Kinetic limitations of stress relaxation and generation in GaN/AlN and AlGaN: Si/AlN heterostructures grown on c-sapphire by plasma-assisted molecular beam epitaxy

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Abstract. The paper describes experimental study of stress relaxation and generation in (1-2)-µm-thick GaN and AlGaN layers grown on AlN/c-Al2O3 buffer layers by low temperature (<720 °C) metal-rich plasma-assisted molecular beam epitaxy (PA MBE). The atomically smooth undoped GaN layers demonstrate only gradual relaxation of the compressive stress, which is probably related to thermodynamically driven inclination of threading dislocations (TDs). The slower stress relaxation at the lower growth temperature is explained by kinetic limitation of this process. The switch of compressive to tensile stress in the less-strained undoped Al0.7Ga0.3N layers, attributed mostly to the same effect of TD inclination, occurs in the low-temperature PA MBE conditions at much larger thickness (~0.6 µm) as compared to MOVPE ones. Introduction of high Si doping (n~10 19 cm-3) reduces noticeably the initial compressive stress in the AlGaN film due to substitution of small Si atoms in the group-III sublattice. At larger thickness, Si atoms seem to effect the TD propagation and suppress generation of tensile stress related to TD inclination, which makes possible to grow ~1-µm-thick Al0.7Ga0.3N: Si films without cracking.

Introduction

(Al,Ga)N-based binary and ternary compounds are basic materials for novel devices of ultraviolet (UV) photonics and high-frequency/power electronics [1, 2]. Due to low commercial competitiveness of native substrates for these compounds, the device heterostructures are used to grow on various heterosubstrates (c-Al2O3, 6H-SiC and Si (111) etc.). An AlN/c-sapphire heterostructure with moderate values of crystallographic lattice mismatch (aAl2O3-aAlN)/aAlN= -11.7% and thermal mismatch Δαθ= αAlN - α Al2O3= -4.12·10-6 K-1 [3] is the most suitable template for mass-production of devices in which the substrate transparency (for UV-optoelectronics), large diameter and low cost are the key factors when choosing a substrate.

In general, significant stresses generating at all stages of growth of the heterostructures are relaxed in different ways, including the generation of various bulk extended defects, the formation of developed surface morphology, etc. Among the former, the misfit dislocations at the AlN/c-Al2O3 interface are the most important, since threading dislocations (TDs) arising from them can reach the upper (active) regions of the device heterostructures and deteriorate their optical and electrical properties. To reduce the concentration of TDs the AlN buffer layers are commonly grown for a thickness of a few microns, which is sufficient for effective interaction of TDs with each other as well as with filtering super lattices or interlayers [4, 5]. As a result, the TD density can be reduced to a level of 108-109 cm-2. On the other hand, the increasing thickness of AlN leads, as a rule, to transition from the initial compressive mismatch stress to tensile one [6], which, in general, can result in cracking of the film. To overcome this issue, the growth of compressively strained GaN or AlGaN layers on the
AlN buffer layers is used to compensate of the harmful tensile stress. However, unfortunately, these layers also demonstrate a fairly fast transition to an incremental tensile stress [7, 8].

Plasma-assisted molecular beam epitaxy (PA MBE) is one of the main technologies currently being developed for production of various III-Nitrides-based devices. Among its unique features is the possibility of epitaxial growth of (Al,Ga)N compounds at extremely low substrate temperatures (<<1000 °C), which causes specific kinetics and thermodynamics of epitaxial growth of the alloys. In principle, the growth temperature should play an important role in the relaxation and generation of stresses in the heterostructures, but this influence for (Al,Ga)N/c-AlN heterostructures has not been sufficiently studied. Thus, only one paper by Okumura et al. [9] has reported a critical thickness of 900-nm necessary to introduce dislocations into an AlN buffer layer grown on a 6H-SiC substrate, which is more than two orders of magnitude greater than the thickness estimated in accordance with a Matthews–Blakeslee model. Even less is known about influence of Si atoms on the stresses in n-AlGaN: Si layers grown by PA MBE, although creation of an additional tensile stress during MOVPE growth of AlGaN: Si epilayers has been studied by several groups and a few explanations of this phenomenon have been proposed [9, 10].

This paper describes the behavior of stresses in the GaN and AlGaN layers grown by PA MBE on AlN/c-AlN buffer layers. The former is studied as a function of the substrate temperature (T_s) whereas the influence of high Si doping on the stress variation is evaluated for the latter.

**Experimental**

All samples were grown on c-sapphire substrates by PA MBE setup Compact 21T. The peculiarities of growth of AlN nucleation and buffer layers by migration enhanced epitaxy and metal modulated epitaxy (MME), respectively, were described in our previous papers [11, 12]. The nitrogen flux of 0.47 ML/s, defining the growth rate at the employed metal-rich conditions, was kept constant during growth of all structures. The bottom buffer AlN layers in all structures were grown with the same thickness of about 1µm at T_s=780 °C and slightly metal-rich conditions with a flux ratio of Al/N~ 1.1. The 1-µm-thick GaN layers in two GaN/AlN heterostructures were grown by MME at different temperatures of 690 °C (GaN-LT-sample) and 720 °C (GaN-HT-sample) by using the Ga/N flux ratios of 2.2 and 2.9, respectively. The two samples with undoped and Si-doped Al_0.3Ga_0.7N layers with thicknesses of 1 and 1.8 µm, respectively, were grown on the AlN buffer layers by a standard PA MBE at T_s=700 °C using continuous fluxes with a III/N ratio of about 2.

Laser reflectometry and reflection high energy electron diffraction (RHEED) were used for in situ control of growth rate and surface morphology. The stress in the heterostructures was evaluated in situ by a home-made multi beam optical stress sensor (MOSS), as described in [13]. The incremental stresses σ(h_i) were calculated by using the Stoney differential equation

\[ \sigma(h_i) = \frac{M_s h_i^2}{6} \frac{\partial k}{\partial h_i}, \]

Where M_s is a biaxial elastic modulus of substrate (602 GPa for c-AlN_2O_3 [14]), h_i and h_s are the thicknesses of substrate and epitaxial layer, respectively, while \( \frac{\partial k}{\partial h_i} \) denotes the change of substrate curvature with respect to the layer thickness change. The surface morphology of the samples was studied by optical (OM) and scanning electron (SEM) microscopies. Measurements of the width of x-ray diffraction symmetric and skew-symmetric peaks were used to estimate the screw and edge TD densities in AlN layers. The doping concentration was measured by C-V technique.
**Results and discussion**

The inset in Fig.1 shows typical SEM image and RHEED pattern observed for GaN-LT and GaN-HT layers. They indicate the atomically smooth surface morphology for both of the layers due to appropriate choice of Ga-rich conditions for their MME growth. Also, these layers demonstrate almost the same initial compressive stress of about 10 GPa corresponding to the mismatch stress for GaN/AlN heterostructures $\sigma = M_{\text{GaN}} \varepsilon = 10.8$ GPa, where the biaxial elastic modulus $M_{\text{GaN}} = 450$ GPa and the crystallographic mismatch $\varepsilon = -2.4\%$ [14]. However, Fig. 1a demonstrates the different behavior of the substrate curvature (stress $\times$ thickness) vs thickness dependences during growth of these layers.

![Figure 1](image)

**Figure 1.** (a) Curvatures (stress $\times$ thickness) and (b) incremental stresses (first derivative of the plots in (a)) vs thickness for LT-GaN (dashed) and HT-GaN (solid) layers grown on relaxed AlN/c-Al$_2$O$_3$. The thin grey curves in (a) are the experimental data of curvature change during MME growth. Insertion in (b) shows typical SEM image and streaky RHEED pattern observed for both GaN layers grown by MME.

The slower stress relaxation in LT-GaN compared to HT-GaN, possessing the same surface morphology, can be related apparently with kinetic limitations of this process. Moreover, taking into account XRD data for AlN buffer layers, revealing an approximately the same rather high initial TD density $\sim 10^6$-$10^{10}$ cm$^{-2}$ in the both samples, one can assume that the inclination of TDs with respect to the (0001) growth direction is a major mechanism of the stress relaxation in the compressively strained GaN layers [15]. However, the thermodynamic model by Romanov and Speck [15], considering the energy balance approach in the layers with various TD configurations, can only predict that the inclination of TDs results in decrease in dislocation and system energy, which can be easily realized in case of high temperature epitaxial technology like MOVPE. Slowing down this process with reduction of $T_S$ in PA MBE indicates an existence of the kinetic barrier for the TD inclination, which efficiently prevents the stress relaxation in the GaN overlayers. The using of Ga-rich MME process providing an atomically-smooth featureless surface morphology of the PA MBE films plays a role of additional factor minimizing the density of surface defects which may facilitate the TD bending by local changing the surface crystalline orientation or nucleate new TDs in the lattice-mismatched GaN.

Figure 2 shows the changes of the compressive stresses in undoped and highly Si-doped Al$_{0.7}$Ga$_{0.3}$N layers during growth on AlN buffer layers. The corresponding initial stress values of 3.7 GPa and 2.3 GPa are significantly lower as compared to the GaN/AlN heterosystem due to the smaller lattice mismatch ($\sim 0.8\%$). In addition, high Si doping obviously reduces the compressive stress from the very beginning of growth presumably owing to small covalent radii of Si atoms incorporated into group-III sublattice. The RHEED patterns exhibit only slight degradation of the initial streaky pattern
which acquires additional spotty features at the AlGaN growth. These facts indicate that the relaxation proceeds through the weak generation of misfit dislocations at the AlGaN/AlN interface and/ or some 2D-3D transition of surface morphology of the AlGaN layers facilitating at low temperature the inclination of TDs inherited from the AlN buffer [15]. Importantly, these mechanisms explain the gradual relaxation of the compressive stresses, but they cannot be used for clarifying the reasons for transition from compressive to tensile stresses observed at the thicknesses of 0.6 and −0.9 μm for undoped and Si-doped layers, respectively (Fig. 2a).

A few mechanisms responsible for emergence of so-called intrinsic tensile strain in nominally compressively strained AlGaN/AlN heterostructures have been proposed. Firstly, it can be caused by a gradual coalescence of islands in the imperfect grained layers in accordance with a Nix-Klemens model [16], though this mechanism seems to prevail at the interfaces with higher lattice mismatch (e.g. AlN/c-Al2O3) and is not dominant in the considered case. Also, the relaxation of compressive strain in the AlGaN layer through the inclination of pre-existing TDs was suggested to result in generation of equibiaxial misfit dislocations compensating efficiently the initial compressive strain [17, 18]. It should be emphasized that, in accordance with [15], the angle of inclination remains unchanged during the layer growth and it can even lead to generation of significant tensile stress after some critical thickness, leading finally to plastic relaxation of the layer through cracking.

In addition, the stress developing in the doped AlGaN layers is further complicated by influence of Si atoms, as seen in Fig. 2a. There are also several mechanisms of the introduction of additional tensile strain in Si-doped AlGaN layers. The most obvious explanation of this phenomenon is less dimension of Si atoms than Ga ones that leads to hydrostatic pressure in the doped films. As a result, the doped film has the smaller lattice parameters as compared to the undoped layer, which is displayed in the smaller initial stress in the AlGaN: Si layer, mentioned above. Also, Forghan et al. [10] proposed an alternative mechanism of inducing the tensile strain in the doped AlGaN films related to a selective incorporation of Si atoms around edge TDs resulting in transformation the strain dipole field into predominantly tensile strained dipoles.

Figure2. (a) Substrate curvature (stress × thickness) versus thickness for Al0.7Ga0.3N: Si and Al0.7Ga0.3N layers grown on AlN/c-Al2O3 buffer layers. Cross-sectional (b) and plan-view (c) SEM images of the Al0.7Ga0.3N: Si layer. The inset in (c) shows its surface image obtained by OM.

However, the processes of relaxation of compressive stress and generation of tensile one in the undoped and highly Si-doped Al0.7Ga0.3N/AlN heterostructures grown by PA MBE (Fig. 2a) appears to differ strongly from similar structures grown by MOVPE [10, 19, 20]. The undoped PA MBE film exhibits the compressive incremental stress (negative slope in curves in Fig. 2a) up to the thickness of −0.6 μm, when the curvature slope changes sign to the positive one. In contrast, the Al0.7Ga0.3N/AlN heterostructures grown by high temperature MOVPE at T5= 1100 °C [19] demonstrate the compressive stress only for much higher lattice mismatch (x = 0.2-0.38), whereas the higher Al-content layers show negligible curvature change (at x = 0.8) or even a positive transient slope (at x = 0.86) from the very beginning [19]. This can be explained by the low-temperature growth conditions inherent to
PA MBE, which slowdown the TD inclination process considered as the most probable for generation of tensile stress in the heterostructures with small lattice mismatch.

The effect of high Si doping in PA MBE, well pronounced at the initial stage of the AlGaN: Si growth, also shows different behavior as compared to MOVPE reports [19, 20]. Firstly, it does not reverse the stress sign immediately as it does in low-Al-content AlGaN: Si layers grown by high-temperature MOVPE [19], which is probably related to much lower fraction of Ga atoms exchanged by Si ones. Second, it slows down the stress relaxation process shifting the tensile-stress onset thickness by approximately 30-40 % (to 0.9-1.0µm) as compared with the undoped AlGaN layer case. The latter is assumed to be caused by interaction of the high-density Si atoms with TDs, which was thoroughly studied in Ref. [10]. However, in contrast to high-temperature MOVPE case, in the low-temperature PA MBE with the suppressed surface and bulk Si diffusion, the Si atoms seem to affect the TD propagation process, e.g. by blocking or changing the inclination angle of TDs, rather than creating the tensile strained dipoles along the edge TDs. As a result, the compressively stressed Si-doped high-Al-content AlGaN with an electron concentration up to 10^{19} cm^{-3} can be grown by PA MBE on AlN buffers up to much larger thickness without film cracking as compared to the undoped layers.

**Conclusions**

We have demonstrated the strong influence of kinetic limitations on different processes of compressive stress relaxation and generation of intrinsic tensile stress in the undoped GaN and Al_{0.7}Ga_{0.3}N (undoped and highly doped with Si) layers grown on AlN/c-Al_{2}O_{3} buffer layers by low temperature (T_{S}<720 °C) PA MBE. This allowed us to grow 1-µm-thick GaN and Si-doped Al_{0.7}Ga_{0.3}N (n=10^{19} cm^{-3}) layers on the AlN buffers, preserving the average compressive stress. These heterostructures serve as constituent elements of various UV-optoelectronic and electronic devices where the heterostructure cracking and substrates bowing are the critical issues.

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