting devices.

However, there were some difficulties in achieving the comparable with c-plane results. Mostly, such difficulties are due to high dislocation density [8], to different impurities behavior in c-plane material [9] and another epitaxial growth kinetics [10]. One of the most promising and prospective way to grow high quality nonpolar GaN films is r-sapphire substrate usage [11, 12]. In this work this approach was used to a-GaN films growth. A complex structure investigation by X-ray diffraction, SEM Raman scattering spectra and SIMS allows to enlarge understanding of nonpolar GaN growing process.

2. The experimental procedure

GaN has a hexagonal wurtzite lattice and belongs to the space group C₄ᵥ. The atoms dislocation corresponds to the C₃ᵥ symmetry. GaN films were grown by MOCVD on r-sapphire substrates (11 2 0) under reduced pressure (80 torr) in a horizontal reactor with preliminary surface nitridization. The
sources for III and V components were triethylgallium (TEG) and ammonia (NH₃), respectively. The layered gas flow in the quasi-laminar regime in the reactor was carried out through a porous input. The upper gas mixture flow consisted of N₂ and NH₃ and the lower flow - H₂ and TEG. As sources of donor and acceptor impurities, hydrogen sulphide (H₂S) (0.5% mixture in argon) and biscalicyclohexadienyl magnesium (Cp₂Mg) were used, respectively. Preliminary, the sapphire substrate surface was nitrided at a temperature 950 °C for 10 minutes. For single crystal a-GaN growth MOCVD parameters were optimized. At temperatures above 870 °C, the film became a single crystal due to the fact that in this temperature range the GaN growth rate did not depend on temperature, which was common to ensure the layer thickness reproducibility of the material being grown. At lower temperatures, the kinetic nature of the surface process takes place, and the gallium nitride growth rate is characterized by such temperature dependence. V/III ratio was in range 200 - 1000 for different samples. The sample structure is presented in the Table 1.

| Table 1. InGaN structure. |
|---------------------------|
| 0.3 [μm], Al₀.₁Ga₀.₉N   |
| 0.4 [μm], p-type GaN      |
| 32 [nm], QW               |
| 0.4 [μm], n-type GaN      |
| 0.4 [μm], AlGaN           |
| 1.9 [μm], Al₀.₁Ga₀.₉N     |

3. Results and discussion
In Figure 1 it is shown an image of the a-GaN / r-Al₂O₃ structure based on SEM. As it can be seen in Figure 1a the main defect type are triangle pits, oriented in c-direction. Such defects size is no more than 1 μm, and concentration of such defects is 10⁴ cm⁻². On the cross-section view these defects can be observed as triangle pyramids. The structure of cross section SEM view is familiar with previously achieved results on r-sapphire [13].

![Figure 1. a- grown GaN film surface; b - cross section of the sample.](image)

The film growth rate versus temperature dependence on a constant TEG flow rate is shown in Figure 2.
Figure 2. GaN film growth rate versus temperature at constant flow rate TEG $f = 400 \text{ cm}^3 / \text{min}$: 1) amorphous crystalline phase; 2) crystalline phase.

The diffraction patterns from a two-crystal X-ray diffractometer are presented in Figure 3. It can be seen that the grown film corresponds to a-GaN.

Figure 3. Diffraction pattern of a-GaN film on r-$\text{Al}_2\text{O}_3$ substrate.

X-ray diffraction patterns of gallium nitride films on sapphire are shown in Figure 4.

Figure 4. X-ray spectra of deposited GaN films on the r-sapphire substrate and the sapphire itself.
At temperatures above 870 °C, the film became single crystal, the best morphology was achieved at a temperature - 900-920 °C. From the obtained diffraction patterns, it is seen that single-crystal area films have been grown on the r-substrate. The Raman scattering spectra is presented in Figure 5.

![Figure 5. Raman scattering spectra of deposited GaN films on the r-sapphire substrate and the sapphire itself.](image)

It is seen that the Raman spectrum of the Al₂O₃ – r-sapphire substrate is characterized by peaks - 379, 418, 578, 751 cm⁻¹. For both GaN films types a triple Raman peaks with maxima about 534, 561, 570 and 742 cm⁻¹ are detected.

The carrier concentration dependences versus the film growth parameters are shown in Figure 6.

![Figure 6. Carrier concentration versus the film growth parameters.](image)

It is detected that with doping for n-type the dependence is linear, for p-type the extremum is detected. The obtained spectra for the GaN films under investigation, can be correlated with a gallium nitride film.

The measured half-width of the films rocking curve is 1.5-2 times larger than for films with “polar orientation”. This is due to the different structure defects density in GaN layers with different orientations, namely nanopipes, packing defects, screw, edge and mixed dislocations [14-15]. With film thicknesses rise, the crystal perfection increases, which is due to the decrease edge dislocations influence. Based on the etch pits shape, the dominant dislocations types are mixed dislocations.

The luminescence spectrum at room temperature is shown in Figure 7.
Figure 7. GaN-r film PL on a sapphire substrate.

A clear peak is observed at 370 nm, which corresponds to the GaN band-band transition. In the graph the yellow and green luminescence peaks are clearly seen. These peaks are explained by recombination between the levels created by the defects complexes. The following defects are known, for which the observed luminescence characteristic is: V$_{Ga}$, V$_{Ga-On}$ and Cn Cn-On complexes. It was developed the technology for InGaN growth on the synthesized material. The In concentration measurements by SIMS are shown in Figure 8.

Figure 8. InGaN film elements distribution vs thickness.

4. Conclusions

By the original method, a-GaN was successfully grown on r-sapphire by MOCVD. Using the X-ray and Raman scattering spectrum, it was confirmed that the grown films are a-GaN single-crystal films. The dominant defects type on the film surface were investigated by SEM: the defects similar by nature to V-defects on the c-plane. This defect type has been investigated for non-polar orientation films for the first time. Decrease in the V / III ratio upto 950 at the stage of the precipitated growing low-temperature nuclei leads to the growth islands formation, and it also increases the growth rate in the lateral direction. This leads to a decrease in the dislocations density. a-GaN films on the r-Al$_2$O$_3$ substrate were grown by the
MOCVD with good surface morphology. The acceptor and donor impurities concentrations were $8 \cdot 10^{17} \text{cm}^{-3}$ and $4 \cdot 10^{18} \text{cm}^{-3}$, correspondently.

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