***Temperature dependence of the crystalline quality of AlN layer grown on
sapphire substrates by metalorganic chemical vapor deposition***

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Abstract

We studied temperature dependence of crystalline quality of AlN layers at 1050-1250 °C with a fine increment step of around 18 °C. The AlN layers were grown on *c*-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD) and characterized by X-ray diffraction (XRD) ω -scans and atomic force microscopy (AFM). At 1050-1068 °C, the templates exhibited poor quality with surface pits and higher XRD (002) and (102) full-width at half maximum (FWHM) because of insufficient Al atom mobility. At 1086 °C, the surface became smooth suggesting sufficient Al atom mobility. Above 1086 °C, the (102) FWHM and thus edge dislocation density increased with temperatures which may be attributed to the shorter growth

mode transition from three-dimension (3D) to two-dimension (2D). Above 1212 °C, surface macro-steps were formed due to the longer diffusion length of Al atoms than the expected step terrace width. The edge dislocation density increased rapidly above 1212 °C, indicating this temperature may be a threshold above which the impact of the transition from 3D to 2D is more significant. The (002) FWHM and thus screw dislocation density were insensitive to the temperature change. This study suggests that high-quality AlN/sapphire templates may be potentially achieved at temperatures as low as 1086 °C which is accessible by most of the III-nitride MOCVD systems.

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1. Introduction

Deep-ultraviolet (DUV) emitters based on III-nitrides including light-emitting diodes (LEDs) and laser diodes (LDs) can be applied to important areas such as disinfection and digital data storage. Although bulk AlN substrates are ideal for the growth of DUV emitters due to their low-dislocation density as well as reduced lattice and thermal mismatch with high-Al content III-nitrides [1], the application is constrained by limited supply, high cost, DUV absorption, and small substrate size. Thus commercialization of the III-nitride DUV emitters still largely relies on the use of AlN heteroepitaxial templates grown on the vastly-available, low-cost, DUV-transparent, and larger foreign substrates especially *c*-plane sapphire substrates. However, the large lattice and thermal mismatch between AlN and sapphire leads to high dislocation density. As performance of III-nitride DUV emitters is very sensitive to the dislocation-related non-radiative recombination centers [2,3], it is crucial to reduce the dislocation density of AlN templates for the devices grown and fabricated thereon.

One of the common approaches to reducing the dislocation density is epitaxial lateral overgrowth (ELO) where AlN layers are re-grown on patterned seeding AlN templates [4-7]. However, because the ELO approach involves cleanroom fabrication like lithography and etching as well as a regrowth process of the several μm thick layer to coalesce and form a flat layer over the patterned templates, it is associated with much more additional cost and processing time, uneven surfaces, and growth complexity. Another common approach, the use of pulsed atomic layer epitaxy (PALE), has been implemented where supplies of N and/or Al sources are supplied in a pulse mode to allow Al atoms additional time to mobilize on the epitaxial surface [3,8,9]. In some studies, the ELO and PALE were both employed to accelerate the coalescence over the patterned templates [5,7].

In addition to the ELO and PALE, high-temperature growth above 1200 °C has been employed independently or jointly with the ELO and PALE to achieve low dislocation density and smooth surface morphology by metalorganic chemical vapor deposition (MOCVD), in that the mobility of Al atoms on the epitaxial surface is enhanced at high temperature [10-17]. However, there are some concerns regarding high-temperature growth. Not only does it require a special reactor configuration and/or part coating to reach high temperature, but it can also cause considerable thermal stress and cracks in the heteroepitaxial film due to the large thermal expansion mismatch between AlN and sapphire [18]. In addition, the serious wafer bowing of AlN templates at high temperature can also deteriorate wafer uniformity in terms of the template thickness and the composition of layers grown heteroepitaxially on the template [19,20]. To overcome these issues, there have been some attempts to grow AlN layers on sapphire [21] and SiC [22] substrates below 1200 °C. However, surface of these AlN templates was found to possess a high density of point defects [21,22]. In other words, there have been very few successful studies of growing high-quality planar AlN templates on the sapphire substrates below 1200 °C to our knowledge. In addition, temperature-dependent experiments were carried out previously to grow AlN templates at 1100-1500 °C [16,17,21]. However, the studies were performed with a large increment step of 100 °C. Hence it was not possible to find out variation of crystalline quality within a smaller range of temperature and thus potential optimum temperatures therein.

In this work, we carried out a temperature-dependent experiment to investigate the temperature influence on the crystalline quality of two-layer AlN templates. The template temperatures T_t ranged from 1050 to 1250 °C with a fine increment step of around 18 °C. The goal was to identify trends of crystalline quality variation and a proper temperature range which

could lead to sufficient Al mobility for the growth of high-quality AlN/sapphire templates. Details of growth process and characterization are presented hereafter. Neither the ELO nor PALE approach was used in this study. The AlN crystalline quality was characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM).

2. Temperature dependence of crystalline quality of AlN template

2.1 Experimental

To investigate the temperature dependence of the AlN template quality, twelve crack-free AlN templates with a simple two-layer structure were grown by MOCVD at various template temperatures T_t on two-inch diameter *c*-plane sapphire substrates with an offcut angle of 0.2° toward the *a*-plane. This offcut angle is expected to lead to an atomic step terrace width of ~ 89 nm. The MOCVD system used in this study was an AIXTRON $3\times 2''$ close-coupled-showerhead (CCS) system. The emissivity-corrected surface temperature was measured by a dual-wavelength multiple-point pyrometric profiling system. Trimethylaluminum (TMAI) and ammonia (NH_3) were used as precursors and hydrogen (H_2) as carrier gas. Prior to the AlN growth, the susceptor and sapphire substrates were baked at 1100°C for five minutes in a H_2 ambient. A dose of $0.57\ \mu\text{mol}$ of TMAI was deposited at 930°C after the bake to pre-condition the sapphire surface for Al-polar AlN layers [23]. It is noted that the dose of TMAI can vary depending on the reactor design. For instance, our similar $6\times 2''$ CCS MOCVD system does not need any TMAI pre-conditioning to grow Al-polar AlN layers on the sapphire substrate. The lack of a requirement for TMAI pre-conditioning was also observed by Reentila, et al., using an $11\times 2''$ planetary MOCVD system [11]. However, with insufficient TMAI pre-conditioning in our $3\times 2''$ CCS MOCVD reactor, the surface of the AlN/sapphire template becomes rough and hazy, which is attributed to the mixed polarity AlN [23,24], as exemplarily exhibited in Figure 1. As shown in

Figure 2, the AlN template structure comprised two layers: (1) a 25-nm thick AlN buffer layer grown on the sapphire substrate at 930 °C after the TMAI pre-conditioning, and (2) subsequently a 780-nm thick AlN template layer grown at one constant template temperature T_t within the range of 1050-1250 °C with an increment step of around 18 °C and a V/III ratio of 77. Except the template temperature T_t , the other growth parameters were kept the same for all of these twelve samples. The total flow rate of precursors and carrier gas was kept constant at 20 slm. The reactor pressure was set at 85 mbar or 64 Torr during the growth of AlN layers. Despite the difference in temperatures, the growth rate of AlN template layer for all the samples measured by the *in-situ* reflectance was around 1.76 $\mu\text{m/h}$.

2.2 Results and discussion

The template temperature T_t dependence of the structural quality of the AlN templates were studied partially in terms of full-width at half maximum (FWHM) of XRD symmetric (002) and asymmetric (102) ω -scans as shown in Figure 3(a). The FWHM's of symmetric (002) ω -scan and asymmetric (102) ω -scans correspond to and are proportional to the screw dislocation density and the edge dislocation density, respectively. The screw dislocation and edge dislocation originate from the stacking faults tilting and twisting grain boundaries, respectively. In addition, Figure 3(b) shows the $5 \times 5 \mu\text{m}^2$ RMS surface roughness as a function of the template temperature T_t , which was extracted from the AFM images of Figures 4(a)-(l). The horizontal temperature coordinates of Figures 3(a)-(b) were aligned vertically. A close examination of Figures 3(a)-(b) reveals different trends of the template temperature T_t dependence of structural and morphological quality in three temperature ranges, as segregated by the dash line and summarized in Table 1.

In the first template temperature T_t range of 1050-1086 °C, the (102) FWHM and especially (002) FWHM at the lower temperature of 1050 °C were significantly higher than those at higher temperatures of 1068 and 1086 °C, indicating poor crystalline quality with high density of dislocations. As shown in Figure 4(a), large and deep pits were found on the surface, leading to high RMS roughness and suggesting incomplete coalescence of initial AlN three-dimensional (3D) islands at 1050 °C attributed to low Al atom mobility. As the template temperature T_t increased to 1068 °C, a steep decrease of the (002) FWHM, (102) FWHM, and RMS roughness was observed, indicating a dramatic improvement of crystalline quality because of the enhanced Al atom mobility. This was also reflected by the significant reduction of surface pit density shown in Figures 4(b)-(c), as compared with Figure 4(a).

In the second template temperature T_t range of 1086-1212 °C, the (002) FWHM stayed relatively constant, indicating the density of screw dislocation and thus the tilting of grain boundaries were not sensitive to the temperature change in this range. On the other hand, the (102) FWHM rose slowly with elevated temperatures, suggesting a gradual increase of the density of twisting boundaries. The surface was very smooth as shown in Figures 4(c)-(i) with RMS roughness between 0.24 nm to 0.34 nm. This suggests that the Al atom mobility was sufficient at template temperatures T_t as low as 1086 °C that had been largely considered to be a relatively low temperature for AlN growth by MOCVD previously.

In the third template temperature T_t range of 1212-1250 °C, the (002) FWHM still stayed relatively constant. But the (102) FWHM increased rapidly with higher template temperatures T_t , suggesting a template temperature T_t of 1212 °C may be a threshold, beyond which the formation of edge dislocations was accelerated. This implied that the tilting of grain boundary was insensitive to the temperature changes in the template temperature T_t range of 1086-1250 °C,

while the twisting became rapidly severe above 1212 °C. Meanwhile, the surface roughness increased due to the gradual formation of periodic macro-steps from 1212 °C as shown in Figures 4(j)-(l). Such surface morphology is undesirable for the fabrication of high-quality heterostructures [25]. A similar surface morphology was also observed by a recent study by Li, et al., who reported growing the AlN template layer at 1250° C [24]. The formation of macro-steps can be attributed to a thermodynamic process wherein the mobility of Al atoms was high enough that the diffusion length of Al atoms was longer than the atomic step terrace width at high temperature [26]. Although the formation of macro-steps appeared simultaneously with the accelerated increase of edge dislocation density, Shen, et al., have shown that the macro-steps can lead to dislocation bending and thus reduction of the dislocation density in GaN and AlN templates grown on sapphire substrates [27-28]. This means that the macro-steps should not be the cause of increased edge dislocation density.

In the growth of AlN templates on sapphire substrates, Okada, et al., have shown that the edge dislocation density was annihilated in the transition from three-dimensional (3D) island growth to two-dimensional (2D) growth and a slower transition leads to more efficient annihilation of threading dislocation originated from buffer layers [13]. In this work, the 3D-island growth dominated in the buffer layer at 930 °C and the template layer grown at or above 1050 °C provided 2D growth. At lower template temperatures T_t , the Al atom mobility was smaller leading to a slower transition from 3D to 2D growth. The slower transition thus enhanced the bending and annihilation of edge threading dislocation. At higher template temperatures T_t , the transition from 3D to 2D growth was shorter, leading to higher edge dislocation density.

Given these results and discussions, it is evident that the higher temperature growth does not necessarily lead to higher-quality AlN/sapphire templates as a result of the increased edge

dislocation density and surface roughness. It is important to note that this conclusion is different from some previous studies, where the high-temperature growth yielded better crystalline quality than the lower-temperature growth [16,17,21]. The discrepancy may result from different growth conditions including the use of PALE, temperature range, growth rate, V/III ratio, reactor condition, and layer structure. However, herein the AlN templates with a simple two-layer structure already shows relatively low surface roughness without the use of PALE which indicates adequate Al atom mobility can be obtained at temperatures as low as 1086 °C. Hence with further optimizations, high-quality planar AlN/sapphire templates may be potentially obtained at such reduced temperatures which are reachable by most of the III-nitride MOCVD reactors.

3. Conclusion

The dependence on template temperatures T_t of crystalline quality of two-layer planar AlN/sapphire templates grown by MOCVD was studied with a fine increment step of around 18 °C at 1050-1250 °C. Below 1068 °C, the templates showed poor crystalline quality with large and dense pits and high XRD (002) and (102) FWHM's, which were caused by incomplete coalescence of 3D AlN islands as a result of the low Al atom mobility. The template surface became pit-free and smooth at 1086 °C, indicating sufficient Al atom mobility. Above 1086 °C, the edge dislocation density increased with temperatures, which may be attributed to the shorter 3D to 2D growth mode transition. Above 1212 °C, surface macro-steps were formed due to longer diffusion length of Al atoms than the expected step terrace width. In addition, the edge dislocation density increased quickly which may be caused by an enhanced effect of the shorter 3D to 2D growth transition. The screw dislocation density was insensitive to the temperature change. This study suggests that high temperature growth does not necessarily lead to high-

quality AlN/sapphire templates, which however can be potentially achieved at reduced temperatures of around 1086 °C with further optimization, a temperature range accessible by most of the modern III-nitride MOCVD systems.

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Table 1. Trends of template temperature T_t dependence of FWHM's of XRD (002) and (102) ω -scans as well as $5 \times 5 \mu\text{m}^2$ RMS roughness of the two-layer AlN templates at 1050-1250 °C.

T_t Range °C	(002) FWHM	(102) FWHM	$5 \times 5 \mu\text{m}^2$ RMS roughness
(1) 1050-1086	Decrease	Decrease	Decrease
(2) 1086-1212	Constant	Constant	Constant
(3) 1212-1250	Constant	Increase fast	Increase fast

Figure captions

Figure 1. Photograph of the AlN/sapphire template grown by the AIXTRON 3×2” CCS MOCVD system with insufficient dose of TMAI pre-conditioning showing rough and hazy surface because of mixed polarity.

Figure 2. Cross-sectional schematic diagram of the two-layer AlN templates structures grown on the (0001) sapphire substrates with different template layer temperatures T_t at 1050-1250 °C.

Figure 3. (a) FWHM's of XRD (002) and (102) ω -scans, and (b) $5 \times 5 \mu\text{m}^2$ RMS roughness extracted from Figure 4 of the two-layer AlN/sapphire templates as a function of temperatures T_t .

Figure 4. (a)-(l) $5 \times 5 \mu\text{m}^2$ AFM images of the AlN templates at different template layer temperatures T_t at 1050-1250 °C. The RMS roughness for each sample is included.

Figures

Figure 1 of 4, Li et al.

Figure 2 of 4, Li et al.

Figure 3 of 4, Li et al.

Figure 4 of 4, Li et al.