Standard pressure deposition of crack-free AlN buffer layer grown on c-plane sapphire by PALE technique via MOCVD

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ABSTRACT

A high-quality aluminium nitride buffer layers were grown on (0 0 0 1) sapphire substrate at standard pressure with a subsequent low growth temperature via metal organic chemical vapour deposition. The preparation of aluminium nitride buffer layers was accomplished by growing a thin aluminium nitride nucleation layer through a nominal growth condition followed by deposition of a thick aluminium nitride film using pulsed atomic-layer epitaxy technique. In 13.3 kPa ambient, the influence of aluminium nitride nucleation layer on the crystal quality of the aluminium nitride film atop was studied by varying the nucleation layer growth temperature at 700, 800, 900, 1000 and 1100 °C, respectively. It was observed that the growth temperature of nucleation layer substantially affected the structural properties of the top aluminium nitride film where the lowest value for symmetric (0 0 0 2) and asymmetric (1 0 – 1 2) x-ray rocking curve analysis were achieved at 1100 °C, indicating the reduction of dislocation density in the aluminium nitride films. In line with that, this result was sustained by the root mean square surface roughness evaluated via atomic force microscopy. Moreover, an atomically-flat crack-free aluminium nitride buffer layer was demonstrated by field emission scanning electron microscopy measurement.

1. Introduction

Recently, the evolution of solid state optoelectronic devices such as laser diodes (LDs) and light emitting diodes (LEDs) operating in the ultraviolet (UV) region has attracted considerable interest due to their applications in a variety fields. Indeed, high brightness of LDs or LEDs operating in the deep-UV region (wavelengths of 200–270 nm) are extensively applied for biagent detection, water or air purification, material sterilization as well as the light sources for a short-range line-of-sight communication [1,2]. The fabrication of these devices typically involves the deposition of a buffer layer on top of a c-plane sapphire substrate. Traditionally, gallium nitride (GaN) epilayer was grown before the growth of subsequent device structures in order to overcome most of the epitaxial issues during growth [3]. However, GaN has strong optical absorption in the UV region, and thus is detrimental to the performance of the entire device [4]. It is thus imperative that a GaN-free technology on c-plane sapphire substrates be developed for the fabrication of deep-UV optoelectronic devices.

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A promising material for the buffer layer is aluminium nitride (AlN) due to its large intrinsic bandgap, high thermal conductivity as well as high temperature and chemical stability [5]. Furthermore, AlN epilayers grown on sapphire have very good lattice and thermal expansion coefficients matching as compared to GaN epilayers for heterostructures growth devices [6]. For AlN to be suitable as a buffer layer, it has to be atomically flat with a crack-free surface, has low threading dislocation density (TDDs) and has stable in Al (+c) polarity [7,8]. However, the large lattice mismatch between sapphire and AlN (∼13.3%) as well as the need to grow at high temperature (>1250 °C), have generally yielded AlN layers with a low emission efficiency due to low internal quantum efficiencies (IQE) of the Al-rich deep-UV emitters.

Despite these challenges, recent research made significant progress in the growth of high quality AlN buffer layers on c-plane sapphire substrates for deep-UV epitaxy. The general technique for the fabrication of such devices via MOCVD includes the careful selection of the V/III ratio, the introduction of flow-modulation growth process as well as by the careful control of temperature and pressure for the AlN nucleation layer [9]. M. Takeuchi et al. has reported the growth on c-plane sapphire substrate of Al- and N-polar AlN layers by introducing flow-modulation MOCVD, whereby the flow of the Al gas is modulated while a steady flow of NH3 is maintained during the growth process. In their report, the surface polarities were distinguished by introducing a surface pre-treatment technique prior to the growth of AlN seeding layer. This method is believed to avoid the strong vapour-phase reaction between the ammonia gas (NH3) and trimethylaluminum (TMA) precursor and improve the surface migration of Al atoms [10]. More recently, H. Wang et al. [11] has demonstrated good quality AlN films using pulsed atomic-layer epitaxy (PALE) technique on sapphire substrate while varying the AlN nucleation layer growth temperature through the nominal growth process. The growth was prepared at low temperature and at a very low pressure (5 kPa) in order to enhance the Al ad-atoms mobility, as the growth of AlN epilayer at low temperatures is challenging due to the shorter diffusion length unless done at very low pressures. The relationship between vacuum pressure and temperature on the growth of AlN epilayers was studied in detail by M. Takeuchi et al. [12] by employing the flow-modulation MOCVD technique who found that the low temperature and low-pressure growth condition produces AlN crystals with the best quality. This is thought to be due to the suppression of the vapour-phase reaction, producing clear oscillation between both atoms and maintaining the Al-rich growth condition. However, epilayers grown at low pressures have been shown to exhibit a higher probability of non-radiative recombination due to a higher carbon content from the TMAI precursor and may be minimized by growing the epilayer at standard pressure [13]. Furthermore, low pressure growth typically has a lower growth rate, and thus will have longer deposition period in order to get the desired epilayer thickness [14]. Therefore, it is preferable to grow at standard pressure even at low temperature if the crystal quality of the AlN epilayer can be maintained.

In this study, we demonstrate standard vacuum pressure deposition of crack-free atomically-flat surface AlN buffer layer grown on c-plane sapphire substrate using PALE technique via MOCVD at the standard vacuum pressure of 13.3 kPa. This was accomplished by growing a thin AlN nucleation layer (NL) through nominal growth process, followed by the deposition of thick AlN films using the PALE technique. The temperature of AlN NL was set at 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C to optimize the quality of top AlN films grown using PALE technique at 1180 °C. The effect of the temperature on the surface roughness, dislocation density and structure quality are also studied.

2. Experimental procedure

In this work, a 2-inch sapphire substrate with a (0 0 0 1)-crystal orientations was employed. The epitaxial growth was attained in a horizontal reactor MOCVD operating at a pressure of 13.3 kPa with a continuous flow of hydrogen (H2) gas as the gas carrier. The ammonia gas (NH3) and trimethylaluminum (TMAI) metal organic (MO) precursor were used as the nitrogen (N) and aluminium (Al) reactant source materials for the epitaxial growth. All the processes were done at an ambient vacuum pressure of 13.3 kPa.

Initially, the substrate was baked inside the reactor under H2 ambiance at 1000 °C for 10 min to remove the native oxides on the substrate surface [15]. This thermal cleaning process did not exceed 1500 °C in order to avoid the sapphire structure from deteriorated [2]. In order to prepare the sapphire substrate before the growth of AlN film by the PALE techniques, a 30 nm thick AlN nucleation layer (NL) was first been grown by simultaneously supplying TMAI and NH3 flows of 53 sccm and 5 SLM at 700 °C, respectively. After the deposition of AlN NL, a 250 nm thick of AlN film was deposited on top at 1180 °C by TMAI and NH3 pulsed-flow growth method [15]. The pulsed-flow was achieved by flowing TMAI and NH3 gases for 4 and 2 s alternately until the desired thickness was achieved. This procedure corresponds to the growth rate of 3.75 nm/min. The epitaxial growth process was then repeated with temperatures of 800 °C, 900 °C, 1000 °C and 1100 °C to study the effect of temperature on the quality of the top grown AlN films. However, the epitaxial growth temperature did not exceed 1200 °C due to the limitations of the reactor. Fig. 1(a) schematically shows the gas flow sequence used for TMAI and NH3 pulse-flow growth and Fig. 1(b) present the schematic diagram of the epitaxial growth structure. The samples were then analysed using atomic force microscopy (AFM), field effect scanning electron microscopy (FESEM) and high-resolution x-ray diffractometer (HR-XRD) for x-ray rocking curve (XRC) measurement in order to study the morphological and structural properties of the resulting AlN films.
3. Result and discussion

The growth temperature of AlN NL is an essential parameter for high quality AlN film grown using PALE techniques on c-plane sapphire substrates. The effect of AlN NL temperature on the surface quality of the top PALE AlN films deposited at standard pressure is studied with AFM, presented in Table 1. It is clear from Table 1 that the root mean square (RMS) roughness value for the top PALE AlN films decreased from 6.76 to 0.49 nm with the increase of the nucleation layer temperature from 700 °C to 1100 °C. The result also showed that at the highest temperature of 1100 °C, the surface of top PALE AlN films appeared to be more homogenous and uniform. Indeed, despite aligned pits clearly visible, the substrate is nonetheless completely covered by AlN with an atomically near-flat surface [2]. Since a normal-oriented c-plane sapphire substrate is used for the growth, there are no sites for Al atoms to incorporate into, resulting in high atom concentrations on the surface exceeding the critical super-saturation point [16]. From Table 1, a large reduction in the RMS value occurred between 800 °C and 900 °C. This may be explained from the fact that at low NL growth temperatures, Al adatoms have relatively low mobility, creating many nucleation sites [11]. As the deposition of top PALE AlN films was done at a higher temperature of 1180 °C, the Al adatoms have sufficient mobility to move to energetically favourable sites, thus forming AlN islands with random sizes. As the film thickens, some larger islands may inhibit the growth of smaller ones, leading to the formation of the observed pits and resulting in the higher RMS value. In contrast, at higher NL growth temperatures, the Al adatoms mobility is enhanced, causing fewer nucleation sites to be created and uniformly distributing the AlN islands. This began at a NL growth temperature of 900 °C, forming near atomically-flat surface after the deposition of top PALE AlN films as the growth window of AlN NL begins to widen and the Al adatoms have higher diffusion length, providing nearly stoichiometric composition of the vapour phase [17]. At 1100 °C, the AlN NL has sufficient surface energy generated from the higher surface mobility and is able to overcome the mismatch issue with the substrate, producing the lowest RMS value. This thus reduces the grain boundaries and maximize the coalescence surface ratios [18,19].

The five samples were then further characterized using FESEM under 1000 times magnification, presented in Fig. 2. The morphological evolution of the five samples can clearly be observed in the images, where faceted crystallites structure being present on the surface of top PALE AlN films grown at low temperatures NL and gradually smoothens until becoming nearly atomically-flat as the temperature is increased. The deep valleys between islands observed at low temperatures NL may be attributed to the segregation of excess TMAl. This is not present at higher NL growth temperatures due to the high surface energies and fewer nucleation sites are created. The growth mode at the higher temperatures therefore transitioned from being dominated by 3D growth to dominated by 2D growth, indicating the completion of the coalescence process after the deposition of top PALE AlN films [16]. In addition, the growth mode of the AlN films transitioned from layer-by-layer to island growth as the growth temperature is increased from 700 to 1100 °C. The FESEM image of AlN NL grown at 1100 °C also show a crack-free surface of top the PALE AlN film. The high growth temperature exhibited high diffusion lengths and strong lateral growth which allows the smoothening of the top PALE AlN films as well as restraining the propagation of dislocations [20]. This results provides additional evidence to support the notion that a higher surface mobility with maximal surface coalescence ratios of top PALE AlN films was obtained for an AlN NL grown at 1100 °C. In order to verify this, x-ray rocking curve measurements was done for all the grown samples.

The significance of AlN NL temperature on the structural properties of top PALE AlN films grown on c-plane sapphire substrate
Table 1
The AFM images of the PALE AlN/sapphire surface morphologies with 30 nm AlN NL deposited at 700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C under vacuum pressure of 13.3 kPa.

<table>
<thead>
<tr>
<th>AIN-NL Temperature (°C)</th>
<th>2-Dimensional</th>
<th>3-Dimensional</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>6.76</td>
</tr>
<tr>
<td>800</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>6.10</td>
</tr>
<tr>
<td>900</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>1.21</td>
</tr>
<tr>
<td>1000</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>0.98</td>
</tr>
<tr>
<td>1100</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>0.49</td>
</tr>
</tbody>
</table>
was further studied via XRC analysis. Two different XRC analysis were performed, namely, the symmetric (0 0 0 2) and the asymmetric (1 0 –1 2) analyses, with the former employed to investigate the screw dislocation and the latter to study the edge and mixed dislocation that occurred in the top PALE AlN films [22]. The full width-at-half maximum (FWHM) values for both analyses with their threading dislocation densities (TDDs) are plotted in Fig 4(a) and (b). The graph shows that the FWHM and TDDs values for both analyses decrease with increasing of AlN NL temperature. Indeed, at an AlN NL temperature of 1100 °C, the lowest FWHM values were recorded - 86.4 arcsec for the (0 0 0 2) analysis and 820.8 arcsec for the (1 0 –1 2) analysis. The decrease in the FWHM values for both symmetry and asymmetry analyses with the increase of AlN NL temperature indicate a reduction of dislocation density in the top PALE AlN films. From the XRC analysis results, the TDDs for screw (\(D_S\)) as well as mixed and edge (\(D_E\)) may be estimated from Ref. [23]:

\[ D_S = \frac{\beta_S^2}{4.35 |b_S|^2} \]  

\[ D_E = \frac{\beta_E^2}{4.35 |b_E|^2} \]  

where \(b_S\) and \(b_E\) are the Burgers vector sizes of the screw and, mixed and edge TDDs, respectively, with \(\beta_S\) and \(\beta_E\) being the FWHM value in radiant. Here, \(b_S = 0.4982\) nm and \(b_E = 0.3112\) nm. The values of the TDDs are given in Table 2.
The minimum values recorded were $1.63 \times 10^{-7}$ cm$^{-2}$ for screw dislocation and $3.76 \times 10^{-9}$ cm$^{-2}$ for edge and mixed dislocation, respectively. This trend is thought to be due to the enhancement of Al ad-atoms surface diffusion caused by a smaller probability to react with N ad-atoms and is in agreement with previous work which showed a positive correlation between the coalescence of AlN epilayers with the increase in growth temperature [24,25].

The existence of the edge dislocation may be explained as follows: during the initial stage of the growth, small three-dimensional grain islands are deposited and subsequently incorporated into bigger grains resulting in much larger grains, with the edge dislocations being produced during the incorporation process [26]. This results also support the notion that the compressive stress induced by the AlN NL grow at 1100 °C is minimized, effectively restraining the crack generation while simultaneously reducing the dislocation density. The increasing AlN NL growth temperature thus result in decreasing densities of TDs in top PALE AlN films. Here, the elongated AlN islands NL grown at high temperature form larger and relatively uniform grains, resulting in atomically flat surface without pits with smaller threading dislocation density forming during the coalescence process after the deposition of the top PALE AlN films. It is however essential to note that the FWHM value may be further reduced if the thickness of the top PALE AlN films are increased as the incident x-ray beam will be detecting only the AlN lattice and not the sapphire lattice [19,27]. Hence, these results are comparable with other publication, by which the FWHM value was around 80–140 arcsec for AlN buffer layer at thickness 300 nm grow at low pressure [10].

### Table 2
Summary of XRC measurement and threading dislocation density at various AlN NL growth temperature.

<table>
<thead>
<tr>
<th>AlN NL Temperature (°C)</th>
<th>FWHM (0002) (arcsec)</th>
<th>FWHM (10–12) (arcsec)</th>
<th>TDDs (0002) (cm$^{-2}$)</th>
<th>TDDs (10–12) (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>759.6</td>
<td>2847.6</td>
<td>$1.26 \times 10^9$</td>
<td>$4.53 \times 10^{10}$</td>
</tr>
<tr>
<td>800</td>
<td>601.2</td>
<td>2653.2</td>
<td>$7.87 \times 10^8$</td>
<td>$3.93 \times 10^{10}$</td>
</tr>
<tr>
<td>900</td>
<td>136.8</td>
<td>1422.0</td>
<td>$4.08 \times 10^7$</td>
<td>$1.13 \times 10^9$</td>
</tr>
<tr>
<td>1000</td>
<td>126.0</td>
<td>1144.8</td>
<td>$3.46 \times 10^7$</td>
<td>$7.31 \times 10^8$</td>
</tr>
<tr>
<td>1100</td>
<td>86.4</td>
<td>820.8</td>
<td>$1.63 \times 10^7$</td>
<td>$3.76 \times 10^7$</td>
</tr>
</tbody>
</table>
4. Conclusion

This paper discusses the effect of in situ aluminium nitride nucleation layer temperature on the morphological and structural properties of the top aluminium nitride films grown by metal organic chemical vapour deposition using pulsed atomic-layer epitaxy techniques at standard vacuum pressure on c-plane sapphire substrate. It was then being investigated through field emission scanning electron microscopy, atomic force microscopy and x-ray rocking curve analysis. The outcomes promote the morphological and crystal quality of the top aluminium nitride films tremendously improved after the aluminium nitride nucleation layer grown at 1100 °C under 13.3 kPa ambient. Where the root mean square value for top aluminium nitride films surface roughness was 0.49 nm. Furthermore, we also determined the images obtained using field emission scanning electron microscopy for sample with 1100 °C of aluminium nitride nucleation layer growth temperature showed a crack-free with almost atomically-flat surface. So, we justified that the compressive stress induced by the aluminium nitride nucleation layer grown at 1100 °C has effectively restraint the crack generation.

Moreover, in the symmetric and asymmetric x-ray rocking curve analysis, the samples with aluminium nitride nucleation layer grown at 1100 °C exhibited the lowest full width at half maximum value with 86.4 arcsec and 820.8 arcsec, respectively. The reduction value of full width at half maximum denoted the reduction of dislocation density for screw as well as edge and mix dislocation density in the top aluminium nitride film with 1.50 × 10^6 cm^−2 and 3.58 × 10^5 cm^−2, respectively. Hence, an initiation growth of a high quality aluminium nitride buffer layer has well been developed on c-plane sapphire substrate by a combination of nominal growth and pulsed-flow growth technique with nucleation layer grow at 1100 °C under 13.3 kPa ambient.

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