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Impact of Strained Periodic Multilayer on the Surface and Crystal Quality of Semi-polar (11-22) GaN Template

Abdullah Haaziq Ahmad Makinudin a, Al-Zuhairi Omar a, Afiq Anuar a, Ahmad Shuhaimi Abu Bakar a, Steven P. DenBaars b, Azzuliani Supangat *a.

a Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

b Materials Department, University of California, Santa Barbara, United States

*Corresponding author’s e-mail address: azzuliani@um.edu.my

Abstract

Efficient reduction of defects and dislocations in semi-polar (11-22) GaN epilayer with the use of AlN/GaN strained periodic multilayer is demonstrated. On- and off-axis x-ray rocking curve analyses have shown significant improvement in the crystalline qualities with remarkable narrowing in their respective full width at half maximum upon utilization of increased AlN/GaN pairs. X-ray reciprocal space mapping revealed a prominent increment in the degree of relaxation state, with notable shrinkage in the diffuse scattering streak. Structural evaluation via transmission electron microscope illuminates the interruption of defect and dislocation propagation due to the strained periodic multilayers. It was observed that the first 20th pairs exhibited a three dimensional growth mode owning to numerous defects originating from the AlN/sapphire interface. Such phenomenon was found to have a positive impact towards accumulating the propagation of defects. The surface morphology analysis elucidates the reduced stripe-like undulations, whereby the terrace-like features in the lower scales endured an enhanced rearrangement favoring the reduced defect density.

Introduction

III-nitride materials are well known to exhibit remarkable performance in various optoelectronic applications such as light emitting diodes (LEDs) and laser diodes (LD) due to its considerably wide tunable bandgap 1-2. Commercially, these nitride based LEDs are grown along the polar c-axis direction on c-plane sapphire (Al2O3)1. The performance of blue GaN based LEDs on c-plane sapphire have shown significant improvement over the last decade 3-4. Even so, LEDs grown on c-plane sapphire suffers from the quantum confined stark effect (QCSE) resulted from the concomitant piezoelectric polarizations 3-4. Such phenomenon give rise to the separation of electron-hole wave function within the quantum wells (QW) 5. The impact of the QCSE becomes more prominent in longer-wavelength LEDs as the higher Indium content promotes increased lattice mismatch within the multi quantum wells 3-6.

Alternatively, the growth of GaN-based LEDs on different orientations such as non- and semi-polar orientation would enable the overcoming of such issues 7-8. Numerous reports have demonstrated high efficiency LEDs on non- and semi-polar bulk GaN substrates 2, 9. However, such substrates are not available in bulk sizes and cost ineffective. On the contrary, the growth of non- and semi-polar GaN based LEDs on foreign substrates such as sapphire (Al2O3) would be more cost effective. The disadvantages however, lies with the quality of the epilayers being degraded with numerous defect densities affecting the device performance 10-
In addition, non-polar based devices are mainly utilized in shorter wavelength LEDs as the indium adsorption efficiency is less inversely with semi-polar LEDs.

Semi-polar GaN have been exploited intensively currently as it possess the ability to reduce the piezoelectric polarization related QCSE as well as it holds the advantage of easily adsorbing indium atoms in the QWs. Various substrates are currently available for the growth of semi-polar GaN depending on the tilt angle of the desired semi-polar orientations. As semi-polar GaN epilayers are known to suffer from high density of basal stacking faults (BSFs), and partial/perfect dislocations, efforts have been made to encounter them by patterning the substrates with SiO₂ mask prior to the well-known epitaxial lateral overgrowth (ELOG). Some studies have also conducted chemical mechanical planarization (CMP) on a semi-polar GaN template prior to the deposition of thick GaN layer. Although such techniques have shown remarkable enhancement in the semi-polar GaN crystal qualities, such methods require complex preparation as well as tedious growth optimizations. However, a few studies have proven that the utilization of simpler yet effective approaches would attain high quality semi-polar GaN. This includes the use of double aluminum nitride (AlN) or GaN nucleation layer, in-situ thermal etching I-STEP technique, silicon nitride (SiN) interlayer, indium nitride (InN) interlayer, in-situ asymmetric island sidewall growth (AISG) technique, and graded superlattices of AlN/AlGaN as well as AlGaN/AlGaN.

Despite the mentioned novel techniques, there is yet a well-established research conducted in order to thoroughly investigates the use of AlN and GaN alternating multilayers (ML) for defect reduction in semi-polar (11-22) on planar m-plane. In this work, the use of a strained periodic ML consists of alternating AlN/GaN epilayers for enhanced semi-polar (11-22) GaN template grown on planar m-plane (10-10) sapphire substrate is demonstrated. Structural properties enhancement were analyzed via HR-XRD and TEM whilst the surface morphology was characterized via AFM and FESEM.

**Experimental Method:**

The semi-polar (11-22) GaN epilayer with AlN/GaN ML was grown on planar m-plane (10-10) Al₂O₃ substrates via a metal-organic chemical vapor deposition system (SR-2000, Taiyo Nippon Sanso, Japan). The reactant source material utilized was TMA for aluminum, TMG for gallium, and NH₃ for nitrogen. The sequence for the growth procedure is as follows: A nitridation step was implemented prior to the growth of the AlN nucleation layer (thickness ~80nm). Subsequently, three different periods of AlN/GaN ML with thickness of ~4.5/20 nm, respectively, was grown and denoted as 60 pairs (ML-I), 80 pairs (ML-II), and 100 pairs (ML-III). TMA and TMG flow for AlN and GaN were kept at 98.3 and 22.6 sccm, respectively. Finally, a 4.5 µm thick Uid-GaN with similar growth conditions was grown as to ensure the resulting outcome being purely influenced by the AlN/GaN ML.

Structural properties of the semi-polar (11-22) GaN were examined via Rigaku HR-XRD X-ray rocking curve (XRC) on- and off-axis measurement as well as reciprocal space mapping (RSM). Morphological analysis was conducted via atomic force microscopy (AFM-AFM5000II) and field emission scanning electron microscope (FESEM-SU8200). Finally, the structure of the sapphire/AlN/GaN was evaluated via high-resolution transmission electron microscope (HR-TEM) (JEOL, JEM-2100F).
Results and Discussion:

On-axis X-ray rocking curve (XRC) as a function of the azimuthal angle (Φ) was conducted to evaluate the anisotropic properties of the semi-polar (11-22) GaN is shown in Figure 1(a). Semi-polar (11-22) GaN is well known to exhibit anisotropic broadening XRCs in which the FWHM along \([1-100]\) is always observed to be broader than the FWHM along \([-1-123]\). Such phenomenon is mainly owing to the lattice mismatch between the semi-polar GaN and the sapphire \(^{19,26}\). It can be deduced that the increment in the AlN/GaN period up to 100 pairs, significant narrowing in the full width at half maximum (FWHM) at both \([-1-123]\) and \([1-100]\) can be observed. In addition, the degree of narrowing in the FWHM along \([1-100]\) was observed to be larger upon further imbedding additional AlN/GaN pairs (up to 100 pairs) signifying the reduced anisotropy \(^{27-28}\). Such decrement in the FWHM values along the \([-1-123]\) and \([1-100]\) is an indication of the crystal quality enhancement \(^{20}\). Studies have shown that based on the visibility criteria for x-ray diffraction, the basal stacking fault neither type \(I_1, I_2\) nor \(E\) would be visible under the (11-22) diffraction \(^{28}\). However their respective partial dislocations would broaden the on-axis XRCs. In addition, the prismatic stacking faults (PSFs) would also affect the on-axis XRCs at \(\Phi = 90^\circ\) with a displacement vector \(\mathbf{R} = 1/2\langle10-11\rangle\) \(^{28-30}\).

Consequently, further evaluation of the crystal quality via the off-axis XRC measurement was implemented for various diffraction planes with an inclination angle (χ) respect to the (11-22) plane at different azimuth. Many have reported that with the use of the off-axis XRC
analysis, various commonly existing in-plane misalignments within the epilayers of the semi-
polar GaN such as basal stacking faults (BSFs), partial and perfect dislocations would be
revealed $^{20, 28-29}$. Figure 1(b) depicts the off-axis XRCs for the diffraction planes of (10-11)
and (11-20). From the figure, a clear trend in reduction of the XRCs FWHM for the
diffraction plane (10-11) and (11-20) value is observed as the ML period was increased. Such
narrowing in the XRCs FWHM is an indication of crystal quality enhancement with higher
number of AlN/GaN periods. Based on the visibility criterion, the XRCs for the diffraction
planes of (10-11) and (11-20) would correspond to the density of perfect dislocations with
Burgers vector of $b = 1/3<11-20>$ and PSFs with its displacement vector $R = 1/2[10-11]$, respectively $^{15, 31}$.

It should be noted, that the (n0-n0) plane XRCs are greatly influenced by the BSFs whilst the
(000n) plane XRCs are correlated with the partial dislocations and/or perfect dislocations $^{20, 28-29, 32}$. The (n0-n0) series measurement in Figure 1(c) suggests that the density of the BSFs
type $I_1$ (in conjunction with (10-10) plane XRC) and $I_2$ (in conjunction with (20-20) plane
XRC) is reduced as the AlN/GaN period was increased. This might be due to the fact that the
increase in the ML period would further facilitate the reduction of the BSFs. However,
studies have shown that the (30-30) plane XRC is insensitive to the BSFs presence, in turn
deviate from the (10-10) and (20-20) trend $^{15, 31}$. Additionally, the (000n) series measurement
in Figure 1(d) also portrayed similar trend in the FWHM decrement in conjunction with other
diffraction planes. The trend suggest that the higher number of AlN/GaN period would also
impact the partial dislocations and/or perfect dislocations with Burgers vectors having c-axis
component.

Table 1: Diffuse scattering streak extension and tilt values of ML-I, ML-II, ML-III, based on
the x-ray reciprocal space maps.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DS streak ($\text{Å}^{-1}$)</th>
<th>Tilt (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML-I</td>
<td>0.0365</td>
<td>1.4135</td>
</tr>
<tr>
<td>ML-II</td>
<td>0.0325</td>
<td>1.6132</td>
</tr>
<tr>
<td>ML-III</td>
<td>0.0248</td>
<td>1.6653</td>
</tr>
</tbody>
</table>

The strain state of the semi-polar GaN epilayer was evaluated via XRC reciprocal space
mapping (RSM). Figure 2(a-c) depicts the on-axis RSM of the (11-22) reflections along [-1-1-23] for ML-I, -II and -III with its corresponding tilt and diffuse scattering (DS) streak values
are tabulated in Table 1. Significant offsets in $Q_x$ were observed for all samples between the
substrate and the epilayer peaks. This indicates a macroscopic tilt in the epilayers crystal
lattice. It has been reported that the microscopic tilts corresponds to the formation of misfit
dislocations (MDs) at the hetero-interface $^{33-34}$. The generation of the MDs have shown to
help facilitate the relaxation of the epilayers $^{26, 33}$. Comparing all three samples, an increase in
the tilt can be observed as the number of AlN/GaN period was increased. In addition, the
diffuse scattering streak can be seen in all three RSMs indicating the presence of PSFs $^{20}$. However, the elongation of the DS streak for ML-I was observed to be longer if compared to
ML-II and ML-III as depicted in Table 1. ML-III exerts the lowest DS streak extension indicating lower presence of PSFs, which further supports the XRC analysis.
Figure 2: X-ray reciprocal space maps of the semi-polar (11-22) GaN along [-1-123] with Qz (out-plane) and Qx (in-plane) of the space maps for (a) ML-I, (b) ML-II, and (c) ML-III.

As the crystal quality was observed to have a positive impact upon the utilization of additional periods of the AlN/GaN ML, the surface morphology has also seen to be evolving. Figure 3 shows the 5×5 µm AFM 2D and 3D micrograph of ML-I to ML-III with the average line profile plot for its respective images. From the figure, it is safe to presume that the higher number of AlN/GaN pairs would further facilitates the surface quality enhancement with lower density of undulations. The contrast scale of the AFM images represent the height difference along the scan area, it would seem that ML-III exhibits the least arrowhead-like features. This can also be observed from the average line profile whereby ML-III exerts a fairly even surface with lower number of sharp protruding peaks/valleys as compared with the lower AlN/GaN pairs. Studies have shown that the typical undulated features of semi-polar GaN is well correlated to the defect propagations \(^{24, 32}\). It is presumed that the higher density of the undulations is a consequence of higher defect density propagating throughout the epilayer \(^{24}\).
Figure 3: 2D and 3D 5×5 µm AFM micrographs with the average line profile for (a) ML-I, (b) ML-II and (c) ML-III.
Figure 4: 2D and 3D 500×500 nm AFM micrographs with its line profile for (a) ML-I, (b) ML-II and (c) ML-III.
In order to further clarify the origins of the undulations, higher magnification of the surface was conducted with the scan size of 500x500 nm. Figure 4(a-c) shows the 2D and 3D AFM images with its respective line profiles. The higher magnification scan area reveals that there is indeed a lower scale surface evolution where the terrace-like structures of the surface undergo a deformation upon increasing the AlN/GaN pairs from 60 to 100 pairs. It can be deduced from the images that ML-III having the highest AlN/GaN pairs yields the highest density of such terrace-like structures with smaller surface area whilst lower number of AlN/GaN pairs result in larger terrace sizes. The line profile further proves the number of the steps becomes higher (regardless of the step height) as the step sizes was reduced whereby the average terrace length was found to be as low as ~22 nm as compared with ML-I and ML-II of ~60 and ~33 nm, respectively. Longer terrace length facilitates loosely packed steps resulting in the lengthy interval between the protruding peaks in the line profile. The relatively lower scan sizes would relate closely to the microscale surface properties where the closely-packed (in length) step terraces would result in lower density of surface undulations (striations) in the lower magnification scan areas. Semi-polar GaN are well known to exhibit such terrace like structure originating from the atomic-scale terraces\(^{14}\). Such structures have been proven to assist the indium adsorption during the growth of the quantum well (QW) for longer wavelength emissions\(^{14}\).

![Figure 5: FESEM cross-section of (a) full structure including AlN nucleation layer (NL), AlN/GaN ML and Uid-GaN, and (b) higher magnification of the AlN/GaN ML interface near the first 20\(^{th}\) pair.](image)

Due to the significant evolution in the surface morphology, cross-sectional FESEM imaging was conducted as to verify the structural interfaces prior to the thick GaN epilayers. Figure 5(a) depicts the cross-sectional imaging of the 100 pairs of AlN/GaN ML. Higher magnification of the ML reveals that around the first 20 periods of the AlN/GaN pairs, it was undergoing a 3-dimensional deformation as shown in Figure 5(b). It can be observed from the image; the interface between the AlN and GaN was completely disfigured with discontinued/wavy lines (highlighted in white circle). However, upon reaching the subsequent periods of the ML, the interfaces rearranged in rather an orderly manner continuing the rest of the periods. It should be noted here that all the AlN/GaN pairs from the first pair up to the 60, 80 and 100\(^{th}\) were grown under the exact same conditions; hence, the
growth mode variation between the earliest and its subsequent pairs implies a secluded phenomenon occurring within the hetero-interface.

Figure 6: Bright field TEM image along [10-10] zone axis with g = (11-20) (a) low magnification of the full structure, (b) high magnification at the sapphire-AlN NL-AlN/GaN ML, (c) high magnification at the 20\textsuperscript{th} - 40\textsuperscript{th} ML and (d) high magnification at the 60\textsuperscript{th} ML.

Further evaluation of the phenomenon was conducted via a transmission electron microscope (TEM). Figure 6 represents the cross-sectional image of the sample ML-III taken along the [10-10] zone axis with g = (11-20). Low magnification bright field (BF) imaging reveals the full structure of AlN/GaN multilayers inclusive of the sapphire, the AlN NL, until the semi-polar GaN epilayer as shown in Figure 6(a). It is safe to presume that the first 20 periods of the multilayers indeed underwent a 3-dimensional growth mode with absence of continuous lines representing the AlN/GaN ML interfaces. The predominant defect observable from the images is the intrinsic BSFs of the I\textsubscript{1}-type with the associated partial dislocations (highlighted in orange circle) as well as a few PSFs (highlighted in blue circle).
From Figure 6(a-d) with respect to its schematic illustration in Figure 7, three main phases of defects propagation/termination/annihilation was observed to occur. (i) The BSFs along with its associated partial dislocations, originating from the AlN/sapphire interface propagates along the c-plane to the subsequent epilayer. Higher magnification imaging depicted in Figure 6(b) reveals the numerous defects generated from the AlN NL and sapphire interface was seen propagating/accumulating towards the first pair of the AlN/GaN ML causing a disturbance during the epilayer growth. Such phenomenon continued to reoccur until ~20th pair of the AlN/GaN. (ii) Due to the tensile/compressive strain exerted by the subsequent alternating AlN/GaN ML, the BSFs were terminated by its associated partial dislocations. It is well known that the $I_1$-type BSFs can be terminated by the partial dislocations or folded by the PSFs $^{15, 31}$ as seen from the higher magnification image of Figure 6(c-d). (iii) Consequently, the partial dislocations being affected by the alternating ML accumulates and propagates in unison deviating from its original path to an undesired propagation direction. This can be clearly observed as the consequent 40th AlN/GaN pairs (highlighted in orange circle in Figure 6(c)) and above exerting significant interfacial abruptness (Figure 6(d)) portraying prominent absence of the mentioned defect in certain areas. In addition, the partial dislocations associated BSFs starts to converge around the 60th ML pair unitedly propagating into the semi-polar GaN epilayer (inverted V-shape/arrowhead). (iv) When the propagation enters the Uid-GaN interface, the strain difference separates the union whilst bending them in a manner which loops the propagation creating a closed-loop effect of the defects $^{24}$. However, certain propagation of the defects still reaches the surface of the epilayer conversely with a lower density.
This illuminates the fact that utilization of a strained alternating ML consists of AlN/GaN, would be beneficial in reducing the defect densities. However, as mentioned in previous section, the growth conditions of the ML were kept constant for all epilayers. In other words, the effect observed in this work solely influenced by the period of the ML. Higher numbers of AlN/GaN period yields lower density of defects. Referring to the schematic illustration of the proposed defect termination in Figure 7(a-b), if the growth was stopped at the 20th pair of the AlN/GaN ML, the defect accumulation would be in a state where nothing would stop their propagation into the Uid-GaN epilayer. Conversely, with the addition of the subsequent periods of the ML, defect blocking/termination would occur as described in the 2nd and 3rd phase of the defect reduction phenomenon. Consequently, if the period of the AlN/GaN ML was further increased, convergence of the defect unison propagation would increase yielding lower number of defect free to enter the Uid-GaN. In addition, the density of the defects propagation would also affect the surface properties of the semi-polar (11-22) GaN as depicted in Figure 7(a-b). The greater the number of defects enabled to propagate through would result in higher density of the arrowhead-like features on the surface of the semi-polar (11-22) GaN as previously seen by the AFM measurements.

Conclusions

Structural quality via TEM imaging concurs well with the XRC measurement indicating enhanced crystal quality with significant defects reduction. Surface morphological correlations on the other hand have shown that the defect propagations did induce steps evolutions resulting in the stripe-like undulation density to be lowered. This correlates well with other studies presuming such stripe-like undulated features are well affected by the defect densities 24, 32. It is clear that the presence of the ML following the AlN NL would induce tensile/compressive strain resulting in forced annihilation of the existing defect generated at the AlN/sapphire interface. Stimulating the termination of the BSFs via its associated partial dislocations and PSFs is deemed effective. In summary, the use of higher number of AlN/GaN ML period yielded spectacular reduction in the defect density including BSFs and its associated partial dislocations as well as the PSFs.

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a Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

b Materials Department, University of California, Santa Barbara, United States

*Corresponding author’s e-mail address: azzuliani@um.edu.my

This paper demonstrates the impact the strain periodic alternating multi-layer towards the improvement of crystal quality of the semi-polar (11-22) grown on m-plane (10-10) sapphire substrate. The correlation between the surface morphology and defect reduction within the epi-layers is thoroughly discussed.