In situ observation of two-step growth of AlN on sapphire using high-temperature metal–organic chemical vapour deposition

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We studied the two-step growth of AlN using high-temperature (HT) metal–organic chemical vapour deposition (MOCVD) using a 405 nm short-wavelength in situ monitoring system. First, an AlN nucleation layer (NL) was grown on sapphire at 950 °C before deposition of the HT-AlN film at 1300 °C. The 405 nm wavelength in situ reflectance-transient curves revealed the evolution of AlN growth. The reflectance intensity of the 405 nm signal first decreased during AlN growth and then became stronger until it reached a steady state at large and equal amplitude, revealing that the AlN growth underwent a transition from nuclei to nuclei decomposed island recovery to quasi-layer-by-layer growth. The effect of different initial growth conditions on the AlN growth mode was also studied using the in situ monitoring system. The growth mechanism for the films was proposed based on the 405 nm in situ reflectance curves and atomic force microscopy observations. By optimizing the NL growth conditions, we obtained a high-quality AlN/sapphire template with full width at half maxima for the (0002) and (10–12) planes of 60 arcsec and 550 arcsec, respectively. Finally, a high performance PIN-AlGaN detector was fabricated on the AlN template, which further demonstrated its high quality.

1 Introduction

The growth of high-quality AlN has received much attention because of its promising applications in AlGaN-based deep-UV optoelectronic devices and AlGaN-based power electronic devices.1–3 Because of its direct and tunable band gap, AlGaN optoelectronic devices cover the ultraviolet (UV) region of the spectrum from 200 nm to 365 nm. AlGaN semiconductors are thus key for solar-blind detectors, UV light-emitting diodes (LED), and laser diodes. However, the performance of AlGaN-based devices is limited by the high threading dislocation density of AlGaN epilayers.4–6 The dislocations act as nonradiative recombination centers and charge scattering centers for carriers, causing low mobilities.7,8 Dislocations are also associated with leakage current in AlGaN-based Schottky contacts.9,10

Until now, growth of AlGaN has mainly been performed on AlN layers nucleated on lattice-mismatched sapphire substrates due to the lack of commercially available AlN substrates. In other words, the crystal quality of the AlGaN epilayer is key in determining the amount of dislocation density in the AlGaN material because the majority of threading dislocations in a AlGaN epilayer are generated in the AlN layer. However, the growth of high-quality AlN is extremely difficult owing to the weak surface migration of Al adatoms. Many techniques have been employed to decrease the dislocation density and improve the crystallinity of AlN, such as migration-enhanced metal–organic chemical vapour deposition (MEMOCVD), modified MEMOCVD, flow-modulated MOCVD, and the ammonia (NH₃) pulse-flow multilayer AlN growth method.11–14 For each of these techniques, at least one of the source flows (metal–organic source or NH₃) is modulated to serve as an input to the reactor to enhance the Al atomic migration on the substrate surface, and thus improve the AlN quality. In addition, high-temperature (>1300 °C) MOCVD (HT-MOCVD)15,16 or hydride vapor phase epitaxy17 are the other choices for the growth of high-quality AlN films because high growth temperatures can also improve the migration of atomic Al on the substrate surface. However, until now, there have been few in situ observations of the AlN growth process because of technical limitations. Many studies focusing on the two-step growth of GaN have been carried out with in situ 950 nm or 633 nm optical monitoring, because these wavelengths enable the entire growth process of GaN to be observed, especially for the nucleation layer or low-temperature buffer layer. However, because the band gap of...
AIN is wider than that of GaN, the intensity-modulation and phase difference of the reflectance transients during AlN growth cannot be clearly distinguished for 950 nm or 633 nm incoming light. So 950 nm or 633 nm wavelength in situ optical monitoring is not powerful enough to reveal the AlN growth mechanism in detail, especially at the initial stage. Most reports on the growth mechanism of AlN are based on indirect, ex situ experimental results. Therefore, much shorter wavelength in situ optical monitoring is required to directly explore the growth mechanism of AlN. In this paper, we investigated the two-step growth of AlN by HT-MOCVD with a simultaneous source using short-wavelength (405 nm) in situ monitoring. The effects of different initial growth conditions on the AlN growth modes and crystal quality were studied in detail and a growth mechanism for the two-step growth of AlN films using HT-MOCVD on sapphire was proposed. Finally, a high performance AlGaN PIN-type detector was fabricated on the AlN/sapphire template to reflect the high-quality AlN template. It is believed that the results obtained here are a significant step towards the realization of high-quality AlN and AlGaN films and high efficiency AlGaN-based deep-UV optoelectronic devices and power electronic devices.

2 Experimental

The AlN films were grown on just-cut (0001) plane sapphire substrates using low-pressure HT-MOCVD with LayTec 405 nm short-wavelength in situ optical monitoring. According to Fabry–Perot oscillation, the phase and amplitude of oscillations depend on the wavelength of the incident light as well as the optical constants of the materials and thickness of the growing layer. Maximum reflectance occurs if the product of the refractive index and layer thickness is equal to the even number of the half wavelength. This means that the 405 nm wavelength in situ monitoring system used herein is very suitable for large band gap materials such as AlN. Moreover, the 405 nm short wavelength monitoring system had a higher surface sensitivity than that of 950 nm or 633 nm systems. Thus, the 405 nm wavelength in situ monitoring system was able to simultaneously observe the evolution of AlN growth for deeper mechanistic understanding. Besides, surface roughness was another important parameter influencing the reflectance transients, increasing roughness resulted in low amplitude or damping oscillations; otherwise, the oscillations should be stable or ramping reflectance transients. Usually, rougher surface causes lower oscillation intensity. The two-step growth process was as follows: first, a ~50 nm-thick AlN nucleation layer (NL) was grown on sapphire at 950 °C under optimized growth conditions. The temperature was increased to 1300 °C and a 1 μm-thick HT-AlN film was deposited. The growth rate for the HT-AlN was 1 μm h⁻¹. Trimethylaluminium (TMA) and ammonia (NH₃) were used as Al and N precursors, respectively. Prior to AlN NL growth, thermal cleaning of the sapphire substrate was carried out at 1100 °C for 10 min. To evaluate the role of the NL, HT-AlN films were also grown under the following different initial growth conditions: i) without a nucleation layer or sapphire cleaning treatment (sample A); ii) with only a nucleation layer (sample B); iii) with nitridation at 950 °C for 5 min and an added nucleation layer (sample C); and iv) with TMA pretreatment for 2 s and an added nucleation layer (sample D). Note that all the nucleation layers and the HT-AlN layers were grown under the same parameters. Based on the two-step growth of the AlN template, AlₓGa₀.₄₋ₓN PIN-type ultraviolet layers were fabricated using the traditional standard technology. SiH₄ and Cp₂Mg were used as the n- and p-type dopants, respectively. The n-AlGaN and p-AlGaN doping levels were up to 10¹⁸ cm⁻³. Ti/Al/Ni/Au (5 nm/10 nm/15 nm/50 nm) and Ni/Au(5 nm/5 nm) were used as the Ohmic contacts for the n-AlGaN and p-AlGaN, respectively.

Veeco multi-mode atomic force microscopy and a Bruker D8 high-resolution X-ray diffractometer (XRD) with Cu Kα radiation were employed to further confirm the surface morphology evolution of the HT-AlN and the crystallinity of the obtained AlN film. A Shimadzu UV-3101PC dual beam scanning photometer was used to measure the transmittance properties of the AlN film. Details of the spectral responsivity measurement of the AlGaN PIN detector are described in ref. 8.

3 Results and discussion

Fig. 1 a) shows the in situ monitoring curves for four samples with different oscillations. For sample A, which was grown directly onto the sapphire, the reflectance intensity of the 405 nm signal during the HT-AlN growth damped as the growth time increased, indicating that slight intensity and phase modulation occurred because the surface morphology of sample A became rough and the growth process was three-dimensional (3D) island growth. A similar phenomenon has been observed during the direct growth of GaN on sapphire, which was dominated by a 3D growth mode because of their large lattice mismatch (~16.1%). Similarly, for AlN directly grown on sapphire, the large lattice mismatch (~13.3%) between AlN and sapphire also could cause 3D growth. Fig. 1 b1) shows the schematic atomic structure of AlN directly grown on sapphire substrate. The large lattice mismatch between AlN and sapphire made the formation of AlN nuclei difficult. The AlN nuclei that formed grew continuously to create AlN islands. Because the AlN nuclei density were too low to coalesce, the AlN islands evolved separately from each other, as shown in Fig. 1 b1). Furthermore, the diffusion length of an Al adatom is smaller than that of a Ga adatom. Thus, it is much easier for AlN growth to form AlN islands and result in 3D growth than for GaN.

For sample B, which was grown with only a nucleation layer, the reflectance intensity of the 405 nm in situ monitoring curve during the HT-AlN growth first decreased and then became stronger until it reached a steady state. This indicated that the growth mode of sample B underwent a transition from 3D island growth to quasi-two-dimensional (2D) layer-by-layer growth. Obviously, in contrast to that of sample A, the 2D
layer-by-layer growth mode was governed by the presence of the AlN nucleation layer. Fig. 1 b2) shows schematic atomic structures for the growth process of sample B. The low-temperature AlN nucleation layer provided nuclei for further AlN growth, causing the separate AlN islands to coalesce, resulting in 2D layer growth. In addition, the AlN nucleation layer decreased the surface energy of the sapphire substrate and reduced the lattice mismatch between the HT-AlN and sapphire, causing quasi 2D growth.

For sample C, the reflectance intensity observed during the HT-AlN growth decreased to a certain value and then remained constant, which implied a transition from a 3D growth mode to a mixture of 3D and 2D growth. For sample D, the reflectance intensity increased to a steady state, indicating that 2D growth dominated the whole HT-AlN growth process. This difference between the two samples was mainly governed by their different surface polarity. For sample C, the mixture of 3D and 2D growth modes resulted from the limited Al adatom surface migration; the N-rich polar surface was predominantly terminated by N atoms, with each N atom being bonded to an Al atom leaving three dangling bonds behind, as shown in Fig. 1 b3).19 It is reasonable to deduce that this high density of dangling bonds limited the surface migration of Al atoms. The only way to increase the migration of Al atoms is to break the strong Al–N bonds, which at about 2.88 eV are difficult to break. Thus, the weakened surface migration of Al adatoms resulted in the subsequent mixed-growth mode of HT-AlN for the nitridation pretreated surface. However, the 2D growth mode for the Al-rich conditions, as shown in Fig. 1 b4), resulted from the excess Al atoms. After pretreatment with TMA, excess Al atoms adhered to the growing AlN surface of sample D. These were bonded by weak metallic Al–Al bonds and formed a saturated Al film surface, reducing the energy barrier for the surface migration of N atoms. Thus, the N atom diffusion length was enhanced and the N atoms were able to move to preferable incorporation sites. As a result, both the suitable availability of Al adatoms and the enhanced N adatom diffusion length caused the AlN growth to evolve to 2D layer-by-layer growth under Al-rich conditions.20

The full width at half maximum (FWHM) of the HT-AlN (0002) and (10–12) planes was measured to confirm the growth evolution of the four samples (Fig. 2). FWHM values are widely used to calculate the dislocations in AlN film.21,22 If the diffraction vector $\mathbf{g}$ satisfies the condition of $\mathbf{g} \cdot \mathbf{b} = 0$, the existence of screw dislocations results in the widening of the FWHM. If the diffraction vector $\mathbf{g}$ satisfies the condition of both $\mathbf{g} \cdot \mathbf{b} = 0$ and $\mathbf{g} \cdot \mathbf{t} = 0$ ($\mathbf{t}$ is the dislocation line vector), the amount of edge dislocations is proportional to the FWHM.23,24 Thus, the (0002) FWHM is usually used to calculate the screw dislocations, and the wider the (0002) FWHM, the more screw dislocations are present. Similarly, the value of the (10–12) FWHM is proportional to the amount of

![Fig. 1](image_url)  
**Fig. 1** a) In situ monitoring curves for HT-AlN, and b) schematic atomic structure of HT-AlN.

![Fig. 2](image_url)  
**Fig. 2** FWHM of the (0002) and (10–12) planes of HT-AlN grown under different initial conditions.
edge dislocations. Comparing the FWHM values of the four samples, it can be seen that the initial growth conditions have an obvious effect on the FWHM values. The smallest FWHM values of both (0002) and (10 12) are obtained for sample B. These indicate that the HT-AlN grown with only the nucleation layer had the lowest dislocation density and high crystallinity.

AFM images of the four samples were taken to further explore the origins of the different FWHM values of the HT-MOCVD grown AlN under different initial growth conditions (Fig. 3). As can be seen, both sample A and C were formed of 3D islands, and especially sample A was dominated by isolated islands. In contrast, the surface morphology of samples B and D was smooth, with sample B much smoother, with obvious atomic steps observed, compared to that of sample D. It is worth noting that the AFM image (Fig. 3b) of sample B shows macrostep morphology. It has been reported that a vicinal substrate could cause a macrostep morphology for AlN grown by MBE.²⁵ In our case, it is impossible for the macrosteps to have originated from a vicinal substrate since the sapphire substrate is the normal (0001) plane without off-cutting. Thus, the most likely possible cause is the change in growth mode. Bai et al. have observed similar macrosteps on AlN/sapphire by TEM during growth mode transition from 3D to 2D layer-by-layer growth.²⁶ These results correspond with the in situ monitoring results and further confirm the occurrence of different growth modes when the initial growth conditions were varied. As is known, 3D growth usually produces many isolated islands, in particular for AlN growth because of the short diffusion length of the Al adatom. The isolated AlN islands of sample A and mixture of AlN islands and layer of sample C mean that the dislocation density in both of the samples was very high, leading to the larger FWHM values observed. The smooth surface of sample D is obviously associated with the 2D growth mode. However, high-density threading dislocations formed at the surface of sample D from the initial layer, which lowered the quality of the AlN film. The main reason for sample B having the highest crystallinity with the narrowest FWHM values is that its growth process experienced a transition from 3D to 2D growth. During this transition, the dislocations have been bent at the 3D growth to 2D growth transition interface, which can dramatically reduce the threading dislocation density. According to the reflectance transients, AFM results, and the above analysis, it can be concluded that the different growth modes are responsible for

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**Fig. 3** AFM images of HT-AlN grown under different initial conditions: a) sample A, b) sample B, c) sample C and d) sample D.
the different crystalline quality and that the two-step growth can produce high-quality HT-AlN, which is better than that reported.\textsuperscript{13,21}

To further investigate the mechanism of the two-step HT-MOCVD growth of AlN, the growth process was divided into six stages: I) nucleation layer; II) nucleation layer after annealing; III) 2 min growth for HT-AlN; IV) the lowest point of reflectance intensity (8 min); V) coalescence (22 min); and VI) 47 min growth, as shown in Fig. 4 a). After each stage of growth ended, we removed the sample from the reactor and measured its surface morphology using AFM (Fig. 4 b)). According to the 405 nm wavelength \textit{in situ} monitoring signal, the appearance of the increased reflectance curve indicates the formation of the nucleation layer, as shown in Fig. 4 a) I. The decrease in the reflectance intensity of the 405 nm reflectance curve indicates that the surface morphology of the AlN nucleation layer became increasingly rough, as shown in Fig. 4 a) II, III and IV. Subsequently, the enhanced intensity of the 405 nm reflectance-transient curves of step V suggests that the HT-AlN growth underwent a transition to islands coalescence leading to decreased surface roughness. The reflectance intensity further increased to a constant swing, indicating that the coalescence transformed to layer-by-layer AlN growth, and an AlN film with a smooth surface was subsequently obtained.

Comparing Fig. 4 b) with Fig. 4 a), the surface morphology evolution of HT-AlN measured by AFM is in good agreement with the reflectance curve of the 405 nm \textit{in situ} monitoring system. Fig. 4 b) I shows the surface of the deposited nucleation layer, which consisted of isolated islands with high density. After annealing, the island size became larger but the density decreased due to the recrystallization and coalescence of the nucleation layer (Fig. 4 b) II). The continuous enlargement of the islands caused the growth surface to become increasingly rough, as shown in Fig. 4 b) III and IV. The results of Fig. 4 b) II, III and IV correspond to the 405 nm signals of Fig. 4 a) II, III and IV, in which the reflectance intensity decreased to the lowest point. As the growth time increased, the islands became large enough to coalesce, as
shown in Fig. 4 b) V. This caused the surface roughness to decrease and resulted in the enhanced intensity of 405 nm in situ monitoring reflectance transient observed in Fig. 4 a) V. Finally, a high quality AlN epilayer with smooth surface and obvious atom steps was obtained after 47 min growth, as shown in Fig. 4 b) VI. This agrees with the increasing and then constant reflectance intensity of the 405 nm reflectance curves observed in Fig. 4 a) VI. Thus, the surface morphology measured using AFM further supports the in situ monitoring results and confirms that the two-step growth of AlN underwent a transition from nuclei (3D island) to nuclei decomposed coalescence to layer-by-layer (2D) growth. Based on the above analysis, a schematic of the two-step AlN growth is shown in Fig. 5.

The transmittance of the HT-AlN film was measured to further evaluate the quality of the two-step grown HT-AlN epilayer, as shown in Fig. 6. It was seen that the transmittance of the AlN epilayer dropped sharply around the absorption band gap of AlN, at a wavelength of 200 nm, which indicated that there were few dislocation-associated intermediate bands. Fig. 6 also shows that at wavelengths larger than 200 nm, Fabry–Perot interference occurred as a result of the AlN film reflecting the light more than once, which also suggests the high quality of the AlN film. Furthermore, based on the relationship between the absorption coefficient $\alpha$ and the incident photon energy $E$:

$$\alpha E = A(E - E_g)^{1/2}$$

where $A$ is the material constant and $E_g$ is the band gap as shown in the inset of Fig. 6, the band gap of the two-step growth AlN was obtained to be about 6.13 eV. These results further confirm that the AlN film had high quality.

Using the two-step growth of AlN as a template, a high quality AlGaN epilayer was deposited and a PIN-type AlGaN detector structure was grown. Fig. 7 a) shows the schematic structure of the obtained PIN-AlGaN ultraviolet detector while Fig. 7 b) shows the responsivity of the detector. The AlGaN PIN detector exhibited a high responsivity near 290 nm which slightly decreased with wavelength due to the reduced photo-penetration depth and increasing recombination of surface photogenerated carriers. This good performance of the PIN-AlGaN detector is attributed to the high quality of the AlN template grown by the present two-step HT-MOCVD.

![Fig. 5 Schematic for the two-step growth of AlN.](image)

![Fig. 6 Transmittance of the HT-AlN film and plot of incident photon energy ($E$) versus ($\alpha E)^2$ (inset).](image)
Conclusions

In summary, the two-step HT-MOCVD growth of AlN was investigated in detail using a 405 nm short wavelength in situ monitoring system, and high-crystalline-quality AlN was obtained with XRC-FWHM of 60 arcsec and 550 arcsec for the (0002) and (10\,\overline{12}) planes, respectively. According to the 405 nm in situ reflectance curves, the two-step AlN growth experienced a transition from 3D island growth to 2D growth, which resulted in the growth of high-quality HT-AlN. The 405 nm signal revealed that the crystallinity of the AlN was strongly affected by the initial growth conditions. The reasons for this were investigated and different growth modes were proposed for different initial AlN growth conditions. In addition, a growth mechanism for the two-step growth of AlN films using HT-MOCVD was proposed based on the obtained 405 nm in situ reflectance curves and atomic force microscopy observations. The two-step grown AlN showed good transmittance and high performing PIN-AlGaN detectors based on the AlN film were fabricated.

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Notes and references