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# Influence of the nucleation layer morphology on the structural property of AlN films grown on c-plane sapphire by MOCVD

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The influence of nucleation layer (NL) morphology on the structural property of AlN films grown by metal organic chemical vapor deposition (MOCVD) has been investigated using atomic force microscopy (AFM). It is found that the initial V/III ratio of the NL effectively controls the polarity, size, density, and coalescence rate of the islands, which is one of the most critical parameters determining the crystalline polarity and surface morphology. Due to difference adatom diffusion on the growth surfaces, it is observed that AlN films grown under high initial V/III ratios exhibit N polarity with rough surface, while that grown under low initial V/III ratios show Al polarity with smooth surface. And high quality crack-free AlN film with thickness about 1.4 μm has been obtained by optimizing initial V/III ratios during the NL deposition stage.



## 1. Introduction

In the past decades, AlN has attracted considerable attention because of its unique combination of remarkable properties. It is a material of great potential for high power electronic devices [1,2], ultraviolet (UV) photonic devices [3,4] as well as acoustic devices [5,6] due to its wide band gap (6.2 eV), high breakdown voltage, high thermal conductivity, and high piezoelectric constant. However, the main issues for the growth of AlN are the lack of large area bulk AlN wafers and the difficulty for the epitaxial AlN growth with high-quality and crack-free on foreign substrates such as sapphire, Si and SiC [7–9]. For the crystal growth of AlN, c-plane sapphire is still one of the most popular substrate for the fabrication of III–nitride-based UV devices due to their low cost, stability at high temperature and the transparency at ultraviolet wavelength, although there is a large lattice mismatch and difference in thermal expansion coefficient between AlN and sapphire. The large band gap of sapphire makes it is possible to extract UV light from the AlGaN active layer through the bottom of the substrate. In recent years, many methods have been developed to improve the epitaxial quality and reduce the strain of AlN epilayers grown on sapphire, such as two-step growth [10,11], multiple-step V/III growth [12], alternating supply of precursors [13], precursor preflow [14], epitaxial lateral overgrowth (ELO) [15], and so on. Usually, AlN layers on sapphire are used as templates for deep ultraviolet light emitting devices due to their UV transparency as well as their small lattice mismatch to AlGaN with high Al-content.

AlN with Al polarity usually exhibits smooth surface while AlN with mixed Al and N polarity has rough surface morphology [16]. And the polarity is a key factor that affects the electrical and optical properties [17]. Therefore, the investigation for polarity-controlled epitaxy processes is very important to grow high quality AlN epilayer. It is believed that the polarity of the layers grown on c-plane sapphire is related to the presurface treatment and the succeeding growth conditions, which are extremely sensitive to the initial chemical condition of the reactor, and that small changes can have significant effects on growth [18,19]. In the past few years, growth temperature of the NLs, thickness of the NLs, the density and the size of the nucleation islands have been found to influence the quality of the AlN layers [20,21]. However, studies on the initial

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stages of AlN growth are still scarce, when compared to GaN. In the case of the GaN, several authors have described the formation of the microstructure of GaN films directly grown on sapphire [22–25]. The NLs deposited at 500–600 °C is composed of highly metastable cubic GaN and the stable hexagonal GaN grains. The microstructure of the GaN NL changes drastically when it is heated to the growth temperature. A phase transformation from cubic to hexagonal is occurred. The recrystallization of the crystallites in NLs takes place during the ramping period. Then high density of islands cover the substrate, which lead to growing in 3D mode at initial stages of HT-GaN growth. For 3D growth mode, the islands grow in both lateral and vertical direction, resulting in coalescence of the large size islands. As the islands begin to coalesce, more vertical direction growth (quasi-2D growth) has taken on. And GaN with flat surface has been obtained finally. It is found that the 3D growth mode at initial stages of HT-GaN growth can significantly reduce the density of edge type dislocations [24,25]. However, in the case of AlN, the low surface mobility of Al atoms due to their high adsorption energy make it more difficult to grow high quality AlN films than GaN on sapphire. Especially for the initial stages of AlN growth, such as the polarity and growth mode changing process, are still not well understood, and concern still exists for growing low defects AlN materials on sapphire.

In this work, the influence of NL morphology on the structural property of AlN films has been studied carefully, and high quality crack-free AlN film with thickness about 1.4 μm is obtained by optimizing V/III ratios during the NL deposition stage. A systematic optimization study of the nucleation layer reveals that the V/III ratio is one of most critical parameter which has a major effect on the surface morphology and crystalline quality [26–28]. It is found that the NL morphology strongly depends on the surface N/Al ratio in the initial NL growth stage. It is well known that heteroepitaxial growth of GaN thin films on sapphire initiates as an assemblage of crystallites, or grains, that coalesce into flat film [24,25]. In this work, we investigated the morphology of the NL grown under different V/III ratios. It is found that the initial V/III ratio effectively controls the size, density, and coalescence rate of the islands, and thus determines the polarity in AlN. We also discuss the relationship between the diffusion behaviors of adatoms and the crystalline surface morphology.

## 2. Experimental

All of the samples in this study were grown on 2 inch c-plane sapphire substrates by low-pressure metal organic chemical vapor deposition. Trimethylaluminum (TMA) and high-purity ammonia ($NH_3$) were used as precursors for Al and N, respectively. Hydrogen was used as the carrier gas. Before the growth, thermal cleaning of the substrate was carried out for 5 min in hydrogen ambient at 1100 °C. The two-step growth method was used to prepare all samples. Firstly, a 30 nm thick AlN NL was deposited on sapphire at 850 °C with V/III ratio varying from 1360 to 136. After the NL growth, the temperature was ramped to the growth temperature of 1200 °C. The ramping time (400s) and the stabilization time (150s) were kept constant for all runs. The annealing process was carried out during the ramping period and the stabilization stage, during which the recrystallization of the crystallites in NL has taken place. Then, a HT-AlN top layer was grown at the growth temperature with a V/III ratio of 512. And the reactor pressure was maintained at 50 Torr during growth. Here, the growth temperature, pressure and V/III ratio of the HT-AlN top layer were kept identical for all samples. In order to understand the influence of NL morphology on the structural property of AlN films, several AlN NLs were grown under different III/V ratios, which were accomplished by varying ammonia flow rate. The amount of TMA flow during growth was fixed at 40 μmol/min. The total flow was constant.

The surface morphology of AlN films were characterized by AFM of Digital Instruments Nanoscope III. The surface roughness was obtained by extracting root mean square (RMS) values from 5 μm × 5 μm AFM images. Crystalline quality was evaluated using high-resolution X-ray diffraction, which were carried out by using Bruker D8 Discovery system, delivering a pure $CuK_{\alpha1}$ line (λ = 0.1540598 nm). Both ω-scan rocking curves of symmetrical (002) and asymmetrical (102) reflections were measured. The dislocation densities were estimated using the experimental values of full width at half maximum (FWHM) for symmetric (002) and asymmetric (102) rocking curves of the thin AlN layers. Selective etching of the Al-polar and N-polar surface was obtained using KOH aqueous solution. Etching temperature was maintained at 70 °C, and the concentration of KOH was approximately 50 wt%. All samples etched for 3 min. AFM was used to determine the effects of the etchant on the surface morphology of the AlN. The optical transmittance spectrum of the AlN epitaxial layer on sapphire in the 190–500 nm wave-length range (i.e., photon energies ranging from 2.5 eV to 6.5 eV) was measured at room temperature using a Perkin-Elmer Lambda 950 UV spectrometer. Tungsten and deuterium (for wavelengths shorter than 319 nm) lamps are used as light sources. The average thickness of AlN NLs was measured by X-ray reflectivity (XRR) using the Bruker D8 Discovery system and simulated by software. And cross sectional the field-emission scanning electron microscopy (FE-SEM) analysis were carried out to make sure the thickness of HT-AlN samples.

## 3. Results and discussion

In order to investigate comprehensively the influence of the NL morphology on the structural property of AlN films, four group samples (A-D) with different NL V/III ratios were prepared aiming at understanding the growth mechanism. For the group A, B, C and D, samples were deposited with NL V/III ratios of 1360, 453, 272, 136 at 850°C respectively. The evolution of the surface morphology of the AlN film with thickness varying from 30 nm to 300 nm is clearly shown in the Fig. 1 (from bottom to top in the first column). The 5 μm × 5 μm AFM image in Fig. 1(a) shows that hexagonal-prism-shaped islands dominate the surface, size of which is largely increased with the thickness. And the root-mean square (RMS) roughness value of the surface is about 2.9 nm. These islands in shape of hexagonal prism lead to growing in column growth mode during HT-AlN growth. For column growth mode, the islands grow in both lateral and vertical direction, which coalesce in large size sub-grains (as shown in the Fig. 1(e)). Then the RMS roughness value of the surface (Fig. 1(i)) increases to about 19 nm with the thickness adding to 300 nm. For the group B, as the decrease of NL V/III ratios, the shape of islands have turned into hexagonal pyramid which are in smaller size and higher density than that of group A. And the surface RMS value reduced to 14 nm (Fig. 1(j)). While, for the group C, as the further decrease of NL V/III ratios, the islands begin to coalesce partially with each other, resulting in more flatten surface (as shown in the Fig. 1(k), the surface RMS value of which has reduced to 10 nm). When the NL V/III ratios are reduced massively to 136 for the group D, which is shown in the last column of Fig. 1. It can be clearly observed that hexagonal pyramids disappeared completely, and the islands coalesce with each other even in the thin NL films, which can be seen in the Fig. 1(d). As we know, growth kinetics of the flat islands is much different to the hexagonal ones. Then, growth takes place in quasi-2D mode directly at initial stage of HT-AlN growth in the Fig. 1(h), where number of small size pits can be seen, the RMS roughness value is reduced to 1.3 nm. As the coalescence of islands, more vertical direction growth (2D growth) has carried on. Finally, atomic smooth surface