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Featured Letter

Study of dual nitridation processes in growth of non-polar *a*-plane AlGaN epi-layers

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ABSTRACT

The effect of dual nitridation processes for both *r*-plane sapphire and low temperature-grown AlN (LT-AlN) nucleation layer on non-polar *a*-plane AlGaN epi-layer was studied intensively. A root-mean-square value as small as 1.54 nm for *a*-plane $Al_{0.53}Ga_{0.47}N$ epi-layer was achieved. It was revealed that the generation of AlN grains as well as the coalescence and recrystallization of LT-AlN islands were the key factors for growing *a*-plane AlGaN epi-layers with smooth surface morphology. Meanwhile, the evolution of surface morphology with varied nitridation processes and the mechanisms for improving surface morphology of *a*-plane AlGaN epi-layers were also investigated.

1. Introduction

The non-polar $\left(11\bar{2}0\right)$-oriented *a*-plane AlGaN-based light emitting diodes (LEDs) and laser diodes are desirable for achieving high efficiency in deep-ultraviolet (DUV) range due to the elimination of quantum confined Stark effect [1]. However, as a result of the anisotropic growth rates along various directions for *a*-plane AlGaN-based materials [2], undulation structures along (0001) *c*-axis will be generated on the surface of *a*-plane GaN epi-layers [3] and dense superficial pyramidal defects distributed along *c*-axis will also be generated on the surface of *a*-plane AlGaN epi-layers [4,5]. These typical structure features result in a much poorer surface morphology for the non-polar *a*-plane AlGaN epi-layer than their polar counterparts grown on *c*-plane sapphire substrates.

Recently, a root-mean-square (RMS) value of 2.02 nm for *a*-plane $Al_{0.68}Ga_{0.32}N$ epi-layer was achieved with a two-way pulsed-flow metal organic chemical vapor deposition (MOCVD) technology [4]. However, as the Al composition was decreased to be around 0.5 which is essential to make the emission wavelength of the AlGaN alloy in the DUV range, the RMS value was found to be approximately 5 nm. This value is obviously too large to grow a quantum well structure.

In this work, a RMS value as small as 1.54 nm was achieved for *a*-plane $Al_{0.53}Ga_{0.47}N$ epi-layer grown with an optimized nitridation process for both the *r*-plane sapphire substrate and the low temperature-grown AlN nucleation layer (LT-AlN NL).

2. Experimental

The *a*-plane AlGaN epi-layers used in this study were grown with a low pressure (40 Torr) two-way pulsed-flow MOCVD technology. Ammonia (NH_3), trimethyl-aluminum (TMAl), and triethyl-gallium (TEGa) were used as the precursors for N, Al, and Ga, respectively. Prior to the epitaxial growth, the *r*-plane sapphire substrate was heated up to 1060 °C in H_2 ambience to remove surface contamination. Then, NH_3 was fed with a flow rate of 100 mmol/min to conduct the first nitridation process for the sapphire substrate with a duration of t_{n1}. Subsequently, the temperature was decreased to 600 °C to deposit a 30 nm-thick LT-AlN NL·NH_3 flow was switched off during the temperature declining (from 1060 °C to 600 °C) process to ensure an accurate nitridation duration for the *r*-plane sapphire substrate. Then, the temperature was raised to 1100 °C in 4200 s and stabilized for a time of t_{n2} which is just equal to the duration of the second nitridation process for the LT-AlN NL. Then, the high temperature-grown AlN (HT-AlN) buffer layer was deposited on LT-AlN NL with two-way pulsed-flow

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growth method [4]. Finally, the temperature was fixed at 1060 °C to grow an 80 nm-thick AlGaN epitaxial layer with an Al composition of 0.53. Two groups of samples were named as samples A_1–A_5 and samples A_{31}–A_{34}, respectively, and grown with varied t_{n1} and t_{n2} to study the effect of the nitridation processes on the growth of the non-polar *a*-plane AlGaN epi-layers. The detailed nitridation process parameters for samples A_1–A_5 and A_{31}–A_{34} are summarized in Table 1. In addition, to investigate the evolution of the surface morphology of *r*-plane sapphire substrate, a series of *r*-plane sapphire substrate samples S_1-S_5 were treated at 1060 °C in NH_3 ambience with t_{n1} = 150, 240, 330, 480, and 660 s, respectively. Another *r*-plane sapphire substrate named as sample S_0 which was in its original epi-ready state was used as the reference sample.

Atomic force microscopy (AFM) was employed to characterize the evolution of the surface morphology with varied nitridation process duration for the non-polar *a*-plane AlGaN epi-layers and the *r*-plane sapphire substrates. The Al composition and the crystalline quality for the grown *a*-plane AlGaN epi-layers were evaluated with ultraviolet-visible spectrophotometer and high-resolution X-ray diffraction (HR-XRD), respectively.

3. Results and discussions

As shown clearly in Fig. 1(f), the RMS value decreased monotonously from 5.33 nm for sample A_1 to 2.50 nm for sample A_3 as t_{n1} was increased from 150 to 330 s. However, the RMS value increased monotonously from 2.50 nm for sample A_3 to 4.55 nm for sample A_5 while t_{n1} was further increased from 330 to 660 s. This fact indicates that a relatively smooth morphology can be achieved by carefully optimizing this important growth process. Moreover, the pyramidal defects that are distributing along *c*-direction on the surfaces and are the typical features for the *a*-plane AlGaN-based epi-layers [5], were identified to be more evident for samples A_4 and A_5 than sample A_3 as shown in Fig. 1(c)–(e). Therefore, it was inferred that the emergence of the evident pyramidal defects on the surfaces of samples A_4 and A_5 were due to the overlong nitridation duration for the sapphire substrates. Meanwhile, it is shown in Fig. 1(k) that the RMS value further decreased monotonously from 2.50 nm for sample A_3 to 1.54 nm for sample A_{32} as t_{n2} increased from 330 to 780 s and then increased monotonously from 1.54 nm for sample A_{32} to 2.63 nm for sample A_{34} when t_{n2} was further increased from 780 to 1380 s. This behavior is very similar to that associated with the RMS value variation as a function of t_{n1} for samples A_1–A_5 plotted in Fig. 1(f). It is well known that the LT-AlN islands will coalesce and recrystallize under high temperature conditions during the nitridation process of LT-AlN NL [6]. The LT-AlN NL with appropriate nitridation duration can promote the two-dimensional growth of the subsequently-grown HT-AlN buffer layer and thus result in smooth surface morphology for the topmost AlGaN epi-layer. As a result, a RMS value as small as 1.54 nm was achieved for sample A_{32} with t_{n2} = 780 s. Moreover, the pyramidal defects distributed along *c*-direction on the surfaces were observed to be more evident for samples A_{33} and A_{34} than samples A_{31} and A_{32} from Fig. 1(g)–(j). This feature and the increased RMS values for samples A_{33} and A_{34} reveal that the overlong nitridation process duration could trigger three-dimensional-like growth and hinder the coalescence of subsequently grown epi-layers [7].

To further investigate how the nitridation process of sapphire substrates affect the growth of *a*-plane AlGaN epi-layers, a series of sapphire substrate samples S_0-S_5 were prepared and evaluated by measuring AFM images within a detection area of $2 \times 2\ \mu m^2$. It was reported that the main phase of the nano-scale crystal nucleus distributed along a specific direction as demonstrated evidently in Fig. 1(m)–(q) was AlN grain with a preferred $\left(11\bar{2}0\right)$-orientation and the specific distribution direction is parallel to the sapphire $\left(\bar{1}102\right)$ axis [8]. Meanwhile, it was remarkable that both the density and the height of the AlN grains increased gradually as t_{n1} extended from 150 s for sample S_1 to 660 s for sample S_5 and the RMS values increased monotonously from 0.43 to 1.10 nm. Since the AlN grains with proper density and height benefits the growth of the subsequent LT-AlN NL which plays a critical role in the MOCVD growth of the non-polar *a*-plane AlGaN epi-layer, the RMS values for samples A_1–A_5 varies as a function of t_{n1}. Needless to say, improper density and height of the AlN grains will lead to poor surface morphology for *a*-plane AlGaN epi-layers since the superfluous AlN grains can trigger three-dimensional-like growth and hinder the coalescence of the subsequently grown epi-layers [7]. This is why the RMS values for samples A_4–A_5 increased as t_{n1} further extended.

The ultraviolet-visible relative light transmittance (RLT) spectra and the corresponding first-order derivative of RLT for samples A_1–A_5 and A_{31}–A_{34} were depicted in Fig. 2(a) and (b), respectively. It can be clearly observed that the absorption edges for the nine *a*-plane AlGaN samples A_1–A_5 and A_{31}–A_{34} are all located at approximately 265 nm, implying that the Al composition in all of the nine samples is primarily the same, and was determined to be 0.53. Fig. 3(a) demonstrates the HR-XRD ω-2θ scanning curve for sample A_1. The peaks located at 29.30 and 29.67° were identified to be the XRDs from the *a*-plane $Al_{0.53}Ga_{0.47}N$ and AlN epi-layers, respectively, indicating an excellent mono-crystal property. On the other hand, the X-ray rocking curves (XRCs) for samples A_1 and A_{32} were measured along *c*-direction ($\varphi = 0°$) and *m*-direction ($\varphi = 90°$), respectively. It was found that the full width at half maximum (FWHM) values in XRCs measured at $\varphi = 0°$ and $\varphi = 90°$ were reduced from 0.61 to 0.56° and from 1.03 to 0.96°, respectively. The decrease in FWHM value also implied the improvement in crystalline quality induced by the newly-developed dual nitridation processes.

4. Conclusions

A RMS value as small as 1.54 nm for the *a*-plane $Al_{0.53}Ga_{0.47}N$ epi-layer was achieved by carefully optimizing the first and the second nitridation process for the *r*-plane sapphire substrate and the LT-AlN NL, respectively. It was revealed that the generation of the AlN grains in the first nitridation process for the *r*-plane sapphire substrate as well as the coalescence and the recrystallization

Table 1
Summary of the nitridation process durations for samples A_1–A_5 and A_{31}–A_{34} used in this study.

Samples A_1–A_5 with varied t_{n1} and a fixed t_{n2} of 180 s					
Sample	A_1	A_2	A_3	A_4	A_5
t_{n1} (s)	150	240	330	480	660

Samples A_{31}–A_{34} with varied t_{n2} and a fixed t_{n1} of 330 s				
Sample	A_{31}	A_{32}	A_{33}	A_{34}
t_{n2} (s)	480	780	1080	1380