Growth of semi-polar (11\textbar 22) GaN on m-plane sapphire via In-Situ Multiple Ammonia Treatment (I-SMAT) method

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\textbf{ABSTRACT}

Enhanced surface morphological properties of semi-polar (11\textbar 22) gallium nitride (GaN) were successfully achieved via implementing an In-Situ Multiple Ammonia Treatment (I-SMAT) method. Utilization of an optimized flow of ammonia (1 SLM), surface striations of semi-polar (11\textbar 22) GaN was reduced yielding RMS roughness of 4.20 nm. Low scan sizes of the surface reveal an evolution of the atomic-sized terraces to a rather uniformly arranged distribution resulting in narrowing/shallowing of the interfacial valleys. X-ray rocking curve (XRC) analysis implies that I-SMAT would facilitate dislocation reduction through a selective-area etching process Consequently enhancing the crystal quality. Conversely, excessive ammonia flux during the I-SMAT would degrade the structural and morphological properties of the semi-polar epilayer whereby the alternating thin GaN epilayer would undergo the selective-area etching to the extreme. This in turn exposes the etched sites significantly prior to the subsequent thick semi-polar (11\textbar 22) GaN epilayer resulting in a polarity change in the crystal orientation.

1. Introduction

Semi-polar gallium nitride (GaN) has been the topic of interest in the field of light emitting diodes (LEDs) and laser diodes (LDs) for the past years. Such interests arise due to the “Green-Gap” issue of c-plane polar GaN-based devices, whereby an increase of indium (In) composition within the InGaN active region for longer wavelength emission would increase the strain in the lattice structure resulting in device performance degradation [1–6]. In addition, the commonly known piezoelectric fields that will perturb the holes and electrons wave-function within the GaN crystal would be greatly reduced with the use of semi-polar GaN in LED [4,7]. This is due to the arrangement of gallium and nitrogen atoms in semi-polar GaN lattice are tilted to the c-plane GaN which reduces the alternating distance of both atoms [8]. However, semi-polar GaN suffers from numerous crystal defects during the epitaxial process such as the basal stacking faults (BSFs) leading to a poor crystal quality as well as surface properties [9]. For decades, various approaches have been implemented to achieve an enhanced morphological and crystal quality of semi-polar (11\textbar 22) GaN. These approaches include the epitaxial lateral overgrowth (ELOG), surface selective growth on patterned substrates (SSG), and overgrowth on nano-rod array templates [10–12]. However, such approaches require additional complex in-situ processes with the use of dielectric materials. In addition, studies have also shown enhanced crystal qualities upon utilization of in-situ techniques such as AlN/GaN multilayer and SiN interlayer [13,14]. Nonetheless, such techniques require additional metal sources.

On the other hand, several works have devised an implementation of an in-situ thermal treatment of the semi-polar GaN epilayer with the use of various gas flux such as H\textsubscript{2} and NH\textsubscript{3} for crystal quality and surface morphology enhancement [15,16]. It was shown that the use of such treatments would help facilitate dislocation termination resulting in enhanced semi-polar GaN epilayer [15,16]. However, none have reported on the use of such treatment techniques with multiple gas treatment alternating between thin GaN epilayers. In this study, semi-polar (11\textbar 22) GaN epilayer will be grown with the assist of an in-situ multiple ammonia treatment (I-SMAT) technique: whereby a selective-area etching process occurs for multiple periods to obtain an

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enhanced structural and morphological properties of semi-polar (1122) GaN epilayer.

2. Methodology

The semi-polar (1122) GaN epi-layers were grown on 2-inch m-plane (10-10) sapphire substrates via metal organic chemical vapor deposition (MOCVD) (SR-2000, Taiyo Nippon Sanso, Japan). Trimethylgallium (TMG) and ammonia (NH₃) were used as the precursors for gallium (Ga) and nitrogen (N), respectively. Schematic illustration of the steps involved during the growth is depicted in Fig. 1: (a) substrate cleaning via hydrogen ambient at 1125 °C for 10 min to remove any contaminated oxides layer on the surface of the substrate, (b) nitridation of the substrate, (c) subsequent growth of 20 nm semi-polar (1122) GaN prior to (d) the I-SMAT process; NH₃ flowing alternately with 20 nm of GaN epilayer repeatedly for 60 times, and followed by (e) the growth of a 4.5 μm thick Unintentional-doped GaN (Uid-GaN) epilayer. Variation of the NH₃ flux was carried out at 0, 1, 2.3 and 4 SLM and denoted as T0, T1, T2, and T3, respectively. For instant NH₃ flux alteration, two dissimilar pipe lines of NH₃ flow were utilized for the NH₃ flux treatment and growth of thin GaN epilayer. The time of the 20 nm GaN growth was kept constant at 14.5 s with the growth rate of approximately 1.38 nm/s. In addition, the growth of the 4.5 μm thick Uid-GaN epilayer was kept at similar conditions for all samples to ensure the sole impact of the I-SMAT technique. All samples were characterized via SU8200 field emission scanning electron spectroscopy (FESEM), AFM5000II atomic force microscopy (AFM) for morphological analysis, and Rigaku High Resolution X-ray Diffraction (HR-XRD), including 2θ-ω scans, X-ray rocking curve (XRC) on- and off-axis measurements for crystal quality analysis. Compositional analysis was conducted via X-ray Photoelectron Spectroscopy (XPS; ULVAC-PHI500 Versa Probe II) at Synchrotron Light Research Institute, Thailand using monochromatized Al Kα radiation at 1486.6 eV as an excitation source. During the XPS measurement, the dual beam charge neutralization using low-energy electron beam and ion beam was used to minimize charging effect [17]. The XPS measurement was calibrated with C1s peak of adventitious carbon at 284.6 eV with an error in binding energy interpretation of approximately 1.44 eV due to variation in work function of the samples [18–20]. The recorded spectra were carefully analyzed using CasaXPS software.

3. Results and discussion

Fig. 2a-h depicts the FESEM and AFM images of the surface for samples with and without the I-SMAT technique. Fig. 2a depicts the FESEM images of T0 whereby the existence of the commonly known undulated arrowhead features is clearly observed. However, such features were hardly visible on samples that was treated with the I-SMAT for NH₃ flux of 1 and 2.3 SLM as depicted in Fig. 2b and c. However, upon increasing the NH₃ flux to 4 SLM as shown in Fig. 2d, an observable generation of dark small regions which might be attributed to formation of deep valleys. In order to determine the causality of such phenomenon,
AFM measurement was implemented to further analyze the morphological differences between the samples.

Fig. 2e–h shows the 5 × 5 μm scan size of four different NH$_3$ flow rates, confirming the presence of the arrowhead-like features. Such features may arise due to the lower diffusion length along [1T00] direction compared to [TT23] [21]. Based on the lattice structure of semi-polar (1122) GaN, the surface atomic spacing along [1T00] and [TT23] are 5.53 Å and 3.04 Å, respectively, in which the adatoms diffusion length along [TT23] orientation is longer than [1T00] orientation [21]. However, the density of the arrowhead-like features was observed to decrease upon utilizing the I-SMAT technique with NH$_3$ flux of 1 SLM. Conversely, higher NH$_3$ flux exhibit shorter undulation length along [1T00] which increases the density of the arrowhead-like features leading to a rougher surface.

In order to evaluate the morphological properties further, 0.5 × 0.5 μm$^2$ AFM scans were implemented. Fig. 3a–h presents the higher magnification of the AFM scans with its grain size distribution histogram. It can be observed that all the samples exhibit a terrace-like structure which is the common morphological properties of semi-polar (1122) GaN [13,15,22]. However, sample T0 induced a large valley between the terraces (highlighted in black dashed circle) as shown in Fig. 3a. Comparing T1 and T0, the terrace size becomes smaller,

![AFM images](image-url)
resulting a more compact arrangement leading to the narrowing of the valley sizes. However, the density and size of the valley increases and deepened in T2 and T3 suggesting that the excessive NH₃ flux would disfigure the terrace-like features, degrading the terrace arrangement. Fig. 3e–h depicts the terrace size distribution based on the 0.5 × 0.5 μm² AFM images. From the figures, all graph exhibits small terrace sizes (less than 500 nm) which generally dominated the surfaces. However, the normal line of T1 sample is more shifted to the right with the widest distribution compared to others. This indicates that T1 induced the various terrace size density with the lowest counts of terraces <500 nm of ~80 counts as compared with T0, T2 and T3. T2 yielded the highest counts of small terraces ~400 counts followed by T0 and T3. It is presumed that the formation of various terrace sizes would help facilitate the compact yet homogeneously distributed terraces with lower density of deep valley formation.

Schematic illustration of the valley formation is depicted in Fig. 4a–d. The dissimilar terrace features are presumed to originate from the I-SMAT interruptions prior to the thick semi-polar GaN epilayer. Based on the figures, the low NH₃ flux during the I-SMAT would induce the rearrangement of the terrace features due to reactivity of NH₃ with the thin GaN layer at elevated temperatures (>1000 °C). Studies have shown that such phenomena would promote surface etching of the GaN epilayer [15]. However, it can be observed that excessive flow of NH₃ would degrade the morphology as the etch rate would increase and widening/deepening of the valley resulting in a rougher surface site for the subsequent thin GaN layer deposition. As the step was repeatedly applied, the final deposition of GaN epilayer would exert significant roughening in the terraces, thus revealing the significant valley sizes between the terraces as illustrated in line profile of T2 and T3 in Fig. 4f and h, respectively. Such occurrences are presumed to yield an increased density of the arrowhead-like features that can be seen at the higher scan size areas. The line profiles in Fig. 4e and f shows the peak to valley value for T0 and T1 is 9.41 nm and 3.73 nm, respectively, indicating the shallowing of the valley depth. However, the density and size of the valley increases and deepened in T2 and T3 suggesting that the excessive NH₃ flux would disfigure the terrace-like features leading to a degradation of the terrace arrangement. The peak to valley value of T2 and T3 was recorded to increase up to 4.51 nm and 9.26 nm, respectively.

As the impact of the I-SMAT technique towards the surface morphology of GaN epilayer was seen, HR-XRD 2θ–ω scans were implemented to determine, if any, the presence of crystal orientation deviation. Fig. 5a depicts the HR-XRD 2θ–ω scans revealing a mixed phase of semi-polar (1122) and (10T3) with sample T3. However, absence of the (10T3) phase was observed for all T0, T1 and T2 indicating single crystal of semi-polar (1122) GaN was attained. The 2θ–ω scans correlates well with the AFM analysis suggesting that the excessive flow of NH₃ during the I-SMAT would promote an uncontrollable etch rate deforming the area continuously as the process was repeatedly occurring. This in turn would lead to a change in the polarity of the growth direction. Such occurrence facilitates the twinned-grain formation of semi-polar (1122) and (10T3) in the lower scales resulting a significantly higher surface roughness [23,24].

Crystal quality enhancement was analyzed via implementing the on-axis XRC measurement with various azimuthal angle Φ as shown in Fig. 5b. The on-axis analysis was taken from 0° (equivalent to [1112] direction) to 360° with an interval of 30° whereas at 90°, the scanning direction is along [10T0]. A strong anisotropic property was observed for all samples owing to the lattice mismatch between the semi-polar GaN and the sapphire whereby the XRC FWHMs along [10T0] is broader than along [1112]. However, T1 exhibit the least broadened FWHM along [1112] indicating a reduced anisotropy resulted from the enhanced crystal quality. Studies have shown that the narrowing of the on-axis XRCs would be in direct correlation with the reduction of dislocation densities [22]. The value of FWHM XRCs on [10T0] direction can also be broaden by Prismatic Stacking Fault (PSF) with a displacement vector of 1/2[1011] [23,25] which causes the FWHM at [10T0] to be broader than at [1112] direction for all samples. Fig. 5c shows the experimental geometry of XRD measurement depicting relationship between the heteroepitaxy.

In order to analyze further the dislocations and stacking faults formed within the microcrystal, the off-axis XRCs was implemented with various diffraction planes inclined respect to the (1112) plane at dissimilar azimuthal angle as depicted in Fig. 6a and b. From the figure, T1 exerts significant narrowing of the FWHMs for (10T1) and (1110) diffraction planes elucidating the reduced density of perfect dislocations and prismatic stacking faults (PSFs) [22]. Additionally, the (n0nm) and (000n) planes XRCs showed similar trend by which T1 exhibits the lowest FWHMs. Reports have shown that the (n0nm) plane XRCs would reveal the 11- and 12-type BSFs whereby the narrowing in the (10T0) and (2020) plane would indicate enhanced BSF densities reduction [13,22]. The BSF type I1 is formed by either insertion or removal of a basal plane with a basal shear of 1/4[1100] to reduce the fault energy [25]. Furthermore, the BSF type I1 is also connected by a sessile Frank-Shockley dislocation with burger vector b = 1/2[003] and related with one PSF by displacement vector b = 1/2[1011]. Since the BSF Type I1 have a low fault energy it would be the most probable occurring type of stacking faults the growth process. In addition, for BSF Type I2, the basal plane also slides by 1/4[1100] in one part of the crystal generated by the dissociation of a perfect dislocation with b = 1/12[20] into two Shockley partials with b = 1/4[1000]. Narrowing of the (000n) FWHMs on the other hand would be owing to the partial dislocations and/or perfect dislocations (having a fault vector along c-axis) reduction [22]. All FWHM values for T1 narrowed down to 90% compared to T0 indicating a low NH₃ treatment can effectively reduce the dislocation densities. It is reported that strain from dislocations at the interface between p-GaN and indium tin oxide layer significantly reduce the LED’s light output performance by altering its electronic structure [27]. Therefore, the I-SMAT has
application for not only to create semi-polar GaN \( \langle 11 \overline{2}2 \rangle \) template, but also has potential to enhance the LED performance by reducing the dislocation in p-GaN epilayer. However, upon implementing higher NH\(_3\) flux during the I-SMAT to 2.3 and 4.0 SLM, an increase in the FWHMs for all the off-axis diffraction plane was observed to increase. Such phenomenon relates well with the on-axis measurements as well as the surface observations whereby the increase in NH\(_3\) flux would exert an excessive etching of the surface resulting in crystal quality degradation. Single ammonia treatment introduced by Song et al. \cite{15,16}, recorded 23 nm and 828 arsec for the RMS roughness and \( \langle \overline{1}1 \overline{2}3 \rangle \) XRC FWHM, respectively, while I-SMAT has improved the RMS roughness and \( \langle \overline{1}1 \overline{2}3 \rangle \) XRC FWHM values to 4.20 nm and 700.34 arsec, respectively. These prove that I-SMAT provides greater semi-polar \( \langle 11 \overline{2}2 \rangle \) GaN epilayer surface and crystal enhancement. It can be presumed that the enhancement of crystal quality semi-polar \( \langle 11 \overline{2}2 \rangle \) GaN via an optimized NH\(_3\) flux during I-SMAT would be owing to the multiple selective-area etching of dislocation sites \cite{15,26}. The thermal instability and differing bounding energy of dislocation sites existing on the GaN surface would be etched by NH\(_3\) \( (>1000^\circ C) \) \cite{15,26,28}. The reduction of \( \langle \overline{1}1 \overline{2}3 \rangle \) FWHM XRC might be due to the etched-facet by the lateral flow of NH\(_3\) on the crystal defect along the \( \langle \overline{1}1 \overline{2}3 \rangle \) direction \cite{15}. In turn, the subsequent GaN deposition will not follow the underlying dislocation further improving the crystal quality. Moreover, annealing with ambient NH\(_3\) would act as an in-situ cleaning for removal of contaminated carbon and oxygen on the GaN surface \cite{29,30}. Carbon and oxygen can easily be adsorbed onto GaN surface at macroscopic defects \cite{31–33}. Therefore, removal of contaminated carbon and oxygen on GaN surface would help with the enhancement of the crystal quality of the subsequent deposited GaN \cite{30}. However, excessive NH\(_3\) flux during the I-SMAT would extremely widen/deepen the dislocation sites deforming the area, which might cause for increased dislocation formation in the subsequent GaN deposition \cite{34}. Consequently, the growth direction would also be affected resulting in a polycrystalline epilayer.

Raman spectroscopy was used to determine the compressive stress of the GaN epilayers in conjunction to the I-SMAT technique with various NH\(_3\) flux. As shown in Fig. 7a, the \( \langle 10\overline{1}0 \rangle \) oriented sapphire substrate induced three peaks located at 378, 416, 740 cm\(^{-1}\) and are seen for all samples. \( E_2 \) (high), \( E_1 \) (TO) and \( A_1 \) (TO) peaks indicated as the active phonon modes for the semi-polar \( \langle 11 \overline{2}2 \rangle \) GaN epitaxial layers are also observed \cite{35}. The \( E_2 \) (high) phonon mode in the spectra can be used to
analyze the in-plane stress. $E_2$ mode is sensitive to strain of the GaN crystal. The standard compressive stress-free GaN $E_2$ (high) is located at 568 cm$^{-1}$, and a shift in the peak of $E_2$ (high) is proportional to the stress magnitude. All samples show the $E_2$ (high) phonon modes peaks located at 568 cm$^{-1}$. This indicates that all samples are compressive stress free in the GaN epitaxial layers. The FWHM of $E_2$ (high) phonon mode exhibits the crystalline quality of the GaN film. Fig. 7b shows the FWHM of GaN $E_2$ (high) mode peaks of all samples with T1 exhibits the smallest FWHM value if compared to others. This concurs with the previous XRC measurements where I-SMAT technique can be said to have efficiently treated the defects between the interlayers, leading to the enhancement of the crystal quality [36].

X-Ray Photoelectron Spectroscopy (XPS) was conducted by using synchrotron source (1400 eV) to study the effect of carbon and oxygen contamination in relation to the gallium ratio on the surface (Fig. 8a). Fig. 8b–d shows all XPS measurement calibrated with C1s peak (284.6eV). It is noteworthy that calibration with C 1s may have some error but sufficiently precise for measuring the chemical composition and energy of the samples [18]. The C1s, O1s and Ga 2p3/2 peaks are presented in all samples elucidate GaN surface is not free impurities

![Graph](image1)

**Fig. 7.** (a) Raman spectroscopy of all semi-polar (1122) GaN samples and (b) GaN $E_2$ (high) FWHM (cm$^{-1}$).

![Graph](image2)

![Graph](image3)

![Graph](image4)

**Fig. 8.** The XPS of (a) intensity ratios, (b) C1s, (c) O1s and (d) Ga 2p3/2. (e) XPS valence band (VB) spectra of all samples.
Fig. 8 illustrated the intensity ratio of C1s and O1s relative to Ga 2p3/2 with the surface of sample T1 has the lowest carbon and oxygen content. These results are well correlated with the AFM measurements suggesting carbon and oxygen contamination increases as the GaN surface roughness increases [38,39]. A rough surface exhibit larger surface area in which increases sites for carbon and oxygen atoms to adsorb efficiently surrounding the pitted area [39]. Thus, the I-SMAT technique would reduce the surface contamination leading to lower surface roughness. These contaminations on the GaN surface has proven unfavorable, whereby studies have shown that high carbon and oxygen contents trapped between the GaN and metal electrode interface, would degrade the electrical properties [40–42].  

The XPS valence band (VB) spectra shown in Fig. 8e were used to study the surface polarity of semi-polar (1122) GaN via the I-SMAT technique. The VB spectra mainly consists of S and P-like VB orbital states [43,44]. The denoted S1 peak corresponds to the VB orbital states as well as the surface adsorbates wherein: for Ga-polar surface, the P1 at 5.2 eV dominates and for N-polar, P2 at 9.5 eV dominates [45]. In addition, sample T0 and T1 exerts a dominant P1 peak implying Ga-polarity. However, T1 exhibit significantly higher dominance of P1 relative to P2 as compared with T0. This indicates that the I-SMAT technique with 1 SLM of ammonia flux would enhance the surface polarity (Ga-polar). Conversely, T2 and T3 induce dominant P2 peak denoting an occurrence of surface polarity change from Ga-polar to N-polar upon utilization of higher ammonia flux during the I-SMAT.  

The polarity inversion from Ga to N-polar as higher ammonia flux applied in I-SMAT might be due to high nitrogen content has been adsorbed by the underlying GaN during I-SMAT process [46,47]. As the polarity change from Ga to N, the surface adsorbates (C and O) was observed to increase, yielding higher contamination ratio and deep acceptor level defect relative to the Ga [48]. This indicates an optimum NH3 flux of 1 SLM during the I-SMAT would exhibit lower foreign adsorbates leading to an enhanced surface morphology as well as crystal quality.  

4. Conclusions  

Surface enhancement of semi-polar (1122) GaN epilayers was deemed successful with the use of the I-SMAT approach. Arrowhead-like features corresponding to the defect densities was observed to recede as a deformation of the terrace step to a uniformly distributed arrangement was observed with the use of 1 SLM of NH3. Such occurrence is seen to originate from the crystal quality enhancement where it is presumed that the use of selective-area etching would discard the dislocation propagation. Conversely, higher NH3 flux would facilitate excessive etching of the dislocation sites resulting in the commonly known twinned-grained formation. Additionally, excessive NH3 would also change the surface polarity of the epilayer leading to higher density of surface adsorbates which degrades the crystal quality.  

Declaration of competing interest  

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.  

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