Suppression of Stark effect in ultra-thin stress-free GaN/AlN multiple quantum well structures grown by plasma-assisted molecular beam epitaxy

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Abstract. We report on suppression of the Stark effect in (1.5-2)-monolayer (ML)-thick (GaN/AlN)\textsubscript{100} multiple quantum well (MQW) structures grown on AlN/c-Al\textsubscript{2}O\textsubscript{3} templates by plasma-assisted molecular beam epitaxy. Different stress relaxation mechanisms are revealed in these structures by using a multi-beam optical stress sensor in comparison with the 5ML-MQW structure. The former (with well thicknesses $\leq$2MLs) demonstrate the nearly stress-free growth, whereas the latter structure with thicker wells exhibits the slow stress evolution from the high initial compressive stress to the nearly relaxed state with zero stress. Moreover, the former structures demonstrate a bright room-temperature cathodoluminescence (CL) with the single peak at the shortest wavelength 240 nm (1.5ML-QWs), while the latter shows much weaker multi-peak CL spectra in the spectral range of 270-360 nm.

1. Introduction
Semiconductor optoelectronics devices based on Al\textsubscript{1-x}Ga\textsubscript{x}N compounds with high $x$ (>0.4) emitting in a middle ultraviolet (mid-UV) range (214-300nm) are of great interest for numerous applications in water/air purifications, medical diagnostics, security etc. [1-2]. These devices, having a small size, high efficiency, low operating voltage, and long lifetime, should replace the widely used Hg-based UV vacuum lamps. However, the efficiency and the output power of mid-UV LEDs are much lower as compared to InGaN-based LEDs operating in the visible and near-UV (365nm) ranges. There exist several problems leading to a decrease in the efficiency of radiative recombination in AlGaN-based quantum well (QW) structures, including the strong Stark effect in the relatively thick QWs (1.5-2.5nm), the TE/TM polarization switching for the output emission from AlGaN alloy layers with high Al-content ($x$>0.25) [3,4]. In addition, non-uniform distribution of stress in multiple QW (MQW) structures with a large number of wells can lead to widening the output emission bands due to different Stark effect in the wells.

One of possible effective ways to overcome these problems is the development of ultra-thin GaN/Al(Ga)N MQW structures with a typical well thickness of a few monolayers (MLs) (1ML=0.25nm), which are intensively studied by several theoretical and technological groups [5-7]. Using this approach, both UV LEDs and e-beam pumped UV emitters operating in the sub-240nm spectral range have recently been fabricated. In these work, plasma-assisted molecular beam epitaxy (PA MBE) was successfully employed due to its unique ability of controllable growth of ultra-thin QWs with sharp interfaces owing to the fast (<0.5s) switching of growth fluxes from effusion cells and the low substrate temperatures (<730°C), which suppress any segregation and interdiffusion phenomena in the heterostructures.

Despite it is generally known that elastic stress in (Al,Ga)N MQW structures play an important role in their efficiency and luminescence spectra, the stress appearance and development have not been studied enough so far. Only Bellet-Amalric et al.[8], using reflection high-energy electron diffraction (RHEED) and X-ray diffraction (XRD) measurements, revealed the complex behavior of the in plane lattice parameter (stress) during PA MBE of AlN/GaN and GaN/AlN binary heterostructures with large layer thicknesses. However, these results cannot be used to analyze stress evolution and its effect in the ML-
thick GaN/AlN MQW structures. In addition, the most advanced modern analytical method for observing the stress evolution in heterostructures is based on in situ measurements of substrate curvature, from which the average and incremental stresses can be calculated using the Stoney’s equations [7]. Therefore modern PA-MBE and MOVPE setups are equipped with a multi-beam optical stress sensor (MOSS), however the use of this method to study thin GaN/AlN MQWs is still limited.

This paper reports on the different types of the stress evolution in binary AlN/GaN MQW structures with a well thickness varying from 1.5 to 5MLs, grown by PA MBE on AlN/c-Al2O3 templates. The possible influence of surface morphology on stress in these structures is discussed. A strong suppression of the Stark effect in the cathodoluminescence spectra of MQW structures with the thinnest (1.5-2ML) wells is demonstrated.

2. Experiment

GaN/AlN MQW heterostructures, schematically shown in Fig.1, were grown using PA MBE setup Compact21T on c-Al2O3 templates. First, AlN templates were grown at a growth temperature of 780°C using migration enhanced epitaxy (MEE) for initial growth of the 65nm-thick nucleation layer [10] and metal-modulated epitaxy (MME) for the next 1.45 µm-thick buffer layer [11]. Upper AlN BLs with a thickness of 0.3 µm were grown in a standard PA MBE mode at slightly Me-rich conditions with an Al/N flux ratio of about 1.1 and using a post-growth surface exposure under a plasma-activated nitrogen flux. One AlN template was grown without the MQW structure. Three studied GaN/AlN MQW structures were grown by a combination of MEE and standard MBE growth, using controlled Me-rich conditions for both GaN and AlN growth at a temperature of 700°C, as reported in detail in our previous paper [7]. They included 100-period MQWs with the same thickness of the AlN barrier layers of 4.5 nm (18MLs) and differed in the thickness of the GaN wells as 5, 2 and 1.5 ML, which were used to denote the structures.

![Figure 1. Schematic view of the samples design.](image)

A homemade MOSS system based on a 10 mW solid-state laser (λ=532 nm) and a standard CCD-camera, was used to measure in situ the substrate curvature at a frequency of 15 Hz [9]. Thickness and growth rates of the AlN layers was controlled in situ by laser reflectometry (LR) (λ=532 nm). The surface morphology of the AlN layers and MQW structures was monitored using RHEED and studied ex situ by using atomic-force (AFM) and scanning electron (SEM) microscopies. The optical properties of MQW structures were studied by measuring cathodoluminescence (CL) spectra using an electron beam with a spot diameter of 2 µm and an energy(current) of 10 keV(30 nA).

3. Results and discussion

Figure 2 shows various evidences of the smooth surface morphology of the AlN templates, including the streaky RHEED patterns (Fig.2a), observed during almost the entire template growth, beginning from the upper parts of the NLs. The SEM and AFM images (Fig.2b,c) exhibit an atomically smooth and droplet-free surface morphology with a root-mean-square (RMS) roughness of about 0.7 nm over an area 1×1µm². Moreover, the AFM image shows that the template surface consists of grains with an average diameter of about 1 µm, which have an upward terrace-like morphology due to the step-flow spiral growth at the metal-enriched conditions used in MME.
AFM images showing the surface morphologies of the MQW structures are presented in Fig. 3. Although the AFM images exhibit the conservation of the step-flow growth mode for all samples, the diameter of the terrace-like grains in the studied structures is different. If the 5ML-structure has a grain diameter of ~0.8µm, which is only slightly smaller than that of the AlN template, the 2ML- and 1.5ML-structures have more pronounced boundaries of the grains with average sizes of ~0.3 and ~0.2 µm, respectively. One should note that the RMS roughness in all the MQW structures exceeds the initial value in the AlN BL and varies between 1.6 and 2.7 nm. This dependence may be explained preliminarily by a thicker Ga surfactant adlayer during AlN barrier growth in the 5ML-structure, which improves the low-temperature growth of AlN, though it needs additional experimental confirmation.

Figure 2. RHEED patterns during finishing the AlN template growth (a). Plan-view SEM (b) and AFM (c) images of AlN templates.

Figure 3. AFM images of MQW structures surfaces with QW thickness of 5 ML (a), 2 ML (b) and 1.5 ML (c).

Figure 4 shows the different character of stress evolution during growth of the MQW structures. First, the 5ML-structure demonstrates a gradual transition from a maximum compressive stress of -2.3GPa to an almost relaxed growth, when the structure thickness exceeds ~500 nm. It should be noted that the initial stress observed in this MQW structure with an average composition of \( t_{\text{GaN}}/(t_{\text{GaN}}+t_{\text{AlN}})=0.8 \) (where \( t_{\text{GaN(AlN)}} \) are the thicknesses of GaN(AlN) layers in the MQW structure) corresponds to pseudomorphic growth of Al\(_{0.8}\)Ga\(_{0.2}\)N layer on AlN template (the dashed red line in Fig.4a). Such a gradual relaxation of stress is typical for the growth of the (Al,Ga)N layers and heterostructures in low-temperature PA MBE [8]. In contrast, much weaker stresses with small or almost negligible changes in their magnitudes were observed in the 2ML- and 1.5ML-structures, respectively. Similar behavior of the stress in the GaN/AlN MQW structures with various well thicknesses was observed using MOSS in our previous work [7]. However the X-ray diffraction (XRD) analysis carried out earlier [7] and XRD reciprocal space mapping made recently (not shown here) revealed for the MQW structures with thin QWs (narrower than 2ML) practically unchanged vertical and lateral average lattice constants as compared to the AlN template. This implies that a noticeable compressive stresses should be accumulated in the MQW structures, which disagrees with the MOSS results showing nearly stress-free growth.

The contradiction between the MOSS-data demonstrating a stress-free growth of the GaN/AlN MQW structures and the results of XRD analysis indicating the same lattice constant of the AlN BL and MQW with the thin QWs was explained by the formation of ultra-thin spatially separated GaN platelets with a thicknesses of few MLs instead of a continuous GaN layer in growing MQWs. Indeed, the possibility of elastic relaxation of GaN(AlN) ultra-thin layers grown atop of the AlN(GaN) thick layers by PA MBE at
Me-rich conditions via development of discontinuities in the thin layers was proposed by Bourret et al. [12]. We applied this idea to explain the complete stress relaxation in the GaN/AlN MQW structures with the ultra-thin wells (≤2ML), in which the elastic lateral relaxation of the compressive stress induced in the GaN platelets at the lower interface causes the tensile stress relaxation in AlN barrier at the top interface of the platelets, which result in preserving both vertical and lateral average lattice constants [7].

Thus, it is expected that the same mechanism related to formation of nanoplatelets may be responsible for stress-free or weak-stress growth of the 1.5ML- and 2ML-structures, respectively, observed by MOSS in this study. One should mention that formation of the relatively small grains in 2- and 1.5ML structures, shown in Fig.3, could be considered as an alternative relaxation mechanism for the stress in the grained MQW structures. However, keeping in mind a large size of the grains (several hundred nanometers) as compared to the Ga-rich platelets (below 160 nm) [13], the possible contribution of this mechanism in the stress relaxation was preliminary estimated by us as negligible. In addition, usually the development of such grains, resulting in implementation of this mechanism of stress relaxation, occurs gradually during heteroepitaxial growth that contradicts the observed absence of any stress induced at the beginning of the 1.5ML-structure growth.

Figure 4. The measured by MOSS values of \((\text{stress} \times \text{thickness})\) vs thickness in MQW structures with the QW thicknesses of 5ML (a), 2ML (b) and 1.5ML (c). The curves with oscillations demonstrate experimental data, while the red solid and dashed lines show the average stress values and the pseudomorphic growth lines for the effective alloy composition of MQWs, respectively.
To separate finally the contributions of the formation of platelets and grains in the MQW structures to relaxation of the compressive stress the detailed XRD analysis and CL studies should be performed. The XRD results will be reported elsewhere, whereas the analysis of the CL spectra of the MQW structures is presented below in Fig.5.

Figure 5a shows the CL spectrum of the 5ML-structure, consisting of several peaks distributed between the highest one at 360 nm towards the weakest ones at shorter wavelengths till 270nm. Thus, the full width at half maximum (FWHM) of the envelope curve for this fairly weak CL band is about 50 nm. In contrast, the 2ML- and 1.5ML structures exhibit much more intense and narrower single peaks at 270 and 240nm with the FWHM values of 21 and 13 nm, respectively. If position of the main CL peaks in the MQW structures is determined mainly by the quantum confinement effect, the spectral width depends on the elastic stress and thickness uniformity in the MQW structure.

Consequently, the observed multi-peak CL spectrum apparently corresponds to rather high and strongly varying stress in the 5ML-thick structure, which changes the internal electric field and, hence, the magnitude of the Stark effect in the GaN QWs, causing the blue shift of the CL peaks from the initial MQW region under the compressive stress. The narrower and single CL peaks from the MQW structures with thin QWs provide the convincing evidence of uniform and low stress level in the GaN QWs across the structures. Thus, the observed formation of the terrace-like grains does not cause significant stress relaxation in the MQW structures with the thinnest QWs, where the grain density is higher, but the formation of the small nanoplatelets inside these grains is rather responsible for the stress-free growth of the structures.

4. Conclusion
We demonstrated that the (GaN/AlN)_{100} MQW structures with extremely thin GaN QWs (1–2 MLs) grown by PA MBE on AlN have a constant and small average substrate curvature that means a stress-free growth. In contrast, the 5ML-MQW structure with the average Al content of x_{av}=0.8 exhibits the standard gradual stress relaxation from high level of the compressive stress (-2.3GPa), corresponding to the pseudomorphic growth, to the nearly fully relaxed growth at the surface. Although, the MQW structures with ultra-thin wells (<2ML) demonstrate the formation of the grains with the typically smaller sizes of about 200-300nm than in the 5ML-MQW structure, their contribution to stress relaxation seems to be negligible. The formation of small nanoplatelets is proposed as the main mechanism of elastic lateral relaxation of the local compressive and tensile stresses in the thinnest QWs, which provides a stress-free growth of the QWs and reduced Stark effect. This results in the strengthening and narrowing the single CL peaks from the structures with the shortest observed wavelength of 240nm. For the 5ML-MQW structure, the described mechanism of elastic stress relaxation through formation of separate platelets is apparently broken, that leads to a significant gradient of the compressive stress in the structure and, as a result, to widening the CL spectra consisting of several low-intensity peaks. Thus, development of the GaN/AlN MQW structures with ultra-thin (≤2MLs) wells is a promising way to develop high-power narrow-band sources of UV radiation in the sub-250 nm spectral range.

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