Stress evolution in AlN layers grown on c-Al$_2$O$_3$ by plasma-assisted molecular beam epitaxy at metal-rich conditions

O A Koshelev, D V Nechaev, S V Ivanov, and V N Jmerik
Ioffe Institute, 26 Polytekhniccheskaya Str., St. Petersburg 194021, Russia

Abstract. Stress generation and relaxation in AlN nucleation and buffer layers grown on c-Al$_2$O$_3$ substrates by plasma-assisted molecular beam epitaxy at low (LT, $T_S=780^\circ$C) and high (HT, $T_S=850^\circ$C) substrate temperatures were studied. Oscillation behavior of the wafer curvature (stress $\times$ thickness) was revealed during pulsed deposition of AlN in metal modulated epitaxy and migration enhanced epitaxy modes under the metal-rich conditions, which corresponded to Al bilayer formation and consumption. Minimal average stress ~ $+0.05$ GPa in AlN buffer layers was observed at LT growth, which increased up to $+0.85$ GPa at HT growth. In addition, the LT AlN layers demonstrated lower densities of screw and edge threading dislocations equal to $7.8 \cdot 10^8$ and $5.1 \cdot 10^9$ cm$^{-2}$, respectively, while in the case of HT AlN layers those densities were significantly higher.

1. Introduction
To manufacture III-Nitride-based photonic and electronic devices the c-sapphire substrates are most commonly used. Such parameters as low cost, transparency, chemical and thermal stability make them most suitable for mass-production of III-N devices. However, the relatively high lattice mismatch of c-Al$_2$O$_3$ and AlN (~13%) can lead to an enormous threading dislocation (TD) density ($\sim 10^{10}$ cm$^{-2}$) even in the several-microns-thick AlN buffer layers [1]. This worsens the output parameters of the devices and several techniques have been actively developing to overcome this problem. Elaboration of initial nucleation (NL) and buffer (BL) AlN layers on c-Al$_2$O$_3$ with typical thicknesses of several tens of nanometers and few microns, respectively, plays a key role in reducing the TDs in the device heterostructures.

The growth of AlN NLs on c-Al$_2$O$_3$ substrates has been studied in detail by several groups which employ high-temperature gas-phase technologies, such as metal-organic chemical vapor deposition (MOCVD). They described complex processes of generation and relaxation of internal stresses in these heterostructures, which relate to both crystal mismatch and coalescence of AlN grains during growth. For instance, Radhavan et al. have studied the temperature dependent evolution of both compressive and tensile stresses in the AlN/c-Al$_2$O$_3$ heterostructures during their growth at substrate temperatures $T_S=600$-1100$^\circ$C [2]. They have found that coalescence of grains in NLs can lead to significant tensile stresses in the growing AlN layers, which may cause cracking of the AlN buffer layers at large enough thicknesses. An important role of grain boundaries in the origination of TDs was also c.

In contrast, mechanisms of stress evolution during low-temperature plasma-assisted molecular beam epitaxy (PA MBE) of AlN layers on c-Al$_2$O$_3$ has not been studied enough yet. Recently we have reported a decrease in the TD density in AlN NLs grown on c-Al$_2$O$_3$ by migration enhanced epitaxy (MEE) at a relatively high $T_S=780^\circ$C as compared to a two-stage growth of AlN NLs, starting at low $T_S=550^\circ$C [3]. In this paper, we elucidate the evolution of stresses in AlN NLs and following AlN BLs
during their PA MBE deposition by using pulsed techniques of MEE and metal-modulated epitaxy (MME), respectively, at the metal-rich conditions and different \( T_S = 780 \) and \( 850 \)°C. The structural perfection of resulting hererostructures is also analyzed.

2. Experiment

AlN layers were grown by PA MBE (Riber Compact 21T) on c-Al_{2}O_{3} substrates annealed at \( T_S = 850 \)°C and nitridized for 10 min at \( T_S = 780 \)°C. Figure 1 shows a schematic design of the studied heterostructures and the sequences of Al and plasma-activated nitrogen (N\(_{2}^{*}\)) fluxes during MEE and MME growth modes at fixed \( T_S = 780 \) or 850°C (noted as LT and HT, respectively), as has been reported in details by us previously [3,4]. To study the evolution of the AlN surface morphology during initial growth stage, the series of AlN-NLs with a thickness varied from 7 to 65nm was also grown at LT. The AlN BLs with a thickness of about 300 nm were grown atop by using a continuous (standard) growth mode at the same fluxes and \( T_S \). The N\(_{2}^{*}\) flux was kept constant at 0.45 ML/s, while the Al flux was varied from 0.5 to 0.64 ML/s for LT and HT AlN growth conditions, respectively.

![Figure 1. The design of grown structures and flux diagrams of three main growth modes.](image)

A home-made multi-beam optical stress sensor (MOSS) based on a 10 mW laser emitting at a wavelength of 532 nm and a CCD-camera with recording frequency of 15 Hz was used to evaluate in situ the incremental stresses during growth of AlN NLs and BLs. The surface morphology of the AlN layers was monitored by the reflection high-energy electron diffraction (RHEED) and studied ex situ by atomic-force microscopy (AFM). The structural quality of the AlN layers was estimated by x-ray diffraction (XRD) analysis through measuring the full width at half maximum (FWHM) of \( \omega \)-scans of symmetric AlN (0002) and skew-symmetric AlN (10-15) reflections.

3. Results and discussion

Prior to the growth of LT- and HT- AlN NLs, the RHEED images from the nitrided substrates exhibited a relatively blurred diffraction pattern, that remained unchanged during the initial growth of the NLs, but then it became brighter. Moreover, in the case LT-AlN NL the streaky or two-dimensional (2D) pattern shown in Figure 2a gradually appeared at a thickness of more than 10 nm. Previously, we studied the AlN NL grown by MEE at \( T_S = 750 \)°C and found that these films with a thickness of 65nm had a flat grain morphology [3]. Figure 2b illustrates the evolution of the
morphology of such AlN NLs with thickness varied in the 7-65 nm range. Their AFM images show a monotonous decrease of the grain density and some increase in the surface morphology roughness up to a thickness of 40 nm, followed then by smoothing the layers. This is accompanied by the lateral 2D growth of the initial NL grains with a typical diameter expanding from several tens to hundreds of nanometers.

Figure 2. (a) Evolution of the stress×thickness vs thickness during the growth of 65-nm-thick LT-AlN NL by MEE. (b) The LT-AlN NL RMS roughness and grain density versus thickness. The dotted lines indicate the thicknesses of AlN NLs for which the RHEED (a) or AFM (b) images are related by arrows from the top of the figures.

Figure 2a demonstrates also the oscillatory change in the curvature (stress×thickness), with a period number corresponding to the number of MEE cycles. These oscillations begin at a layer thickness of ~10 nm and continue with the increasing amplitude up to a thickness of 40 nm, where the oscillation amplitude almost saturates. It should be noted that growth at the Al-stage of MEE results in higher values of the substrate curvature with a positive sign (higher tensile stress), while the curvature drops abruptly at the beginning of the N-stage of MEE. Despite the oscillations of the incremental curvature, the average curvature in the LT-AlN NL exhibits a negative slope (the red dashed line in Figure 2a) corresponding to a compressive stress ~1 GPa.

In principle, there are two main sources for the stress generation in the AlN NL grown on c-Al2O3 substrate. In addition to the incomplete relaxation of the crystal mismatch between AlN and the substrate, leading to the induction of a compressive stress, it should be taken into account the generation of the tensile stress due to grain coalescence in growing films in accordance with a model of Nix and Clemens [6]. Figure 2a indicates that the former mechanism dominates in our LT-AlN NLs despite the rather intense coalescence inside. In contrast, AlN/c-Al2O3 heterostructures grown by high-temperature MOCVD exhibit mainly the tensile stress related to the grain coalescence, as has been reported earlier [2].

The study of relation between metallic phase on the AlN surface and MOSS data was continued during the growth of AlN BLs by pulsed MME technique at different growth temperatures. Figures 3a and b shows oscillations of the substrate curvature for LT- and HT- AlN BLs, respectively. Both figures demonstrate the oscillations with the higher values of curvature during the stage of Al-excess accumulation on the surface of the AlN film growing by MME. This corresponds to the above observation in MEE of the introduction of incremental positive (tensile) stress after occurrence of metallic Al on the surface of growing AlN layer.
During the accumulation stage of the AlN BL growth by LT- and HT-MME the MOSS-data demonstrate a transition from initial positive (tensile) to zero incremental stress for a characteristic time \( t_{Al}^{ex} \sim 55 \)s and \( \sim 80 \)s, respectively (see insets in Fig. 3a and b). Then, the films grow with a constant curvature till the beginning of the stage of Al consumption under the nitrogen flux exposure, when the curvature exhibits a compressive incremental stress for a few seconds during incorporation of the Al-excess MLs. Then, a stress-free growth proceeds until the start of a new MME period. The average stresses in that case are calculated based on the minimum stress\times\text{thickness} values of MOSS-data during the Al-excess elimination stage. The nominal amount of Al-excess \( (D_{Al}^{ex}) \) accumulated on the surface of AlN films for the time \( t_{Al}^{ex} \) during the accumulation stage of MME at the Me-rich conditions can be estimated from the flux balance equation as

\[
D_{Al}^{ex} = (F_{Al} - F_{N_{2}^{*}} - F_{Al}^{D}) \times t_{Al}^{ex},
\]

where \( F_{Al} \) and \( F_{N_{2}^{*}} \) are the incident Al and \( N_{2}^{*} \) fluxes (ML/s), \( F_{Al}^{D} \) is a desorbing Al flux which, at the Al-rich conditions used, corresponds to the equilibrium Al pressure over the Al melt [8]. Using the experimental data for the first two terms and reference data for the Al desorbing flux of 0.02 and 0.17ML/s at 780 and 850°C [9], respectively, gives the equal nominal Al-excess amounts at both temperatures as large as \( \sim 1.7 \) ML. This value corresponds to the general view on growth of wurtzite III-N films at the metal-rich conditions resulting in formation of group-III atoms bilayer on their surfaces [8,10]. Further growth of the III-N binaries occurs at this constant coverage of the surface by metal atoms, while the excess metal is accumulated in metallic droplets with gradually increasing dimensions during the accumulation stage and then either incorporated into the AlN BL or evaporated during the Al elimination stage.

It is worth noting that the generation of elastic stress in thin films by the extremely thin metallic adlayers has been reported in the past, e.g. Floro et al. [5] observed generation of compressive stress in GeSi films at the occurrence of Ge-segregated layers. At the moment, we cannot explain the reason of generation of the opposite (tensile) stress in our AlN layers and this issue will be studied elsewhere.

One should also note that LT-AlN BL shows the almost relaxed growth with a negligible average stress of \( \sim 0.05 \) GPa (Figure 3a), while in the case of HT-AlN BL the significant average tensile stress
of 0.85 GPa (Figure 3b) is generated. As a possible explanation of this difference, one can notice that Figure 3b demonstrates the slightly tensile average stress in the HT AlN-NL, which may be caused by a faster relaxation of crystal mismatch at higher $T_s$ and, consequently, a greater contribution of coalescence in the stress generation process. The observation of the MOSS-data oscillations with an increasing amplitude and gradual transition from spotty to streaky RHEED pattern (not shown) during the initial stage of the HT-AlN BL growth can be also related to the coalescence continuing in this layer. In contrast, the LT-AlN NLs generate the average compressive stress (Fig. 3a), and the amplitude of the MOSS oscillations during LT-AlN BL does not increase.

Thus, growth of AlN NL and BL at a moderate temperatures $T_s$~780°C allows one to achieve the almost stress-free growth up to a thickness of 1 µm, that is a big challenge for AlN films grown by high-temperature MOCVD and PA MBE at the relatively high $T_s$ of 850°C. Advantage of the moderate growth temperature in PA MBE is also confirmed by XRD data evaluating the screw and edge TD densities in LT(HT) AlN layers as $7.8 \cdot 10^8(2.3 \cdot 10^6)$ and $5.1 \cdot 10^9(3.2 \cdot 10^6)$ cm$^{-2}$, respectively. Thus, the LT-AlN BLs generate the average compressive stress at the wafer (0.05 GPa) in the LT-AlN layer and 5.1 GPa at moderate and high temperatures revealed the significantly lower average tensile stress (~0.05 GPa) in the former. It was explained preliminarily by a greater role of grain coalescence in the films grown at higher temperatures. In addition, AlN films grown at LT on c-Al$_2$O$_3$ demonstrated much lower densities of screw and edge TDs equal to $7.8 \cdot 10^8$ and $5.1 \cdot 10^9$ cm$^{-2}$, respectively, in comparison with the HT AlN films.

4. Conclusion

In conclusion, the oscillation behavior of the wafer curvature (stress×thickness) data measured by MOSS has been found and analyzed during growth of both AlN NLs and BLs by pulsed MEE and MME modes in PA MBE at the metal-rich conditions and different substrate temperatures. It has been explained by introduction of the incremental tensile (compressive) stress during accumulation (consumption) of an excess Al-bilayer on the AlN surface. Study of the average stresses in ~1-µm-thick AlN films (NL & BL) grown at moderate and high temperatures revealed the significantly lower average tensile stress (~0.05 GPa) in the former. It was explained preliminarily by a greater role of grain coalescence in the films grown at higher temperatures. In addition, AlN films grown at LT on c-Al$_2$O$_3$ demonstrated much lower densities of screw and edge TDs equal to $7.8 \cdot 10^8$ and $5.1 \cdot 10^9$ cm$^{-2}$, respectively, in comparison with the HT AlN films.

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