High indium content homogenous InAlN layers grown by plasma-assisted molecular beam epitaxy

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Abstract

InAlN grown by plasma-assisted molecular beam epitaxy often contains a honeycomb microstructure. The honeycomb microstructure consists of 5-10 nm diameter aluminum-rich regions which are surrounded by indium-rich regions. Layers without this microstructure were previously developed for nominally lattice-matched InAlN and have been developed here for higher indium content InAlN. In this study, InAlN was grown in a nitrogen-rich environment with high indium to aluminum flux ratios at low growth temperatures. Samples were characterized by high-resolution x-ray diffraction, atomic force microscopy, high-angle annular dark-field scanning transmission electron microscopy, and atom probe tomography. Atomic force microscopy showed InAlN layers grown at temperatures below 450 °C under nitrogen-rich conditions were free of droplets. InAlN films with indium contents up to 81% were grown at temperatures between 400 and 440 °C. High-angle annular dark-field scanning transmission electron microscopy and atom probe tomography showed no evidence of honeycomb microstructure for samples with indium contents of 34% and 62%. These layers are homogeneous and follow a random alloy distribution. A growth diagram for InAlN of all indium contents is reported.

Keywords

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1 Introduction

The III-nitrides are used today in both optoelectronic and electronic devices because of their direct bandgaps ranging from 0.7 eV (InN) to 6.2 eV (AlN). Within the III-nitride material system, InAlN is of great interest. It can be grown over the entire composition range including compositions that are lattice-matched and polarization-matched to GaN. InAlN lattice-matched to GaN in the (0001) plane (indium content ~17%) is currently used for barrier layers in high electron mobility transistors (HEMTs), as well as for electron and hole blocking layers (EBLs/HBLs) in lasers and light-emitting diodes (LEDs) [1–6]. InAlN lattice-matched to GaN is advantageous for these applications because of its wide bandgap (4.3 eV), large spontaneous polarization, and stress-free state. InAlN polarization-matched to (0001) oriented GaN (indium content ~32%) has not been widely studied but has many potential applications including back barriers for depletion-mode HEMTs, barrier layers in enhancement-mode HEMTs, and EBLs and HBLs in LEDs and lasers [7]. Higher indium content InAlN can be used in EBLs and HBLs that are polarization-matched to quantum wells.

In conventional plasma-assisted molecular beam epitaxy (PAMBE), the III-nitrides are grown under metal-rich conditions. Growth is performed under a liquid-like chemisorbed metal bilayer. For GaN, two growth regimes are present under metal-rich conditions: the intermediate and droplet regime. Excess gallium will form a wetting layer. The metal adlayer increases adatom diffusivity, allowing for adatoms, particularly atomic nitrogen, to incorporate at favorable step edges. In the droplet regime more than two monolayers develop and droplets form. Material grown under these conditions has smooth surfaces but large depressions can form under the droplets where less nitrogen can diffuse [8]. Above 600 °C, excess gallium desorbs from the growing surface. The rate at which excess gallium desorbs from the surface follows Arrhenius dependence with an activation energy of 2.8 eV [8]. When the gallium desorption rate is great enough, the adlayer has less than full coverage and growth is in the intermediate regime. Growth in the intermediate regime does not result in gallium droplet formation. The surface has a combination of smooth and rough regions. In the smooth regions, excess gallium has residence time before desorption. In the rough regions, there is no adlayer coverage – the surface is dry. Under nitrogen-rich growth conditions the total metal flux delivered to the surface is less than

both the flux incorporated into the growing crystal and the flux desorbing. Nitrogen-rich growth conditions produce rough morphology; adatoms have low surface diffusivity.

Conventional metal-rich PAMBE group-III nitride growth is performed in the droplet regime. Minimal excess gallium is used and periodic desorption of the metal adlayer is performed to reduce droplet formation [9]. Reflection high-energy electron diffraction (RHEED) is used to measure desorption and monitor the growth. Adlayer coverage dims the RHEED. When growth is paused, the adlayer will desorb and the RHEED will regain intensity. Rough surfaces create a spotty RHEED pattern. Layer-by-layer growth will produce oscillations in the RHEED intensity. Step flow growth will show no change in RHEED intensity.

InAlN growth has proven difficult due to the large difference in lattice parameters and bond strength between InN and AlN. The ideal growth temperatures for InN and AlN are also very different, stemming from a significant difference in their melting temperatures. AlN's melting temperature is $\sim 2,200$ °C, while InN's melting temperature is $\sim 1,100$ °C [10,11]. The growth of InAlN by PAMBE often results in a columnar "honeycomb" microstructure. This structure consists of cells with inner regions of high aluminum content that are surrounded by regions of high indium content [12,13]. The cell spacing of these structures is about 5-10 nm [12,13]. Growth of InAlN under indium-rich conditions as well as growth with In/Al flux ratios much less than 1 under nitrogen-rich conditions result in this honeycomb microstructure [12–16]. By growing InAlN under indium-rich conditions, surface clustering [17] is reported in addition to the honeycomb microstructure [10,11,13,18].

PAMBE InN growth is usually performed at much lower temperatures (400-500 °C) than GaN (700 °C) and AlN (740 °C) [8,19,20]. InAlN or InGaN alloys are usually grown at a temperature in between that of InN and AlN or GaN. The maximum achievable indium content is given by its solubility limit in the growing crystal. Above the solubility limit, indium metal starts to form an adlayer on the growing surface, even under nitrogen-rich growth conditions [17,21]. The solubility of indium in a nitride crystal increases significantly as the temperature is reduced [17,21–24]. The maximum indium content for a given nitrogen flux and growth temperature can be found when growth is performed under an indium adlayer. At the low growth temperature needed to incorporate indium, aluminum has very low adatom mobility. Growth under an adlayer should increase the aluminum adatom mobility but layers grown under these conditions still contain honeycomb microstructure [12,13,15,18]. The high growth rates needed to maintain

indium-rich conditions may contribute to the formation of the honeycomb microstructure. Nitrogen fluxes greater than 2 nm/min are needed to maintain a stable RF-plasma in this growth system. Lower growth rates give adatoms more time to diffuse to favorable incorporation sites, even though adatom mobility decreases under nitrogen-rich conditions [25]. Manuel *et al.* reported that lowering the growth rate resulted in homogeneous films [18]. Presumably the homogenous films were grown with a similar nitrogen flux to that of the higher growth rate films in Manuel *et al.*'s study. In this case, the homogenous InAlN in Manuel *et al.*'s study is grown under similar conditions to that used in our study. It is unclear from their work if honeycomb microstructure was eliminated; only cross-sectional transmission electron microscopy (TEM) was presented.

Recently, the growth of homogenous metal-polar and nitrogen-polar lattice-matched InAlN films have been reported by growing at 550 °C under nitrogen-rich conditions with high In/Al flux ratios [3,26]. At temperatures above ~450 °C increasing the indium flux will not produce high indium content films; indium reaches its solubility limit once a saturated metal-adlayer forms on the growth surface. No reports to date have shown the successful growth of homogeneous InAlN films with indium contents greater than 30%. We report InAlN with a wide range of indium contents by growing with high active nitrogen fluxes, and high indium fluxes at low temperatures. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and atom probe tomography (APT) showed InAlN grown under specific conditions followed a random alloy distribution.

A growth diagram for homogenous InAlN with a wide range of indium contents is missing from the literature. A growth diagram relates growth variables, such as temperature and fluxes, to film properties, such as growth mode, surface structure, and resultant microstructure. By mapping the growth mode, surface morphology, and microstructure of films to the growth conditions, we seek to understand the growth regimes present during the growth of InAlN. Previously, InAlN growth diagrams for PAMBE have been generated for N-face growth, low indium content metal-polar growth, and growth on SiC [17,25,27]. Since these films had honeycomb microstructure, we have developed the first growth diagram for InAlN without honeycomb microstructure. We have developed a growth diagram for metal-polar InAlN that covers the growth of InAlN layers with indium contents ranging from ~10% to ~80% by PAMBE.

2 Experimental

InAlN layers were grown on Lumilog GaN-on-sapphire templates ($\sim 5 \times 10^8 \text{ cm}^{-2}$ threading dislocation density). All growths were performed on a Varian Mod Gen II or a Veeco Gen 930 molecular beam epitaxy system. Both systems are equipped with conventional effusion cells for indium, aluminum, and gallium. A standard Veeco RF-plasma was used to achieve an active nitrogen flux of $8.0 \times 10^{14} \text{ atoms/cm}^2\text{s}$ calculated from the growth rate of GaN grown under gallium-rich conditions. All InAlN growths were performed in the nitrogen-rich growth regime where the total metal flux is less than the active nitrogen flux ($\Phi_{\text{In}} + \Phi_{\text{Al}} < \Phi_{\text{N}}$). The aluminum flux was held constant at $3.4 \times 10^{13} \text{ atoms/cm}^2\text{s}$, and the indium BEP was varied from $1.9 \times 10^{13} \text{ atoms/cm}^2\text{s}$ to $5.4 \times 10^{14} \text{ atoms/cm}^2\text{s}$.

The growth rate for these films varied from approximately 0.8 nm/min to 4.5 nm/min with a change in the In/Al flux ratio from 0.5 to 14.5 for growths at 420 °C. The growth of InAlN was systematically studied for different In/Al flux ratios and different growth temperatures. Layers were 15-80 nm thick. Temperatures above 600 °C were not studied. 550 °C was already established as the optimal growth temperature for lattice-matched InAlN, and indium incorporation decreases with increasing temperature [3].

RHEED was used for *in-situ* growth monitoring. The surface morphology of each sample was determined by atomic force microscopy (AFM) on an Asylum MFP3D. High-resolution x-ray diffraction (HRXRD), symmetric ω - 2θ scans of the GaN (0002) reflection were examined on a PANalytical MRD PRO Thin Film Diffractometer. InAlN composition and film thickness was determined by the InAlN-to-GaN (0002) peak separation, Pendellösung satellite fringe spacing, and Vegard's law. Indium content was calculated assuming complete relaxation of the lattice mismatch between InAlN and GaN for films with an indium content greater than 24%. For films with lower indium content than 24%, the indium content was calculated assuming that the InAlN layer is fully coherent to the underlying GaN substrate. All compositions were calculated assuming Vegard's Law. Later publications from our group will show consistency with Vegard's Law. Thorough analyses of stress relaxation mechanisms and critical thickness for compressively strained InAlN will be published elsewhere.

HAADF-STEM and APT were used to examine InAlN alloy homogeneity, and indium and aluminum atomic concentrations of InAlN heterostructures. A thick GaN cap was grown to facilitate the APT experiment by reducing changes in the APT conditions during evaporation of

the GaN/InAlN interface. A nickel cap was deposited via e-beam evaporation to reduce damage during focused ion beam (FIB) milling for TEM and APT sample preparation. The specimens were prepared with a FEI Helios 600 dual beam FIB instrument following standard procedure with final FIB voltage down to 2 kV to minimize gallium induced damage [28]. APT analysis was performed with a Cameca 3000X HR Local Electrode Atom Probe (LEAP) operated in laser-pulse mode (13 ps pulse, 532 nm green laser, 10 μm laser spot size) with a sample based temperature of 35 K. The laser pulse energy was 0.1 nJ and a detection rate of 0.002 atoms per pulse was set during the analysis. APT 3D reconstruction was carried out using commercial software IVAS^{TM}. The thickness of the InAlN layers were measured in STEM and these thicknesses were used as a reference in the APT reconstruction. A FEI Titan FEG Microscope operated at 300 kV was used for HAADF-STEM images.

3 Results and Discussion

3.1 InAlN Growth Development

Lattice-matched InAlN layers were previously grown under nitrogen-rich conditions at ~550 °C with an In/Al flux ratio of 1 and a nitrogen/group-III flux ratio of 4 [3]. APT and TEM analysis showed these layers were free of any characteristics of honeycomb microstructure [3]. Using similar conditions, InAlN layers were grown with indium contents of ~5-20%. Layers grown under these conditions have smooth surfaces and no evidence of droplet formation. By increasing the In/Al flux ratio at 550 °C, indium droplets formed on the surface as indium reached its solubility limit in the InAlN film. Samples were grown at varying growth temperatures and In/Al ratios to find if high indium content InAlN can be grown free of indium droplets.

Representative surface morphologies of InAlN layers grown in this study as well as the morphology of the underlying GaN template are shown in Fig. 1. The AFM images are 5 μm x 5 μm . Figure 1(a) shows the surface of an InAlN layer grown at 585 °C. The InAlN layer had an indium content of 12.5%. The surface morphology shows clear step terrace structure consistent with step flow growth around spiral hillocks. The surface morphology resembles that of InAlN layers grown at 550 °C with an In/Al flux ratio of 1, like the layers grown by Kaun *et al.* [3]. Growths performed at temperatures between ~450 °C and ~575 °C with an In/Al flux ratio of 2 resulted in metal accumulation and droplets on the surface. An AFM image of an InAlN layer with droplets is shown in Fig. 1(b). The droplets are indicated with black arrows. A rough morphology can be seen in between droplets, possibly the initiation of additional droplets. The InAlN layer in Fig. 1(b) was grown at 535 °C with an In/Al flux ratio of 2 and had an indium content of 22%. By growing at temperatures below 450 °C, InAlN layers without surface metal accumulation were realized. An AFM image of InAlN grown at 435 °C and an In/Al flux ratio of 2 is shown in Fig. 1(c). The indium content of the InAlN layer in Fig. 1(c) was 30%. The surface morphology of layers grown at 435 °C and 585 °C resembles that of the underlying GaN layer – terrace structure with step flow growth around spiral hillocks. Figure 1(d) shows a GaN layer grown under standard PAMBE conditions. The layer was grown at 700 °C under metal-rich conditions.

InAlN layers grown between 400 and 440 °C with In/Al flux ratios ranging from 0.5 to 14.5 resulted in similar surface morphologies to Fig. 1(c). Symmetric HRXRD ω - 2θ scans around the GaN (0002) reflection of InAlN layers grown at 390, 420, and 450 °C are shown in Fig. 2. HRXRD scans are of layers with a nominal indium content of ~34% (In/Al flux ratio of 2) and ~62 % (In/Al flux ratio of 6). High-order Pendellösung satellite fringes are seen in the HRXRD scans for InAlN layers grown at 420 °C indicating a high degree of uniformity. InAlN grown at 390 °C showed no Pendellösung satellite fringes in the HRXRD scans. All layers grown at or below 390 °C showed similar HRXRD scans. At low temperature adatoms may not be able to diffuse to favorable step edges. Additional disorder and dislocation density is present in the crystal causing loss of coherency to the GaN surface. Growths at 450 °C resulted in low-order Pendellösung satellite fringes. The reduction in satellite fringes may be due to a reduction in the thickness uniformity. Layers grown with fully formed droplets do not show satellite fringes.

Analysis of off-axis x-ray diffraction peaks for films in this study with indium content greater than 24% showed full relaxation of the InAlN peak. Therefore the indium content for these films was calculated assuming that the InAlN layer is fully relaxed to the underlying GaN substrate. For films with indium content lower than 24%, layers were not seen to relax in reciprocal space maps. Further studies of relaxation have shown these layers to be fully strained. Also tensile strained layers (indium content less than 17%) did not show cracks and therefore were not relaxed. The indium content for these films was calculated assuming that the InAlN layer is fully coherent to the underlying GaN substrate.

The RHEED patterns progressed from a clear 2 x 2 reconstruction preceding the growth of InAlN (characteristic of the low temperature GaN surface), to a 1 x 1 reconstruction during the growth of InAlN for all films investigated grown under nitrogen-rich conditions for InAlN grown under 450 °C. Figure 3 shows the RHEED pattern proceeding, after 2 monolayers, and after 20 nm of InAlN grown at 390 °C, 420 °C and 450 °C with an In/Al flux ratio of 2. No intensity oscillations were observed in the RHEED specular spot during InAlN growth. For growth temperatures greater than 390 °C, the RHEED specular spot intensity decreased as growth proceeded. When growths were performed at or below 390 °C the RHEED pattern did not dim and became immediately spotty. Spotty bright RHEED patterns have been reported for the low temperature growth of InAlN with much lower In/Al flux ratios than reported here [14].

The spotty RHEED pattern indicates growth progressed in an island growth mode and the bright pattern indicates no partial or full metal adlayer is present on the growth surface.

For growth at 420 °C, the RHEED pattern progressed from clear streaks to dimmer undulating streaks. Growth at 450 °C showed a pattern similar to that of growth at 420 °C but the pattern is qualitatively dimmer. Full or partial metal adlayers present on the growth front can dim the RHEED pattern. If the metal shutters are closed and the nitrogen shutter is left open after InAlN growth at these temperatures, the RHEED pattern does not regain its intensity. If an indium adlayer or partial adlayer is present, it may be energetically unfavorable to incorporate into the layer even in the presence of active nitrogen and no additional metal flux – i.e., essentially for specific growth conditions, the indium in the adlayer has the same chemical potential as the indium in the InAlN. A similar dimming in RHEED is seen during the growth of indium containing alloys under ammonia-rich conditions by ammonia-based MBE [30].

3.2 Homogenous InAlN

HAADF-STEM was performed on two InAlN films to examine InAlN homogeneity. The films were grown at 430 °C with In/Al flux ratios of 2 and 6. Indium content was determined by HRXRD to be 34% (In/Al flux ratio of 2) and 62% (In/Al flux ratio of 6) with thicknesses of 15 nm and 13 nm, respectively. Cross-sectional and plan-view HAADF-STEM images of the 34% indium sample are shown in Fig. 4. Cross-sectional and plan-view HAADF-STEM images for the 62% indium sample are shown in Fig. 5. The plan-view HAADF-STEM images were taken along the [0001] zone axis projection. The cross-sectional HAADF-STEM images were taken along the [11 $\bar{2}$ 0] zone axis projection. Contrast in the images is based on atomic number. The higher intensity areas are created from higher atomic number atoms, therefore, the higher intensity areas have higher indium content in these images. Variations in contrast in the images are consistent with damage from the focused ion beam during preparation. No other discernable intensity contrasts can be seen in the layers – no honeycomb microstructure is observed. APT was used to confirm contrast variations were due to ion beam damage.

APT analysis was completed to examine the homogeneity of both InAlN layers on which HAADF-STEM was performed. For the InAlN layer with indium content of 34%, the APT data is shown in Fig. 6. For the InAlN layer with indium content of 62%, the APT data is shown in Fig. 7. APT 3D reconstructions of the volume analyzed are shown in Fig. 6(a) and Fig. 7(a). The

group-III site profiles in the growth direction (*c*-direction, along the tip) are shown in Fig. 6(b) and 7(b). The average group-III site concentrations in the higher indium content InAlN layer were 65% indium and 35% aluminum. The indium and aluminum concentrations differ only slightly from the values calculated by HRXRD of 62% indium and 38% aluminum. For the lower indium content InAlN layer, the average group-III site concentrations were 34.5% indium and 65.5% aluminum. The indium and aluminum concentrations are very close to the values calculated by HRXRD of 34% indium and 66% aluminum. 2D compositional profiles for indium in the *c*-plane are shown in Fig. 6(c) and Fig. 7(c). The profiles are perpendicular to the group-III site profiles in Fig. 6(b) and 7(b). The profiles are taken from a 2 nm thick cylindrical slice taken in the InAlN layers. The diameter of the slice is 20 nm and indium group-III site distribution are measured in 0.4 nm x 0.4 nm x 2 nm sub-volumes.

APT 3D reconstructions were used to determine whether indium in the InAlN layers is randomly distributed or whether it has a tendency to cluster. Nitrogen was first removed from the APT mass spectrum so that only the group-III site atoms contribution in the volume was taken into account. The variation of nitrogen concentration across the volume originates from the APT analysis and does not represent the reality of the sample [31]. A region of interest was then extracted in each layer away from the low density region in the global APT reconstructed volume. This low density region corresponds to the crystallographic direction [0001]. During ion evaporation, the ions' fly away from this direction causing a low density of impacts in the APT detector and a corresponding low density region in the reconstructed volume. The data was then binned into sub-volumes which contain 100 atoms. Indium and aluminum group-III site fraction was then counted in each sub-volume. The real space linear dimension of the sub-volumes is about 2.8 nm in each dimension and has to remain constant to account for the lateral concentration variations in indium and aluminum. With high density variations in the global volume, the sub-volumes with constant number of atoms are no longer constant in the real space dimension [32]. Taking a region of interest away from the low density region ensures the reliability of the distribution. The total number of group-III atoms considered was 16,200 for the high indium content sample and 14,300 ions for the low indium content sample.

Figure 6(d) and 7(d) show the indium concentration of the bins for InAlN with indium content of 34% and 62%. The actual distribution of indium and aluminum are compared with the binomial distribution expected for a random alloy [33]. The binomial distribution for the two

elements are plotted on Fig. 6(d) and 7(d) for their respective indium contents. A quantitative comparison between the observed and the binomial distribution is performed using a χ^2 test. For InAlN with indium content of 34%, the value of χ^2 is 29.7 for 20 degrees of freedom which corresponds to a significance level of p close to 0.1. For InAlN with indium content of 62%, the value of χ^2 is 23.8 for 17 degrees of freedom which corresponds to a significance level of p equal to 0.12. To confirm the hypothesis that the alloy is random and that there is no clustering of indium or aluminum in the sample, a p value above 0.05 is required. Frequency distributions were tested in different regions of interest with constant density in the sample and for different bin sizes and the χ^2 test always confirmed the random distribution of indium in the two samples. Indium appears to be a random alloy with no evidence of phase separation.

3.3 InAlN Growth Diagram

A growth diagram for InAlN without honeycomb microstructure was developed using high In/Al flux ratios under nitrogen-rich growth conditions. To reduce the dimensionality of the growth diagram, aluminum and nitrogen were held at a constant flux of 3.4×10^{13} atoms/cm²s and 8.0×10^{14} atoms/cm²s, respectively. The growth diagram is displayed as a 2D plot in Fig. 8(a), and a 3D bar plot with indium content in the intermediate growth conditions as the z-axis in Fig. 8(b). Three distinct growth regimes were identified: the droplet regime, the intermediate regime, and the dry surface regime. Growth regimes are presented as a function of growth temperature and indium flux and separated by black lines in the growth diagram. The stoichiometric growth condition, impinging metal flux equal to active nitrogen flux, is shown with a dotted line. For layers grown with a greater metal flux than active nitrogen flux (Indium flux greater than 7.7×10^{14} atoms/cm²s), the growth is metal-rich at all temperatures and droplet formation occurs. Layers grown under metal-rich conditions were not focused upon in this diagram since they result in InAlN with the honeycomb microstructure and/or surface metal accumulation.

The growth regions are distinguished by the presence and dominance of different indium removal mechanisms from the growth surface. Indium will desorb from the growth surface, accumulate on the surface, or incorporate in the growing film. In the high temperature intermediate regime, indium desorption dominates indium removal from the growth front. As the temperature decreases, the indium desorption rate decreases and indium accumulates on the

surface. This is the droplet regime. At lower temperatures, a low temperature intermediate regime is seen. Here the flux of indium incorporated into the layer is great enough to prevent indium accumulation on the surface. At even lower temperatures, all indium incorporates into the film, and the growth is in the dry surface regime.

For the intermediate regime, the high temperature region occurs at temperatures above 550 °C at low indium fluxes. Layers grown in this regime have much less indium incorporated into the film than indium supplied to the surface. For the layer in Fig. 1(a) grown at 585 °C, the ratio of In/Al incorporated into the layer (0.14) was much less than the In/Al flux ratio supplied to the surface (2). No droplets were seen on the surface, therefore indium desorption is the primary indium loss mechanism. Some indium resided on the surface acting as a partial adlayer during growth as shown by RHEED. Indium incorporation into the film is significantly affected by growth temperature in the high temperature intermediate regime: InN does not grow under these conditions [34]. Indium incorporation into the layer decreases with increasing growth temperature [17,21,22]. For growths with an indium flux of 3.7×10^{13} atoms/cm²s, InAlN grown at 575 °C had an indium content of 12% while InAlN grown at 525 °C had an indium content of 22%.

As temperature decreased below 550 °C for an indium flux of 3.7×10^{13} atoms/cm²s, indium droplets were observed on the surface. This regime is called the droplet regime. Indium surface accumulation and droplet formation result when the indium desorption rate and the indium incorporated into the layer together are less than the indium supplied to the surface. More indium cannot be incorporated into the crystal: indium has reached its solubility limit.

Strong indium flux dependence for the onset of droplet formation was observed. Indium desorption increases with temperature, obeying an Arrhenius dependence with an activation energy of 2.5 eV in vacuum [34]. At a growth temperature of 600 °C and an indium flux of 1.5×10^{14} atoms/cm²s, droplets were observed, but at an indium flux of 1.1×10^{14} atoms/cm²s, no droplets were observed. While at 575 °C, an indium flux of 9.3×10^{13} atoms/cm²s resulted in droplets. We have included the transition from indium droplets to indium desorption with an activation energy of 2.5 eV and Arrhenius dependence. For layers grown between 450 and 550 °C with an indium flux less than 3.7×10^{13} atoms/cm²s, no droplets were observed. At these low indium fluxes, the indium never reaches the solubility limit in the crystal.

Layers grown at temperatures between 390 and 450 °C and with indium fluxes less than 5.6×10^{14} atoms/cm²s were grown in the low temperature intermediate regime. Indium primarily desorbs from the surface or incorporates into the layer in this regime. Indium build up does not occur but a partial adlayer exists on the surface. The adlayer was observed via RHEED specular spot dimming during growth. For the indium fluxes investigated, group-III site occupation of the growing layer does not significantly change the chemical potential at these lower growth temperatures and layers with a wide range of indium compositions can be grown. The temperature range at which a wide range of indium content InAlN layers can be grown agrees well with Gallinat *et al.* [34], who state InN starts to decompose at 430 °C in vacuum. InN decomposition during growth has been well characterized as a function of temperature by line-of-sight quadrupole mass spectrometry [34]. The activation energy of InN thermal decomposition is 1.92 eV [34]. We have included the transition from the droplet regime to the low temperature intermediate regime with this activation energy and Arrhenius dependence.

The indium loss from the growth front was calculated for InAlN layers grown in the intermediate growth regimes. The indium loss represents all the impinging indium which was not incorporated into the film. It was calculated assuming all the aluminum supplied to the growth surface was incorporated in the film. The loss as a function of indium flux and temperature is shown in Fig. 9. The indium loss is seen to be proportional to the indium flux supplied to the surface. The desorption rate of a species is proportional to the surface concentration of the species in addition to the Arrhenius dependence on temperature. At constant temperature, the indium desorption rate only changes with the surface concentration of indium. If the species has a rate limiting elementary step of 1, the dependence is linear as is the case for indium ($\text{In}_{\text{ads}} \rightarrow \text{In}_g$). A clear linear trend is seen for indium loss versus indium flux for layers grown in the intermediate growth regimes. Therefore a full adlayer is not present in the intermediate growth regime. If a full adlayer was present, the surface concentration of indium would be saturated and the indium loss versus indium flux data would be constant or plateau and indium droplets would form. The partial adlayer present for films grown in the intermediate growth regimes may be related to the layers' homogeneity. Maintaining high In/Al flux ratios without forming droplets would allow for aluminum and indium adatoms to reach favorable incorporation sites without clustering and building up strain gradients.

At temperatures at and below 390 °C, a growth regime opens up where indium incorporates into the layer without having significant residence time on the surface. In this growth diagram, this is considered the dry surface growth regime. Spotty, bright RHEED patterns were observed. Layers grown in this regime have broad HRXRD peaks, possibly due to dislocation generation during growth. Other results have reported the opening of a dry surface growth regime at low temperatures for the growth of InAlN [17,25]. The growth of InGaN and InN by PAMBE have seen the same behavior in which lower temperatures result in the transition from growth with droplets to a dry surface grown with the same flux ratios [21,34].

4 Conclusion

The growth of high indium content InAlN was explored by PAMBE. Growth conditions were found in which InAlN with a wide range of indium contents can be grown with smooth surfaces. Characterization of InAlN layers with indium content of 34% and 62% by HAADF-STEM and APT showed InAlN layers can be grown without columnar microstructure in which indium content follows a random alloy distribution. A growth diagram is presented for the growth of InAlN under high indium fluxes and high active nitrogen flux. Three different growth regimes are identified in the diagram. Surface morphology, HRXRD, RHEED, and indium desorption were used to distinguish the different growth regimes.

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Figure 1. 5 $\mu\text{m} \times 5 \mu\text{m}$ AFM images of InAlN layers or GaN layers. InAlN layers were grown with an aluminum flux of $3.4 \times 10^{13} \text{ atoms/cm}^2\text{s}$ and an indium flux of $7.5 \times 10^{13} \text{ atoms/cm}^2\text{s}$ under nitrogen-rich conditions. (a) InAlN layer with indium content 12.5% grown at 585 °C showed a smooth, droplet-free morphology. (b) InAlN layer with indium content 22% grown at 535 °C showed indium surface accumulation. Indium droplets are indicated by black arrows. (c) InAlN layer with indium content 30% grown at 435 °C showed a smooth, droplet-free morphology. (d) GaN layer grown under standard conditions by PAMBE shown for comparison.

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Figure 5. (a) Cross-sectional and (b) plan-view HAADF-STEM images of the 13 nm thick, 62% indium InAlN film grown on GaN.

(a)

(b)

(c)

(d)

Figure 6. APT analysis of the 15 nm thick, 34% indium InAlN sample. (a) 3D reconstruction (b) Group-III site profile in the *c*-direction. The average indium concentration in the InAlN layer is 34.5% indium as measured by APT and 34% as measured by HRXRD (c) Map of indium content in the InAlN layer averaged over the middle 2 nm of the layer. The diameter of the section is 20 nm (d) Indium content averaged over 100 ion bins compared to a binomial distribution.

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Figure 9. Indium loss as a function of indium flux supplied to the surface for different temperatures. Linear dependence on indium loss indicates the surface concentration of the indium species is not saturated at any growth condition in the intermediate regime.