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The Structural Quality of $Al_xGa_{1-x}N$ Epitaxial Layers Grown by Digitally-Alloyed Modulated Precursor Epitaxy Determined by Transmission Electron Microscopy.

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Abstract

$Al_xGa_{1-x}N$ layers of varying composition ($0.5 < x_{Al} < 1.0$) grown in the digitally-alloyed modulated precursor epitaxial regime employing AlN and GaN binary sub-layers by metal organic chemical vapor deposition on AlN templates were characterized by transmission electron microscopy techniques. Fine lamellae were observed in bright field images that indicate a possible variation in composition due to the modulated nature of growth. In higher Ga content samples ($x_{Al} < 0.75$), a compositional inhomogeniety associated with thicker island regions was observed, which is determined to be due to large Ga-rich areas formed at the base of the layer. Possible causes for the separation of Ga-rich material are discussed in the context of the growth regime used.

By varying the composition of Al and Ga, the band gap of AlGaN can be tuned from 3.4 to 6.2 eV, corresponding to the UV wavelengths of the electromagnetic spectrum. This makes alloys of AlGaN of great interest for optoelectronic applications such as laser diodes and photodiodes that operate in this wavelength range[1].

Growth of good quality material is essential for realizing this potential. Due to a relative lack of native substrates, AlGaN is usually grown on foreign substrates, such as sapphire or Si, that introduce high defect densities into the layer due to large mismatches in the lattice parameter and thermal expansion coefficient. This problem can be relieved somewhat by the use of a buffer layer, usually GaN or AlN[2], or other complex growth structures[3]. However, the layer quality can also be limited by the growth technique used.

In conventional methods, high growth temperatures and low growth pressures must be used to overcome issues with growth of high Al content AlGaN such as the higher reactivity of trimethylaluminum compared to trimethylgallium[4]. Growth at higher temperatures can be avoided using the modulated precursor epitaxial growth (MPEG) regime whereby the group III and V element precursors are introduced into the growth chamber separately in an alternating sequence[5]. However, growth of ternary AlGaN layers using this method (where the composition is controlled by the element ratio in the group III phase of growth) is difficult due to the volatility of Ga atoms in the absence of an NH_3 overpressure, which limits the amount of Ga that can be incorporated into the layer[6].

In this paper, we characterize AlGaN layers of varying composition grown by the digitally alloyed modulated precursor epitaxial growth (DA-MPEG) technique using transmission electron microscopy (TEM) techniques. In this growth method, AlN grown by MPEG is alloyed with conventionally grown GaN in two separate sub-layers, the intention being to overcome the issues of Ga incorporation and differential sticking coefficients inherent to MPEG of ternary AlGaN. While the quality of these layers appear to be quite good, we observe fine lamellae in bright field images that may indicate slight compositional variations not indicated in diffraction patterns. We also observe Ga-rich regions at the base of islands in samples with higher Ga contents that results in a rougher surface morphology.

The $Al_xGa_{1-x}N$ layers were grown by metal organic chemical vapor deposition (MOCVD) in the DA-MPEG regime employing AlN and GaN binary sub-layers on conventionally grown AlN templates. Four samples were studied with Al compositions determined by x-ray diffraction (XRD) of x =1.00, ~ 0.95, ~ 0.75, and ~ 0.50. The details of the sample growth, as well as optical transmittance, XRD and atomic force microscopy data are discussed elsewhere[7]. Cross-sectional TEM specimens were prepared using standard mechanical grinding and dimpling techniques, followed by low energy, low angle Ar ion milling. Samples were examined in a JEOL 3010 TEM operating at 300kV and a Philips Tecnai operating at 200kV equipped with a high angle dark field detector and a Gatan parallel electron energy loss spectrometer capable of collecting energy-filtered TEM images. The templates were around 800 nm thick and the dislocation density at the pit-free surface was ~ 10^{10} cm^{-2}.

In the sample with no Ga, the MPEG layer interface was difficult to observe, as there was no significant change in contrast in cross-sectional TEM images. This is expected, as there is no compositional difference between the template and epilayer. However, fine lamellae of dark/ light contrast 1-3nm thick were observed in some areas of the MPEG layer when imaged under g = (0002) diffraction conditions, as indicated in Fig. 1. The surface of the MPEG layer was smooth, with no indication of pits. Similar observations were made for the sample with x ~ 0.95. Again, the $Al_xGa_{1-x}N$/ template interface was difficult to observe due to the lack of contrast and fine lamellae ~1nm thick were observed in the DA-MPEG layer on occasion. Using the lamellae to reference the interface, the layer thickness was measured to be 30 ± 3nm and 33 ± 2nm in the x = 0 and x ~ 0.95 samples, respectively.

In the x ~ 0.75 and x ~ 0.5 samples, the $Al_xGa_{1-x}N$ layer exhibits thinner uniform areas and occasional thicker "island" areas, as shown in Fig. 2. The thinner areas are around 40 ± 2 nm and 55 ± 5nm thick in the x ~ 0.75 and x ~ 0.5 samples, respectively and show similar quality to the x = 0 and x ~ 0.95 layers with 1-2nm thick lamellae again being observed. The layer quality at the islands is much poorer compared to the thinner uniform regions. Strong lamellae are visible in the upper part of the islands and areas of darker more uniform contrast are observed at the base in bright field images from both samples, as indicated for the x ~ 0.5 sample in Fig. 2(b). The island regions are around 60-80nm and 100-150nm thick and have a density of ~10^6 cm^{-2} and ~ 10^8 cm^{-2} in the x ~

0.75 and x ~ 0.5 samples, respectively. The increasing island density and size results in an increasing overall surface roughness with increasing Ga content.

Fig. 3(a) shows a [1$\underline{1}$00] zone axis selected area diffraction pattern (SADP) from the x ~ 0.5 sample, indicating good crystal perfection. However, a compositional inhomogeniety is indicated in SADP's from island regions, as shown in (b). Knowing that the outermost spot corresponds to the AlN template, the two other spots give lattice spacings corresponding to compositions of x ~ 0.5 and x ~ 0 (i.e. pure GaN) using Vergard's law. This may be compared with the same order diffraction spot from a thin area of the foil in (c) where only one composition of x ~ 0.5 is indicated.

Z-contrast and energy filtered TEM images of the island regions in the x ~ 0.5 sample such as those in Fig. 4 reveal the location of the compositional inhomogeniety. The areas of uniform darker contrast at the base of the islands in bright field TEM images appear as areas of brighter contrast, i.e. higher Z, in high angle annular dark field STEM images (arrowed in Fig. 4(a)). The bright areas are approximately 50 – 80nm thick and their morphologies correspond well to the surface of the layer. Energy filtered TEM images from the same region show that the bright areas correspond to a high Ga content and a low Al content compared to the rest of the layer, consistent with the SADP's. The large Ga-rich regions cover several dislocations, but there is no clear correlation between the two.

The SADP's taken from the uniform areas of the samples indicate that the quality of growth is good. However, the fine lamellae seen in all the samples may indicate a compositional variation below the limits of observation in the SADP's. The bright/ dark contrast variations of the lamellae most likely arise due to mass-thickness contrast from compositionally different sub-layers. This compositional variation may arise due to the MPEG regime used, where the group III and V precursors are separated temporally; the alternating stages of growth may produce group III- and N-rich layers that are dark and bright in mass-thickness contrast, respectively. This effect may be enhanced around dislocations where large numbers of atomic steps favor the accumulation of thicker than expected sub-layers. Alternatively, the Al sub-layer could be oxidized prior to ammonia flow. The lamellae do not arise due to phase separation[8], as there was no indication of this in agreement with diffraction patterns.

The thick island regions in the layers with higher Ga content are clearly related to the presence of the Ga-rich material, possibly pure GaN, accumulated at the base of the layer. The Ga-rich areas are only observed at the base of the AlGaN layer, indicating that they are formed early in the layer growth. We suggest that excess Ga not incorporated into the AlN sub-layer during GaN sub-layer deposition forms the initial Ga-rich areas near the substrate (possibly at dislocations). This is consistent with the increase in island density with increasing Ga content. The increased lattice mismatch with the template at these Ga-rich areas may lead to relaxation by 3-D growth, explaining the size and shape of these areas compared to the rest of the layer growing in a 2-D mode. In addition, these areas have a different sticking coefficient compared to the rest of the layer and favor the

accumulation of more GaN, growing larger with increasing Ga content. Eventually the strain is relieved and 2-D growth resumes, allowing cladding by AlGaN to occur. However, excess GaN is still not incorporated well and the strong lamellae are produced in the upper part of the islands.

In summary, we observed compositional inhomogenieties in $Al_xGa_{1-x}N$ ($0.5 < x < 1.0$) layers grown in the DA-MPEG regime. Fine lamellae were observed throughout all layers that indicated compositional variations not detected in SADP's. However, a significant compositional inhomogeniety was observed in SADP's from samples with greater Ga content ($x < 0.75$). Z-contrast and energy filtered images revealed the presence of large Ga-rich regions at the base of thicker islands in the layer. We suggest that these features arise due to the nature of the DA-MPEG growth regime.

Acknowledgements

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Figure 1: Bright field image of the AlN MPEG layer with line profile between points A and B. Fine lamellae of bright/ dark contrast ~ 2nm thick are visible near dislocations. Similar results were obtained for the $Al_{0.95}Ga_{0.05}N$ DA-MPEG layer.

Figure 2: (a) An isolated island region in the otherwise thin, uniform layer with x ~ 0.75. (b) Several island regions in the layer with x ~ 0.5. The island regions are associated with large areas of darker contrast at the base of the layer ("X").

Figure 3: (a) Selected area diffraction pattern from the epilayer/ template region in the sample with x ~ 0.5 (b) Close-up of the ($\underline{11}$26) order spots (highlighted in (a)) for a diffraction pattern from an island region. (c) The same ($\underline{11}$26) order spots for a diffraction pattern from a thin uniform area. An additional diffraction spot is visible in (b) that corresponds to x ~ 0.

Figure 4: (Color online) (a) Z-contrast image of the x ~ 0.5 epilayer (cf. Fig. 3(b)) showing brighter areas at the base of the islands. Energy filtered images from the same (highlighted) area confirm that the bright areas correspond to Ga-rich (b) and Al-poor (c) regions, consistent with the SADP's.

(a) island

AlGaN

template

100nm

(b) islands

AlGaN

X

template

X

100nm

(a)

(0002)

($\bar{1}\bar{1}20$) ($11\bar{2}0$)

(000$\bar{2}$)

Island Region

AlN

x ~ 0.5

x ~ 0

(b)

Thin Area

AlN

x ~ 0.5

(c)

(a) z-contrast
100nm
(b) Ga
(c) Al