Metal organic chemical vapor deposition of m-plane GaN epi-layer using a three-step approach towards enhanced surface morphology

Adreen Azman*, Ahmad Shuhaimi*, Al-Zuhairi Omar, Anas Kamarundzaman, Muhammad Imran Mustafa Abdul Khudus, Azharul Ariff, M.E.A. Samsudin, Norzaini Zainal, Saadah Abd Rahmana

a Low Dimensional Materials Research Centre (LDMRC), Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia
b School of Physics, Universiti Sains Malaysia, 11800 USM Penang, Malaysia
c School of Physics, Universiti Sains Malaysia, 11800 USM Penang, Malaysia

ABSTRACT

Specular m-plane (10̅10) gallium nitride (m-GaN) epi-layer are grown on m-plane (10̅10) sapphire substrates by metal organic chemical vapor deposition using a three-step approach. A two-step approach was used to grow m-GaN buffer layer (BL), while a three-step approach was applied to improve the surface morphology of the top m-GaN epi-layer at high temperature. The three-step approach started with growing m-aluminum nitride nucleation layer with an optimized ammonia flux during the growth of aluminum nitride. Then the temperature was ramped up during the recrystallization step before the m-GaN BL deposition at low-temperature and the growth of m-GaN layer at high-temperature for the final step. Unexpectedly, when ammonia flow was intentionally halted during the recrystallization step, the surface morphology of the BL drastically changed from three- to two- dimensional with an abrupt cross-sectional structure. This in turn facilitated the complete coalescence of the m-GaN layer as revealed by field emission scanning electron microscopy. The three-step technique was found to affect the quality of m-GaN epi-layer as the samples exhibit improved crystallinity with X-ray diffraction rocking curves widths of 4680 and 1980arcsec along the azimuth, perpendicular and parallel to [10̅10] directions, respectively.

1. Introduction

Gallium nitride (GaN) devices have been traditionally grown on the c-plane (0001) due to their various applications in optoelectronic and high power electronic devices [1,2]. However, the performance of c-plane GaN have been shown to be limited by the piezoelectric polarization along the polar-axis of the quantum well [3]. Therefore, numerous efforts have been undertaken to grow GaN along non-polar directions such as non-polar m- and a-GaN [4,5]. However, studies have failed to yield m-GaN epi-layers with smooth surface morphology grown on m-sapphire substrate [6]. In fact, previous attempts growing GaN on m-sapphire have only yielded semipolar GaN (10̅13) or (11̅22) orientation with rough surface morphology [7,8].

The m-GaN epi-layers grown on m-sapphire typically employ a four-step growth technique consist of (i) nitridation, (ii) aluminum nitride nucleation layer (AlN NL) growth, (iii) recrystallization and (iv) buffer layer (BL) growth [9]. Earlier attempt by Armitage and Hirayama show that by avoiding nitridation and deposition of AlN NL at 500 °C results in single crystal of m-GaN on m- sapphire substrate. Further work has shown that a device quality m-GaN requires the optimization of growth parameters such as the growth temperature and mole ratio of ammonia (NH₃) from group V to group III (V/III ratio) for both the nucleation and epitaxial layers [10-12]. Prior to the optimization of the NL, the polarity of AlN NL can be tuned by avoiding surface nitridation to achieve m-plane (10̅10) template [13,14]. Several groups have also reported two-step growth approaches to determine the crystal quality of the subsequent epi-layer properties just by avoiding nitridation [15,16]. In addition, the growth window for m-GaN layer is narrower as compared to the conventional GaN growth [17,18].

The work here employs a three-step technique to enhance the growth of the top m-GaN epi-layers towards improved surface morphology and crystallinity. In this work, a transition from three-dimensional (3D) to two-dimensional (2D) mode of growth was observed in the absence of NH₃ flow during the recrystallization step for the BL growth. The crystal orientation of m-GaN on m-sapphire using AlN NL is dependent on the nitridation process [19]. The results indicate that m-GaN layer structure using the three-step approach is an alternative method to improve the heteroepitaxy quality of m-GaN epi-layer [20].

* Corresponding authors.
E-mail addresses: adreen@nitride.org.my (A. Azman), shuhaimi@um.edu.my (A. Shuhaimi).

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2. Experimental procedure

Experiments were performed using two-inch \textit{m}-plane sapphire substrate in a low-pressure, three-flow horizontal metal organic chemical vapor deposition reactor from Taiyo Nippon Sanso Corporation. Trimethylgallium, trimethylaluminium, and NH$_3$ were use as precursor with hydrogen (H$_2$)/nitrogen as gas carrier.

First, the substrate was heated for ten minutes at a temperature of 1125°C under H$_2$ ambient. Then, the temperature was ramped down to 600°C for the first-step growth of AlN NL. The thickness of AlN NL is 30.0 nm and the V/III ratio was varied from 100 to 600. After the NL growth, the NH$_3$ flow was stopped during the recrystallization step for 30 min while the temperature was ramped up to 800°C for the second-step growth of m-GaN BL at 200.0 nm thick. Finally, the High Temperature GaN (HT-GaN) was deposited using third-step growth at a temperature of 1125°C. The HT-GaN were grown at two different thickness namely 500.0 nm and 2.0 μm thick. The V/III ratio for the BL was varied from 650 to 2167 and for the HT-GaN, the V/III ratio was fixed at 650. Fig. 1 shows the growth steps of m-plane GaN epi-layers using three-step approach.

The structural properties of the AlN NL and GaN BL were characterized by High Resolution X-Ray Diffraction (HR-XRD). The ω-2θ scan was performed to study the optimization of V/III ratio effect towards the growth of m-(10\textit{m}) AlN NL and m-(10\textit{t}) GaN BL. For thicker m-GaN grown at HT, the crystal quality of the three-step growths was investigated using rocking curve (ω-scans). The surface morphologies of the samples were examined by Field Emission Scanning Electron Microscopy (FESEM) and Atomic Force Microscope (AFM) respectively. The effect of the V/III ratio on surface morphology was analysed to determine the best growth framework for the m-GaN epi-layer.

3. Results and discussion

3.1. Step-1: AlN nucleation layer

The first-step of growing m-GaN epi-layer is the deposition of AlN NL. During deposition, the AlN NL serves as an amorphous template for growing m-GaN epi-layer. In Fig. 2, the HR-XRD of 2θ-ω scans showed the crystal orientation of the AlN NL grown on m-sapphire substrate for different V/III ratio. The grown AlN NL grown on m-sapphire substrate without nitridation step shows three distinct orientation of m-(10\textit{f}), c-(0002) and α-(1120). It is clear that the AlN NL exhibit a strong (10\textit{f}) peak dominant to (1120) diffraction peak at lowest V/III ratio of 112. In contrast, when the V/III ratio was increased to 502, the observed diffraction pattern indicating that the (1120) peak was dominant as compared to lower V/III ratio. A mixed phase of (0002) and (1120) peaks emerge throughout the V/III variation ranging from 195 to 391. The existence of (0002) orientation at intermediate V/III ratio reveals that the growth window to achieve (10\textit{f}) orientation is narrower as compared to c-plane; whereas tuning the NH$_3$ flux at an appropriate range is the key factor to obtain an m-plane AlN template. This phenomenon reveals that to achieve a single non-polar orientation appear to be narrower as compared to polar c-plane AlN. Unlike m-AlN growth, polar c-AlN is relatively easy to grow due to its wide growth windows in terms of pressure, temperature, precursors and NH$_3$ flux [21]. While the m-AlN growth parameters are usually sensitive when the V/III ratio or NH$_3$ flux were increased. Thus, the effect of NH$_3$ flux is crucial in this experiment. Nitridation in this work was avoided prior to NL growth. As the nitridation time was too long, the surface of the substrate can be altered to promote GaN growth with semi-polar orientation [19]. These results demonstrate that single-phase AlN layers having various orientations such as (10\textit{f}), (1120) and (0002) AlN can be grown on m-sapphire by minimizing the V/III ratio. Base on the XRD scan, the intensity of (0002) and (1120) emerge to be high when the V/III ratio was increased.

The morphology of AlN NL with the optimum V/III ratio of 112 was observed by AFM and FESEM cross sectional shown in Fig. 3a and b, respectively. The surface roughness was found to be 0.33 nm. This indicates that the surface of AlN NL is smooth up to 5.0 μm × 5.0 μm region indicating specular surface for all the NL samples. Further analysis from the FESEM cross-sectional image, the AlN NL growths are laterally smooth with stripe-free features, which are the line defects that are often observed aligned perpendicular to c-axis GaN [22]. However, samples with nitridation exhibits semi-polar orientation associates with bad surface morphology [23]. This is because the nitridation process induces the formation of AlN layers consist of rough surface with defect compensation and slanted facets on the surface of the m-sapphire. The FESEM and AFM results corroborates that the cross-section and surface morphology for the AlN NL are inline proven by the abrupt structure with a smooth surface morphology. Therefore, the growth at low V/III ratio of 112 while avoiding nitridation favours m-AlN NL growth with good surface morphology.

3.2. Step-2: m-GaN buffer layer growth

The second step involves the optimization of the m-GaN BL growth at different V/III ratios. In this work, the BL was grown relatively at low temperature to accommodate a relaxation for the growth of a uniform
The growth of HT m-GaN without insertion of BL always results in the formation of 3D adatoms cluster and island formation. The BL structure was designated in a low temperature growth condition to improve the crystal quality of the HT-m-GaN. For a buffer layer that were grown higher than the temperature of 800°C, the epi-layer often featured black and not transparent to the eye. As mentioned earlier, BL growth is highly dependent on NH3 flow during the recrystallization process. In order to optimize the V/III ratio for BL growth parameters, the variation of the V/III ratio was performed as mentioned in Table 1. The V/III ratio for BL growth was set to be at 650 and 2167 to observe the effect of NH3 flow rate on the BL structure at high and low NH3 flux respectively. Fig. 4a and b, show the structure of the m-plane GaN BL/AlN NL/m-plane sapphire substrate and the XRD-2θ/ω scans for the m-GaN BL. The symmetric reflection showed perfectly single orientation of (1010) GaN with optimum AlN NL (V/III ratio = 112) and GaN BL (V/III ratio = 650) as the preferred orientation. The (1122) and (1120) orientation was not observed in the XRD patterns. Furthermore, the existence of AlN NL closed to the (1010) peak reveal that NL served as the template for BL grown. Hence, BL growth at an intermediate V/III ratio of 650 is favoured for the single orientation of (1010) m-GaN BL.

The cross-sectional image I, the surface morphology images II by FESEM, and AFM 3-D III of the m-GaN BL grown with different V/III ratio are depicted in Fig. 5. In order to justify the role of NH3 flow, growth of BL with NH3 flow for sample (A) was carried out during recrystallization step. The cross-sectional structure for sample (A) was mostly influenced by 3-D growth. It can be observed that the presence of NH3 flow during recrystallization step favoured an island growth and the surface roughness increased along [0002] for 500.0nm thick in the BL structure. However, when NH3 flow was stopped during the recrystallization step, the surface morphology of the m-plane GaN BL significantly improved from 3-D to 2-D, promoting lateral growth as reveal by FESEM images for samples (B-E) in Fig. 5. The drastic change in lateral growth and reduction of the defect such as v pits on the surface of BL justify that the role of NH3 flow should obviously discarded during the recrystallization step. At lower V/III ratio, the defect towards the surface has been reduced as sample (E) exhibit less.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Presence of NH3 flow during Recrystallization</th>
<th>AlN NL V/III ratio</th>
<th>m-GaN BL V/III ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>YES</td>
<td>112</td>
<td>2167</td>
</tr>
<tr>
<td>B</td>
<td>NO</td>
<td>502</td>
<td>2167</td>
</tr>
<tr>
<td>C</td>
<td>NO</td>
<td>112</td>
<td>2167</td>
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<tr>
<td>D</td>
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<td>502</td>
<td>650</td>
</tr>
<tr>
<td>E</td>
<td>NO</td>
<td>112</td>
<td>650</td>
</tr>
</tbody>
</table>

Fig. 3. a) AFM image 5 × 5μm² and b) cross sectional image of AlN NL by FESEM at optimized V/III ratio of 112.

Fig. 4. (a) Schematics structure of m-plane GaN BL/AlN NL on m-plane sapphire substrate and (b) the XRD-2θ/ω scans for m-plane GaN BL grown at V/III ratio of 650 for sample E.
striations propagating along the in-plane c-axis of [0002] of the cross-sectional image of sample (E). Therefore, the low NH₃ flux attributed the ideal V/III ratio for m-GaN BL.

Similarly, samples (B, C, D, and E) prepared in the absence of NH₃ flow during recrystallization step were found to have smoother surface at lower V/III ratio. The surface roughness Ra, and root mean square RMS roughness decreased with decreasing V/III ratio. In this case, the RMS value for sample (E), is 15.0 nm while the Ra is 4.0 nm. A significant increase can be observed in RMS value for sample (A) as the RMS value is double from sample (E). In order to justify the appropriate V/III ratio for the BL growth, the variation of V/III ratio and surface morphology indicated that the RMS and Ra corroborated to the effect of V/III ratio along with the AFM measurement. As the V/III ratio was decreased, the surface morphology became dependent towards the NH₃ flow. From this analysis, it is observed that the high Ra of sample (A), Fig. 5(III), results in very poor crystallinity dependent of the NH₃ role presence during recrystallization. Base on this, it is proven that to achieve a better surface morphology for the m-GaN epi-layer, the NH₃ flux should be flown at minimum flow rate. Samples that was grown at high V/III ratio always results in poor surface morphology due to high NH₃ flux. This is attributed to the high NH₃ flux at high V/III ratio which leads to non-uniform surface morphology such as grain structure formation. Formation of 3-D growth at high NH₃ flux was accredited to the diffusion length of adatoms towards the crystallographic direction of (1010) non-polar GaN and m-plane (1010) sapphire substrate [24]. Such evidence can be observed from the FESEM images of the BL growth in Fig. 5 (II). The less striations on the surface at lowest V/III ratio indicating that upon reducing the NH₃ flux, the surface morphology was successfully improved.

Obviously, when the NH₃ flux was increased to high V/III ratio for AlN NL, strong peak such as (0002), (1011), (1120) from the XRD 2θ-ω scans was observed, which could be due to the difference in the crystallographic growth. Some observations in the past has suggested that the surface symmetry of m-sapphire is higher than those of non-polar m-GaN films. The (1010) GaN films have a lower surface energy while the semi-polar tends to have a lower elastic energy [22]. Formation of twinning growths for the (1010) and (1013) oriented GaN films suggests that the growth window for m-plane is narrower as compared to the c-plane GaN growth.

### 3.3. Step-3: HT m-GaN growth

The final step involves HT-GaN growth with improved surface morphology. Here, the HT-GaN were grown at two different thickness, namely 500.0 nm and 2.0 μm as shown in Figs. 6 and 7. In this experiment, both samples exhibit a mirror-like surface which is essential criterion for the fabrication of electronic devices [25]. The FESEM images showed the presence of minor defects such as small striations and reduced triangular faceted pit v-shaped pit features along the c-axis [0002] in Fig. 6 (c). These pits however, can be suppressed by growing under the same condition at thicker sample, namely 2.0 μm thick. As shown in Fig. 6 (b), the 500.0 nm thick m-GaN grown at 1050°C indicated that the surface experience a suave transition from the BL to a smoother surface. When the sample was grown under the same condition but at thickness of 2.0 μm, the surface morphology was successfully ameliorated. This was evidenced by well-defined steps and terraces.
shown by the AFM images in Fig. 7 (d) with a surface roughness of 1.1 nm for m-plane (1010) HT-GaN for the 2.0 μm thick. From this analysis, it is shown that by growing m-GaN under the same V/III ratio condition with a different thickness namely 2.0 μm results in enhanced surface morphology at 1.0 nm of RMS roughness value. The improved surface morphology of the thicker sample is also further supported by FESEM as shown in Fig. 7b. However, the faceted v-shaped pits were absent as illustrated in Fig. 7c. Additionally, the growth of the m-GaN epi-layer at desired thickness promoted the significant improvements in the quality of the m-GaN epi-layer. Hence, the 2.0 μm thickness of m-GaN exhibited a uniform structure with an abrupt cross-sectional structure.

It is crucial to point out that some fissures were observed from the FESEM cross-sectional image in Fig. 6c for 500 nm m-GaN. However, by growing at higher thickness, namely 2.0 μm, these fissures were almost vanished, in which most of these features were generated from the LT-BL growth. Nevertheless, increasing the temperature to 800 °C, the BL experience a modest transition from 3D-2D growth mode as some defects were still observed such as v pits. In theory, the growth of 2D and 3D is often result from the diffusion length of adatoms on the surface. In this experiment, the growth at low V/III ratio exhibited a Ga-rich condition which Ga atoms predominantly cover the surface. This influences the bonding between Ga and nitrogen (N) atoms, thus it is crucial to tune the NH₃ flux at minimum flow in order to maintain good surface morphology with less pits [26]. Upon growing at 1050 °C, the generated pits continuously extent to certain level leaving some fissures from the FESEM cross-sectional image at 500.0 nm thick. Whereas the growth of the GaN (1010) at 2.0 μm was properly uniform as the v pits started to coalesce and form a 2-D constructive layer. Increasing the growth time to the desired thickness is crucial in order to understand the vital formation of layer between 500.0 nm and 2.0 μm.

The methods for evaluating the crystalline quality of the heteroepitaxial film is to measure the XRD rocking curves scan in symmetric configuration and fit the results with a broadening factor as observed in m-GaN epi-layer. Fig. 8 (A-B) shows the ω-scans of (1010) symmetric diffractions with X-ray incident plane aligned and parallel to [0001] direction respectively. The symmetric (1010) diffraction from m-GaN shows a significant reduction in the full width half maximum (FWHM) values. This characteristic was always observed in m-GaN epi-layer, and could be attributed to structural imperfections and anisotropic properties. Based on these results, the quality of 500.0 nm for top m-GaN epi-layer exhibited 6480 and 2880 arcsec along the azimuth perpendicular and parallel to directions, respectively. On the other hands, thicker samples at 2.0 μm for top m-GaN layer exhibited narrower FWHMs of 4680 and 2880 arcsec respectively. This significant change strongly suggested the improvement of the crystalline quality of m-GaN layer for thicker samples. A summary of all data shows the trend of FWHM decreases as a function of surface roughness. The trend indicated that the optimization was in parallel for three-step approach as the surface roughness showed improved surface morphology, which in turn might be resulted from the epi-layer thickness. Thus, it is shown that by growing m-GaN under the same condition but at different thickness, namely 2.0 μm, results in enhanced crystal quality with lower FWHM values and a reduced surface roughness of 1.0 nm.

4. Conclusion

The significant transition towards the enhanced surface morphology showed that the three-step approach is promising to achieve the growth of m-GaN epi-layer. By employing a three-step approach, the m-plane gallium nitride epi-layer grown on m-plane sapphire exhibit enhanced structural and morphological properties. Accordingly, the two-step and
three-step growth showed a transition from 3D to 2D growth mode at lower V/III ratio and enhanced the surface morphology of the $m$-GaN layer.

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References


Fig. 7. (a) Schematic structure, (b) Plain view of FESEM image, (d) Cross-section FESEM image and (d) A 5 × 5 μm AFM image for 2 μm HT $m$-plane GaN.

Fig. 8. Symmetric and asymmetric XRD omega scans for $m$-GaN layer on $m$-sapphire. The two symmetric scans shown correspond to data for x-rays incident perpendicular or parallel to the c-GaN at V/III 112 for AlN NL and 650 for $m$-GaN at (A) 500 nm and (B) 2.0 μm $m$-GaN.


