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Growth and Characterization of Thick Si-Doped AlGaN Epilayers on Sapphire Substrates

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$Al_xGa_{1-x}N$ epilayers with $x = (0.07$ to $0.13)$ were grown by MOCVD on AlGaN nucleation layer deposited on sapphire substrates. The epilayers grown under constant TMA and TMG flows demonstrated a nonuniform in-depth Al distribution. This effect can be suppressed by varying the TMA/(TMA + TMG) mole flow ratio during the growth and by using an AlN-coated susceptor. Photoluminescence (PL) studies revealed the so-called "S-shaped" PL maximum energy shift with increase in the temperature of observation. Rapid thermal annealing at 1100 to 1300 °C for 30 to 120 s resulted in a complete suppression of this behavior and the PL maximum energy was shifted towards the higher-energy side of the spectrum by more than 20 meV. The room-temperature electron mobility was increased from 30 to 40 $cm^2\ V^{-1}\ s^{-1}$ for the as-grown samples to 200 $cm^2\ V^{-1}\ s^{-1}$ for the annealed samples without significant change in the electron concentration $(1.0$ to $1.5) \times 10^{18}\ cm^{-3}$.

1. Introduction

In spite of significant progress in MOVPE growth of III–N structures on sapphire, most of the structures were based on thick GaN buffer layers, and the growth of thick AlGaN layers remained much less studied. At the same time, thick AlGaN layers on sapphire, grown without underlying GaN buffer layer, can serve as wide-bandgap windows for AlGaN/GaN optoelectronic devices [1] and/or as buffer layers in strain-compensated AlGaN/GaN heterostructures [2]. Here we report on properties of Si-doped $Al_xGa_{1-x}N$ epilayers grown directly on sapphire substrate. The AlN mole fraction in the epilayers was in the range of 0.07 to 0.13.

2. Growth and Characterization

The structures were grown in a horizontal flow MOVPE growth machine (Epiquip VP-50 RP redesigned for GaN growth) with quartz reactor and inductively heated un-

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coated (for samples #2, 3) or AlN-coated (for samples #1, 4, 5) graphite susceptor. The $Al_xGa_{1-x}N$ samples are numbered as #2 to 5. The sample #1 represents a GaN epilayer. Trimethylgallium (TMG), trimethyaluminum (TMA) and ammonia were used as component precursors, monosilane was used for doping and hydrogen was used as a carrier gas. During the growth process the hydrogen flow through the reactor was equal to 5 standard liters per minute (SLM) and the reactor pressure was 200 mbar.

The growth of the AlGaN layers was initiated with (0001) sapphire substrate nitridation under ammonia flow at 990 °C for 1 min followed by an AlGaN nucleation layer deposition at 530 °C. During the nucleation layer deposition ammonia, TMA, and TMG flows were 1.5 SLM, 1.5 μmol/min and 48 μmol/min, respectively.

After this, the ammonia flow was increased to 2.5 SLM. Then, the nucleation layer was annealed at 1000 °C, and an AlGaN epilayer was grown at 1050 °C. The thickness of the epilayers was 4 to 5 μm. During the epitaxial growth TMG mole flow was either kept at the constant level of 36 μmol/min (samples #1, #2, and #5) or varied in the range of 24 to 36 μmol/min as described below (samples #3 and #4). TMA mole flow was kept at a constant level in the range of 2 to 3.5 μmol/min depending on the desirable Al content in the epilayer.

The structures were characterized by photoluminescence (PL) and optical transmission (OTr) spectroscopy, Hall effect measurements, electron-probe micro analysis (EPMA), secondary ions mass spectrometry (SIMS), X-ray diffraction (XRD), and atomic force microscopy (AFM).

3. Results and Discussion

PL measurements of AlGaN epilayers reveal near-band-edge emission with full width on half maximum (FWHM) of 25 to 30 meV at 77 K. The FWHM of the X-ray rocking curves recorded on the samples is 8 to 9 arcmin for ω-scan indicating good structural quality. According to AFM measurements all the epilayers have atomically smooth surfaces with well-resolved monolayer steps.

As it was previously observed in SIMS, EPMA, and CL studies of AlGaN epilayers [1], the high-temperature epitaxial growth under constant TMA/(TMA + TMG) mole flow ratio results in formation of 0.3 to 0.5 μm thick low-Al-content AlGaN regions adjacent to the substrate.

The sapphire substrate, being transparent for the exciting photons of both He–Cd and N_2 laser, gives a unique possibility to measure PL spectra of the epilayer also from the AlGaN region near the interface with sapphire. These spectra can be compared to those recorded from the surface. PL can be also excited from the surface and detected from the substrate side, which gives a combination of PL and transmission spectra.

The noticeable difference between the near-band-edge PL peak position for the near-surface region and the region adjacent to the substrate (shown as Δ_1 in Fig. 1a) indicates the presence of a low-Al-content layer near the AlGaN–sapphire interface of sample #2. This layer, having a lower bandgap, shifts the optical transparency edge of the whole AlGaN deposit to longer wavelengths. This layer is only semitransparent for the GaN edge emission and can be hardly used as a wide-band-gap window, e.g. for GaN/AlGaN photodetectors, or GaN-based light-emitting devices with light input or output from the substrate side, respectively.

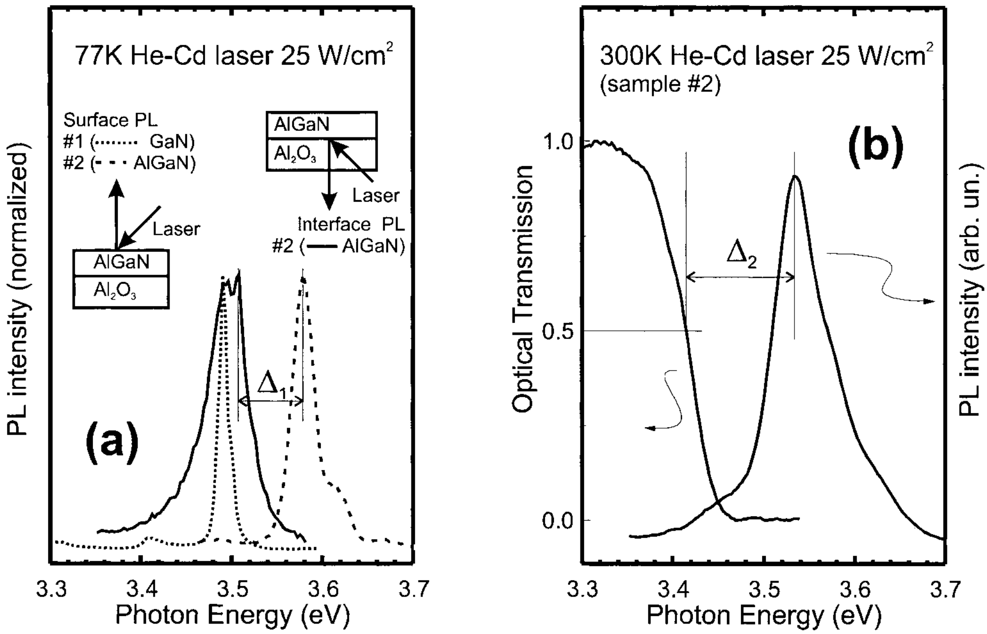

Fig. 1. a) Low temperature PL spectra of the structure grown with constant TMG flow (#2) recorded from near-surface and near-interface regions. b) Room temperature optical transmission and surface PL spectra for the structure grown at constant TMG flow (#2)

The difference between the level of 0.5 transparency and the surface PL peak energy at room temperature (RT) (shown as Δ_2 in Fig. 1b) exceeds 100 meV for this structure, additionally indicating the nonuniformity of the Al distribution along the growth direction.

A simple increase in the TMA/(TMA + TMG) mole flow ratio during the growth of the whole structure leads to an increase in the AlN content in the main part of the epilayer, resulting in a decrease in the electrical conductivity. The obvious way to fabricate uniform AlGaN epilayers with suppressed formation of an Al-depleted interface region is to increase the TMA/(TMA + TMG) mole flow ratio only at the initial stage of the AlGaN deposition. Samples #3 and #4 were grown using exactly this technique. During growth of the first 600 nm of AlGaN, the TMG mole flow was kept at 24 μmol per min and it was increased to 36 μmol/min for the rest of the epilayer.

We also studied the influence of the AlN coating of the graphite susceptor on the Al distribution in the epilayer. The results are summarized in Table 1.

Table 1

sample	$\frac{\text{TMA}}{\text{TMA + TMG}}$	susceptor	77 K PL peak position (eV)	Δ_1 (meV)	Δ_2 (meV)
#1 (GaN)	0	AlN-coated	3.490	>15	>15
#2 ($Al_{0.07}Ga_{0.93}N$)	constant	uncoated	3.628	105	103
#3 ($Al_{0.07}Ga_{0.93}N$)	variable	uncoated	3.637	120	52
#4 ($Al_{0.1}Ga_{0.9}N$)	variable	AlN-coated	3.73	33	37
#5 ($Al_{0.13}Ga_{0.87}N$)	constant	AlN-coated	3.772	57	69

As it can be seen from Table 1, the difference between the PL peak energies for the near-surface region and the $AlGaN/Al_2O_3$ interface (Δ_1) is strongly influenced by the susceptor coating, while the difference between the PL peak position recorded from the surface and the 0.5 transparency level (Δ_2) depends mostly on the TMA/(TMA + TMG) mole flow ratio during the initial stage of the epitaxial growth. The best result (minimal values of Δ_1 and Δ_2) was achieved in the case of simultaneous using of the variable TMA/(TMA + TMG) mole flow ratio and the AlN coating of the susceptor (sample #4). As it was proved by EPMA, in this case the AlN content in the layer adjacent to the substrate is even higher than that of the rest of the structure (see Fig. 2a).

Thus, AlGaN epilayers with relatively low AlN mole fractions grown with this technique are transparent for the GaN edge emission. In Fig. 2b one can see PL spectra of the double heterostructure consisting of 3 μm $Al_{0.1}Ga_{0.9}N$, 0.1 μm GaN and 0.05 μm $Al_{0.1}Ga_{0.9}N$. The structure was excited from the surface side and the PL was detected both from the surface side (dotted) and from the substrate side (solid) propagating in this case through the thick $Al_{0.1}Ga_{0.9}N$ layer and the substrate. Some difference in the intensity and the shape of the GaN-related near-band-edge emission can be explained by the self-absorption effect in GaN.

A temperature-dependent PL study of sample #3 revealed a so-called "S-shaped" emission shift of the PL maximum (see Fig. 3a). This feature indicates the presence of an extended band tail due to the nonuniform Al distribution on a nanoscale level. After rapid thermal annealing (RTA) at 1100 to 1300 °C for 30 to 120 sec this behavior is not observed and the near-band-edge PL peak position is upshifted in energy by more than 20 meV as compared to the non-annealed sample. This indicates an in-

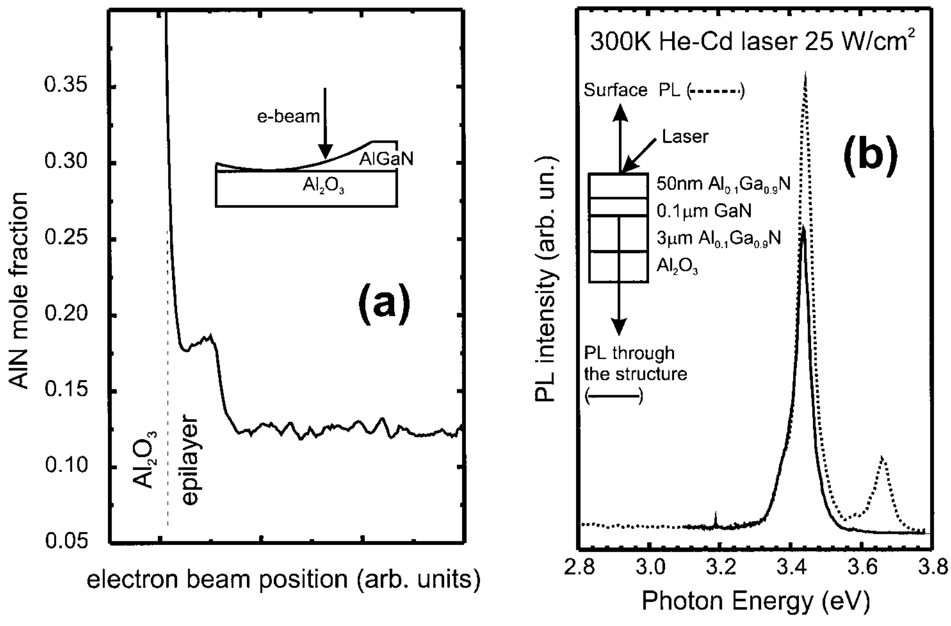

Fig. 2. a) Al distribution for the structure grown with varied TMG flow (#4) and AlN-coated susceptor. b) PL spectra for AlGaN/GaN/AlGaN DHS recorded in two different geometries

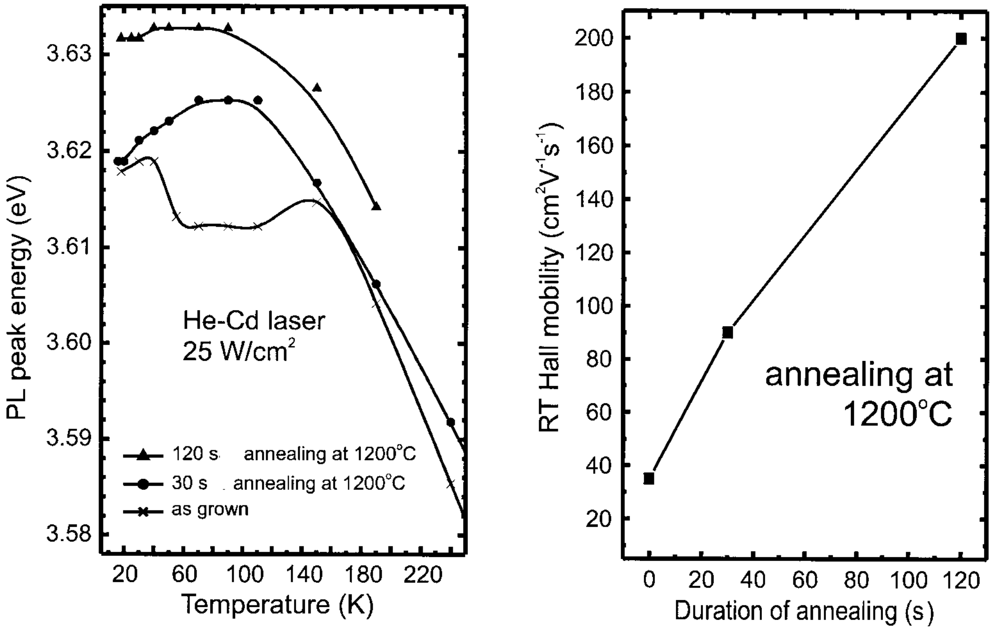

Fig. 3. a) Near-band-edge PL peak energy versus temperature recorded for the as-grown and annealed AlGaN epilayer. b) Dependence of room temperature electron Hall mobility in the AlGaN epilayer on duration of rapid thermal annealing

creased uniformity of the epilayer. The high-energy shift of near-band-edge emission after RTA was also observed in the PL spectra of thin AlGaN epilayers grown on top of GaN epilayers.

RTA also strongly affects the electrical properties of the structure (see Fig. 3b). While the room temperature Hall mobility in the as-grown sample was 30 to 40 $cm^2 V^{-1} s^{-1}$ at $n \sim 1.5 \times 10^{18}$ cm^{-3}, after the RTA the value of the Hall mobility was increased up to 200 $cm^2 V^{-1} s^{-1}$ without significant change in the electron concentration. This value of mobility is comparable to the best published results for GaN epilayers having the same electron concentration; thus, AlGaN:Si layers can be used as contact layers in various optoelectronic devices.

The "S-shaped" temperature dependence of the PL peak energy was also characteristic for sample #4 grown with the AlN-coated susceptor. In contrast, the RT Hall mobility for this sample was at the level of 100 $cm^2 V^{-1} s^{-1}$ for the electron concentration of 1.5×10^{18} cm^{-3} already without any postgrowth annealing.

4. Conclusions

AlGaN:Si epilayers transparent for the GaN edge emission with high electrical conductivity were grown by MOCVD using an AlN-coated susceptor and by varying the TMA/(TMA + TMG) mole flow ratio during the epilayer growth. High crystal perfection of the epilayers allowed us to use them as buffers for strain-compensated AlGaN/GaN distributed Bragg reflectors with high reflectivity [2] served as bottom mirror for photopumped RT operated InGaN/GaN/AlGaN VCSELs [3].

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