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The role of surface kinetics on composition and quality of AlGaN

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ABSTRACT

Metal–polar, Al-rich AlGaN films were grown on both single crystalline AlN and sapphire substrates. The role of surface morphology and surface kinetics on AlGaN composition is presented. With the reduced dislocation density of the films grown on AlN substrates, atomically smooth bilayer stepped surfaces are achieved with RMS roughness of less than 50 pm for a $5 \times 5\ \mu m^2$ AFM scan area. By controlling the surface supersaturation through adjusting the growth rate, a transition from 2D nucleation to step flow was observed. The critical misorientation angle for step-bunching in nominal $Al_{0.70}Ga_{0.30}N$ grown with a growth rate of 600 nm/h on AlN substrates was found to be 0.4°. The composition of bilayer stepped AlGaN was strongly dependent on substrate misorientation angle, where a compositional variation by a factor of two for a change in misorientation angle from 0.05 to 0.40° was observed; this is explained by the different surface diffusion lengths of Ga and Al. Step-bunching resulted in strong compositional inhomogeneity as observed by photoluminescence and scanning transmission electron microscopy studies.

1. Introduction

Al-rich AlGaN alloys are ideal for deep-UV optoelectronic devices due to their direct wide bandgap [1,2]. To operate at their full potential, these devices require epitaxial layers with low dislocation densities and smooth interfaces. To achieve low dislocation density Al-rich AlGaN thin films, the growth on single crystalline native AlN substrates is mandatory. High quality Al-rich AlGaN thin films have been demonstrated on these substrates [3]. By realizing low dislocation density films, the number of non-radiative events and leakage paths is decreased, therefore improving the performance of the device. High quantum efficiencies can be obtained by maintaining atomically smooth interfaces in quantum well structures [4]. Also, the importance of thickness control on an atomic level has been demonstrated in quantum cascade lasers, where the thickness non-uniformity caused by surface roughness hindered the overall performance of the devices [5]. For these reasons, a control scheme is needed to consistently achieve atomically smooth Al-rich AlGaN surfaces with desired composition. To properly formulate such a scheme, an understanding of the surface kinetics during growth is needed.

The compositional uniformity of ternary alloys was shown to be directly related to the surface roughness [6]. This was due to the fact that the surface kinetics of different adatom species of the alloy intrinsically differed from each other and, in addition, it depended on local energetic barriers associated with the steps [7,8]. In particular, step-bunched surface morphology contained seemingly abrupt and undesirable lateral compositional gradients that were correlated with the differences in step densities across such a surface [6,9,10]. The local variations in alloy composition observed on rough surfaces are not desirable since these variations can scatter carriers and broaden or add additional emissions in optoelectronic devices. Therefore, in order to achieve a uniform composition in alloy films and ultimately improve device performance, controlling the surface morphology during AlGaN growth is critical.

This work builds upon and is a logical extension of the work by Bryan et al. that presented an all-inclusive model for controlling the surface morphology in the homoepitaxial growth of AlN on vicinal surfaces [11]. It was shown that the surface kinetics and morphology could be controlled by properly managing the vapor supersaturation and substrate misorientation angle. By understanding the relationship between these two parameters, as they related to the surface supersaturation, one could predictably and reproducibly achieve and transition between 3D island growth, step-flow, or step-bunching in a variety of complementary parameter spaces. Since this framework was developed without a

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specific material in mind, it was suggested to be universally applicable to other materials [11].

In this study, we followed the same framework to understand the surface kinetics and to control surface morphology and composition of Al-rich AlGaN. Al-rich AlGaN films were grown by metalorganic chemical vapor deposition (MOCVD) on vicinal c-plane AlN and sapphire substrates to determine the role of surface steps and dislocations on the resulting surface morphology. The compositional uniformity and Al content in AlGaN as it related to the surface morphology was also studied. The end result of this work was a scheme for controlling the surface, composition, and compositional uniformity of Al-rich AlGaN thin films in MOCVD growth.

2. Experimental procedure

Physical vapor transport deposition was implemented to grow the single crystalline boules used to generate the AlN substrates [12–14]. These boules were cut to fabricate substrates with vicinal (0001) oriented surfaces to grow on. The substrates had a chemo-mechanically polished, atomically smooth surface, free of surface defects based on inspection by optical and atomic force microscopies (AFM). Prior to growth, the AlN substrates were treated following the procedure that included solvent cleaning, acid etch and nitridation of the surface before epilayer deposition [11,15]. All of the films studied here were grown in a rf-heated, vertical, cold-walled, MOCVD reactor [16]. For films grown on sapphire substrates, first an AlN template was grown. These AlN templates had atomically smooth bilayer stepped surfaces with RMS roughnesses of less than 200 pm for $5 \times 5\ \mu m^2$ AFM scan areas [11].

For the results discussed in this study, all surfaces shown are of films that were either grown directly on the AlN substrates or on AlN templates on sapphire. The following growth conditions were used for these films: H_2 was used as the diluent gas with a flow rate of approximately 450 mmol/min during the entire growth; the trimethylaluminum (TMA) flow was varied from 7 to 28 μmol/min, the triethylgallium (TEG) flow was between 2 and 12 μmol/min, while the ammonia (NH_3) was fixed at around 13 mmol/min. All AlGaN epitaxial films were grown at 1100 °C and 20 Torr total pressure.

The Al content of the AlGaN films was determined using reciprocal space mapping by high resolution x-ray diffraction (HRXRD) and a technique developed by Tweedie et al. that allows for separation of strain and composition effects in XRD [17]. The HRXRD measurements were conducted using a Philips X'Pert Materials Research Diffractometer with a Cu Kα x-ray source. Conventional transmission electron microscopy (TEM) was implemented to study extended defects in these films using a JEOL 2000FX operating at 200 kV. TEM samples were prepared by mechanical wedge polishing followed by Ar^+ ion milling with a Fischione Model 1010 Ion Mill. For the films grown on the AlN substrates, TEM analysis confirmed that no new dislocations were introduced in the epitaxial layers, which indicated that the high quality of the substrate was maintained throughout the MOCVD growth and all AlGaN films were pseudomorphic. For films grown on sapphire, similar TEM analysis provided a consistent dislocation density around $1 \times 10^{10}\ cm^{-2}$. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) was performed using a probe corrected FEI Titan G2 60-300kVS/TEM at 200 kV for Z-contrast imaging of AlGaN epitaxial layers. Photoluminescence (PL) spectra were acquired using a pulsed ArF excimer laser ($\lambda = 193$ nm) along with a Princeton Instruments Acton SP2750 0.75 m monochromator, with a 150 grooves/mm grating, and a PIXIS:2KBUV cooled charge-coupled device camera. All measurements were taken with an excitation and detection angle of 45° to the surface normal. An Asylum Research MFP-3D atomic force microscope in tapping mode was used to study the surface morphology of all the films. Before growth, both AlN and sapphire substrate surfaces were characterized by AFM to determine the misorientation angle relative to the [0001] direction. These measurements were further supported using standard HRXRD techniques.

3. Results and discussion

Although the RMS roughness of all Al-rich AlGaN films was below 1 nm, those grown on AlN templates on sapphire were relatively rough compared to those grown on the native AlN substrates. The larger dislocation density present in the films grown on sapphire substrates resulted in step-pinning and a high degree of spiral growth. This spiral growth mechanism resulted in overall rougher surfaces. Fig. 1 shows the surface of an AlN and $Al_{0.60}Ga_{0.40}N$ film grown on sapphire. The AlN surface had a much smoother surface relative to the $Al_{0.60}Ga_{0.40}N$ surface, with over an order of magnitude difference in the RMS roughness. Step-pinning and spiral growth made it difficult to directly observe the long-range surface kinetics as related to different growth modes. Therefore, to properly study the surface kinetics of Al-rich AlGaN, it was necessary to grow films on low dislocation density substrates.

The amount of Ga in the alloy films directly affected the spirals as predicted by the Burton, Cabrera, and Frank (BCF) theory, i.e. the terrace width about a dislocation spiral was inversely proportional to the natural logarithm of the vapor supersaturation [18]:

$$\frac{1}{\lambda_0} \propto ln(1 + \sigma), \tag{1}$$

where λ_0 and σ are the average terrace width and vapor supersaturation, respectively. A $2 \times 2\ \mu m^2$ AFM image of the growth spirals is given in Fig. 2. These spirals formed due to dislocations which had a component of the displacement vector normal to the growth surface, i.e. mixed and screw type dislocations. In particular, the spirals observed in Al-rich AlGaN and AlN were double spirals comprising of two interlocking spiral ramps, each dislocation pinning two steps [19]. By introducing Ga, the supersaturation was reduced since the equilibrium vapor pressure of Ga is much larger than that of Al. Studies on the 60–100% Al content AlGaN films grown on sapphire indicated a direct correlation of increasing terrace width about a spiral with an increase of Ga content. Most importantly, for any further reduction in the RMS roughness of AlGaN films using a sapphire substrate, the dislocation density must be reduced.

For the 60–100% Al content compositional range studied, the observed types of morphology were similar to those observed in AlN homoepitaxy [11]. Because of the low dislocation density of $< 10^3\ cm^{-2}$, spiral growth did not interfere with the steps, allowing for a detailed study of surface kinetics of Al-rich AlGaN. Depending on growth conditions and substrate misorientation, macro-sized 3D islands, bilayer steps, and step-bunches were observed.

Fig. 3 shows two $Al_{0.80}Ga_{0.20}N$ films grown on AlN substrates with different growth rates. The substrate misorientation angle, α, was kept constant at 0.17°. A 3D growth mode appeared for a growth rate of 1200 nm/h. The islands were slightly tilted due to the misorientation angle. By reducing the growth rate to 600 nm/h, a purely step flow growth mode was achieved and resulted in an atomically smooth bilayer step morphology with an RMS roughness < 50 pm for a $5 \times 5\ \mu m^2$ AFM scan area. This demonstrated the transition from the 3D island growth to step flow growth mode by reducing the vapor supersaturation, as predicted