Structural properties, crystal quality and growth modes of MOCVD-grown AlN with TMAI pretreatment of sapphire substrate

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1. Introduction

As members of the III-nitrides family, Al\textsubscript{x}Ga\textsubscript{1-x}N alloys have become a key material for deep ultraviolet (DUV) optoelectronic devices [1–5]. Even though bulk AlN substrates have been developed and are suitable for device applications, they are still expensive and only available in small sizes. Recently, the development of AlN films on silicon (Si) substrates showed the potential for realizing UV devices [6]. However, the crystal quality of AlN on Si was relatively low due to the large lattice and thermal mismatches between AlN and Si. Unlike sapphire, Si is also UV-absorptive. Thus, the growth of AlGaN-based devices is often carried out on AlN film grown on sapphire substrate. Extensive studies have been carried out on the growth optimization of the AlN films on sapphire. In particular, the initial growth conditions including hydrogen (H\textsubscript{2}) annealing [7], growth temperatures [8, 9], thickness control of the nucleation layers (NLs) [10, 11], and the III/V ratio [12] have shown significant impacts on the surface morphology, polarity and crystal quality of the MOCVD-grown AlN.
films. Inappropriate growth temperatures and thicknesses of the NL could lead to generating mixed polarities and inversion domains in AlN films.

Moreover, it has been reported that the pretreatment of sapphire substrates either by ammonia (NH₃) or trimethylaluminum (TMAl) is strongly correlated with the surface morphology [13, 14], polarity [15], and crystal quality [16]. Researchers demonstrated that atomically smooth Al-polar AlN films were obtained without nitridation [16]. Other research group have shown that mixed polarity by pre-growth nitridation of the sapphire substrate results in rough film surfaces because of the different growth rates of N-polar and Al-polar AlN films [8, 17]. Theoretically, from ab initio studies, the nitridation is described as the N-rich limit of growth, with sapphire as the source of Al, and may result in different polarities of AlN films [18]. Experimentally, it was proposed that the formation of AlₓOᵧNₚ is what leads to the rough surfaces and the mixed polarity of the AlN films [19, 20]. Recently, Moh et al achieved Al-polar AlN films on a nitridated sapphire substrate by carefully controlling the AlₓOᵧNₚ intermediate layer followed by a high-temperature annealing process [13].

Nitridation is recognized as a crucial step and thus has been investigated extensively for the sake of achieving desirable AlN or GaN films grown by MOCVD, yet not much attention was paid to understanding the crystallographic polarity and growth evolution of nitride films achieved through TMAl pretreatment (i.e. alumination). The topic of defective and rough-surface AlN/sapphire templates resulting from the TMAl pretreatment has been addressed before [21, 22]. Reentila et al have argued that neither nitridation nor alumination gave the best structural quality [16]. In contrary, studies have shown that better AlN and GaN crystal quality can be achieved after pretreatment using TMAl [23, 24]. Recently, we revealed that it was the carbon presence at the AlN/sapphire interface after TMAl pretreatment that changed the polarity of AlN film. However, the crystal quality of AlN film after the pretreatment was not analyzed [25].

In this study, we present a comprehensive investigation of the structural properties, including surface morphology, polarity, and crystal quality of AlN templates under different TMAl pretreatment durations of sapphire substrates. We also analyzed the correlation between the growth modes induced by different pretreatment and the crystal quality of AlN templates.

2. Experimental details

The AlN heteroepitaxial layers were grown on a c-plane (0001) sapphire substrate using an AIXTRON Closed-Coupled Showerhead metalorganic chemical vapor deposition (MOCVD) system which has a base pressure of ~1.5 × 10⁻² Torr. TMAl and NH₃ were used as precursors and H₂ as a carrier gas. The sapphire substrates were taken from the original package and loaded into the reactor immediately without solvent cleaning. The AlN growth processes comprised four steps. First, the susceptor and sapphire substrates were baked at 1100 °C for 5 min in the H₂ ambient environment. Second, a preflow of TMAl was introduced to the substrate with pretreatment times of 0, 1, 2, 5, 10, and 40 s at a same flow rate of 1.72 × 10⁻⁵ mol. min⁻¹ with a chamber pressure of 85 mbar during the pretreatment. Then the growth started with a 15 nm AlN NL at a temperature of ~900 °C. Last, a ~3 μm AlN layer was grown at ~1100 °C. Except for the pretreatment times of the TMAl, the other growth parameters were the same for all samples. The reactor pressure was 85 mbar during the growth. Besides AlN films, we also prepared two samples with 5 and 40 s TMAl pretreatment (hereafter TMAl-only samples) under the identical MOCVD condition, without the subsequent AlN growth. The surface morphology and roughness of the AlN films and TMAl-only samples were examined by atomic force microscopy (AFM). Microstructures were revealed via high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) at an acceleration voltage of 300 kV in an FEI Titan Probe microscope system. The TEM specimens were prepared by focused ion beam (FIB) using an FEI Helios SEM system with a Ga ion source. High-resolution-x-ray diffraction (HR-XRD) was performed to characterize the crystalline quality.

3. Results and discussions

Figure 1 shows the AFM root mean square (RMS) roughness and surface morphology of the AlN templates. The results exhibit significant difference in surface morphology. Without TMAl pretreatment, the sample exhibited a rough surface with pits. The surface morphology gradually smooths out as the pretreatment time increased from 0 to 5 s. Small pits (threading dislocation centers) are still visible in the sample with the 5 s pretreatment. However, the surface became rougher again with a longer pretreatment time for the sample at 10 s duration. After the 40 s pretreatment, the sample had the roughest surface among the investigated AlN templates. The smoothest AlN film was obtained at under the 5 s pretreatment time with an RMS roughness of less than 1 nm. The sample with the 40 s pretreatment time yielded an RMS value of 80 nm, indicating a 3D growth condition of AlN film might be established after such long pretreatment. Thus, without and excessive pretreatment both led to a rough surface. With proper pretreatment duration, a smooth AlN/sapphire template is achievable.

Next, we carried out detailed TEM analysis of the three AlN/sapphire samples with pretreatment times of 0, 5, and 40 s. Figure 2(a) shows an overall HAADF-STEM image of the AlN/sapphire template without pretreatment. We observed many domains with inverted cone shapes embedded with bright and dark vertical stripes along the growth direction (0001). A rough surface was also observed. Meanwhile a large number of threading dislocations (TDs, in white contrast) were created at the interface but slightly diminished in density as the thickness of the AlN layer increased (fewer TDs above the white dashed line). Nevertheless, the stripes propagated from the interface of the AlN/sapphire to the surface of the AlN template and its contrast alternately changed along the in-plane direction.
Figure 2(b) shows two polarities in two strips next to one another. The left stripe has Al-polarity and the right one has N-polarity, confirming the mixed polarity of the film. There is an inversion domain boundary (IDB), which is marked by the red dashed line. A few groups reported that the mixed polarity is primarily caused by the formation of an Al$_x$O$_y$N interlayer between the sapphire and the AlN-NL. This Al$_x$O$_y$N interlayer causes the polarity to be inverted to the N-polarity [26, 27]. Recent discoveries have also shown that decomposition of sapphire prior to the growth led to the simultaneous growth of N- and Al-polar AlN films [28]. The growth rate of Al-polar film was found to be much higher than that of N-polar films [17], thus leading to a rough surface, as shown in figure 2(a), that is not beneficial to subsequent film growth.

After 5 s pretreatment, the sample exhibits a uniform and smooth surface, as shown in figure 3(a). Although TDs were
crowded throughout the interface between the AlN layer and the sapphire, the TDs rapidly vanished once the thickness increased beyond 1 µm (white dashed line) and only a few TDs propagated to the surface. Interestingly, we observed a high density of small voids in the bottom section of the AlN template. These nanoscale voids could be the result of the incomplete coalescence of the nucleation islands. Literature proposed that a few monolayers of Al were deposited on the sapphire’s surface [29, 30] and formed the nucleation islands before NH3 came into the reaction chamber, creating a quasi-three-dimensional (quasi 3D) growth mode at the beginning of the growth. Later, the high-temperature AlN began to grow on these quasi-3D islands, which was followed by the islands’ coalescing and finally the growth transferred to a 2D mechanism. The voids were suppressed and the TDs were bent and/or annihilated as the film grew thicker [31], forming a uniform and smooth film. The inset image shows the atomic resolution image, confirming the Al-polarity of this film.

Next, we will address the correlation of TMAl-pretreated sapphire surface with the crystal quality and the growth mechanism of AlN films.

The crystal quality of the AlN templates was studied by measuring the full width at half maximum (FWHM) of the XRD symmetric (0 0 2) and asymmetric (1 0 2) ω-scans, as shown in figure 4 [33–35]. Except for the sample with the 40 s pretreatment, the obtained FWHM values of XRD peaks were largely comparable with the ones reported by other groups, falling in the range of 100–500 and 800–1500 arcsec for the (0 0 2) and (1 0 2) plane, respectively [36–39]. The FWHM values of the symmetric (0 0 2) and asymmetric (1 0 2) ω-scans corresponded to and were proportional to the screw dislocation and the edge dislocation densities, respectively. It is generally noted that the screw dislocations and edge dislocations originate from the stacking faults that cause tilting and twisting grain boundaries. A close examination of figure 4 reveals different trends of the crystalline quality with different pretreatment times. The (0 0 2) FWHM (blue curve) is nearly constant during the first 10 s pretreatment, indicating that our relatively lower temperature (~900 °C) pretreatment processes the pretreatment. With the 5 s pretreatment, the formation of N-polarity regions was completely impeded [32].

Figure 3(b) shows that the overall HAADF-STEM image of the AlN/sapphire template with the 40 s pretreatment that exhibited the roughest surface among the investigated samples. The surface had faceted nanocolumns. Meanwhile the AlN/sapphire interface included a high density of voids and TDs. This is primarily due to excessive pretreatment of the sapphire, resulting in the formation of high density large 3D islands (domains) at NL. Thus, a 3D growth mode was immediately established after the pretreatment, creating nanocolumns with well-defined boundaries. Most of the TDs formed at the interface or diminished at the boundary, leaving less density at the top part of the nanocolumns. Similar to the other two samples, the TDs rapidly vanished as the thickness of the AlN layer increased beyond 1 µm (white dashed line). The inset image confirms the Al-polarity of this film.
did not result in a large tilt of AlN nuclei, thus the density of screw dislocation did not change too much. For the (1 0 2) FWHM (red curve), it slightly decreases after the 2 s pretreatment and then increases significantly from 5 to 40 s pretreatment duration, indicating higher density of edge dislocations. The smallest (0 0 2) and (1 0 2) FWHMs were obtained when the pretreatment time was 1–2 s and the (1 0 2) FWHM is more sensitive to the pretreatment time. A similar XRD trend was observed in the study of the pretreatment of sapphire using TMAl [32] for MOCVD-grown GaN templates. However, our observation is contrary to what O. Reentila et al reported earlier [16]. They presented both FWHMs increased dramatically with the increase of TMAl exposure time, and the surface roughness of their films remained below 1 nm, even after the 80 s pretreatment. Thus, we believe the discrepancy is probably due to higher growth temperature of 1500 °C and 1000 °C for their AlN template and AlN-NL respectively. Normally, higher growth temperatures (generally more than 1400 °C) are favorable for the migration of Al adatoms, which benefits the increase of crystal quality of AlN templates [40]. Another study has shown that the roughness of the NL decreased by increasing the growth temperature of the NL ($T_{NL}$) because the diffusion length of Al adatoms and lateral coherence length at sapphire surface increased as $T_{NL}$ was increased [38]. So the growth temperature plays such significant role in the process of AlN film by MOCVD.

Besides the variation of the crystal quality, TEM studies (figures 2 and 3) revealed the drastic microstructure difference between samples underwent various pretreatment conditions. Most notably, the growth modes have undergone significant transformations as a result of changing the pretreatment times. Here we present the investigation on the surface morphology of the TMAl-only samples using AFM prior to the AlN epitaxy, as shown in figure 5. Without pretreatment, the sapphire surface was extremely smooth, with a measured RMS value of 0.2 nm. The cross-section profile across the scanned surface shows less than 1 nm in height. However, after 5 s pretreatment, we clearly observed spotty surface with a measured RMS value of 2.3 nm, indicating a formation of rough surface with small islands on the sapphire substrate. The cross-section profile indicates an 8–10 nm in height. With 40 s pretreatment, irregular nanoscale 3D islands (50–100 nm in horizontal

Figure 5. (a)–(c) are AFM images of surface morphology of TMAl-only samples (without AlN epitaxy) with the 0, 5 and 40 s pretreatment, respectively. The left, middle, and right are the plan-view, 3D image and cross-section profiles, respectively, corresponding to the marked line in the 3D image.
dimension) on sapphire substrates were formed, with a measured RMS value of 6.3 nm. The cross-section profile indicates a measured height ranges of 15–20 nm.

Based on the observation of the structural characteristic of AlN films and TMAl-only samples above, here we propose the growth mechanism under 0, 5 and 40s pretreatment. Figure 6(a) shows the creation of rough AlN films without pretreatment. Although the AlN started nucleation on smooth sapphire, because of the formation of $\text{Al}_x\text{O}_y\text{N}_z$ in the first few monolayers of AlN growth [13, 17], Al-polarity was partially transformed to N-polarity and this has led to the mixed polarity of AlN film, thus created a rough surface. However, after the TMAl pretreatment, the process not only helped establish the Al-polar growth condition but also create a slightly roughened surface due to the TMAl decomposition, confirmed by AFM in figure 5(b) [41]. The residuals of decomposed TMAl formed a cluster of small islands, thus a quasi-3D growth mode was introduced. The formation of small islands, which was accounted for inducing the quasi-3D growth mode, was proved to be beneficial to create higher quality of AlN and GaN films [23, 24]. As the growth continued, these small AlN grains coalesced and the surface became smooth, which meant a 2D-growth (a layer-by-layer growth) was established in the end. This process is similar to the high-quality and smooth GaN growth on sapphire with a combination of quasi-3D and then 2D growth modes [42, 43]. Figure 6(b) presents the schematic of such growth mechanism for the 5s pretreatment. A uniform and smooth surface of AlN template was obtained. In addition to the improvement of surface morphology, an increase of the density of edge dislocations ($\omega$-scan) was observed by increasing the pretreatment time. This might be due to the increasing size of islands formed on sapphire after longer pretreatment time, as shown in figure 5, preventing the migration of arriving Al and N atoms horizontally. These islands facilitated in generating more twisted grain boundaries while establishing the initial quasi-3D growth mode, thus a higher density of edge dislocations. Also, the larger the islands prior to the AlN epitaxy on sapphire, the thicker subsequent AlN film might be required to get fully coalesced while creating small voids in the bottom AlN layer [23]. Nevertheless, these islands did not contribute to the tilt of in-plane AlN nuclei, thus little impact on the density of screw dislocations after increasing the pretreatment time from 1 to 10s. Once the sapphire substrate is over-treated, a high density of larger 3D islands were formed on sapphire (figure 5(c)), leading to extreme rough NL. The NL might act as a mask and further prevent Al-adatoms from diffusion to different nucleation islands, thus leading to a 3D growth mode throughout the subsequent template growth. The Al-polar AlN template with nanocolumns was grown on those islands which are consistent with the AFM measurements, as shown in figure 6(c). Interestingly, Eom et al were able to fabricate AlN 3D nanostructures using KOH etching by controlling the polarity of the AlN films due to the TMAl preflow [44].

Figure 6. Schematic illustration of the growth modes, the evolution of the AlN templates with (a) 0 s, (b) 5 s, and (c) 40 s pretreatment.

4. Conclusions

In conclusion, we have studied the influences of the TMAl pretreatment on the structural properties, crystal quality and growth mode of AlN films on sapphire substrates by MOCVD. Due to the absence of the TMAl pretreatment, the AlN films had a mixed polarity, but after a few seconds of pretreatment, the polarity of AlN films tended to convert to Al-polarity, while the surface roughness and crystal quality were improved according to the FWHM variations of the (102) and (002) rocking curves. However, excessive pretreatment results in poorer crystal quality and a rough surface. A detailed epitaxial growth mechanism under different pretreatment time were presented. A shift of growth mode from quasi-3D to 3D was identified after increasing the pretreatment time. We conclude that pretreatment times that are too short or too long should be avoided as neither is favorable for AlN epitaxy on sapphire. These results give practical advice and guidance in changing the growth mode of AlN film to achieve desirable AlN films.

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