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Thermal stability of $\text{Al}_{1-x}\text{In}_x\text{N}(0001)$ throughout the compositional range as investigated during *in-situ* thermal annealing in a scanning transmission electron microscope

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ABSTRACT

The thermal stability of $\text{Al}_{1-x}\text{In}_x\text{N}$ ($0 \leq x \leq 1$) layers was investigated by scanning transmission electron microscopy (STEM) imaging, electron diffraction, and monochromated valence electron energy loss spectroscopy during *in-situ* annealing from 750 °C to 950 °C. The results show two distinct decomposition paths for the In-richest layers ($\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$) that independently lead to transformation of the layers into an In-deficient, nanocrystalline and a porous structure. The In-richest layer ($\text{Al}_{0.28}\text{In}_{0.72}\text{N}$) decomposes at 750 °C, where the decomposition process is initiated by forming In at grain boundaries and is characterized by an activation energy of 0.62 eV. The loss of In from $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer was initiated at 800 °C through continuous desorption. No In clusters were observed during this decomposition process, which is characterized by an activation energy of 1.95 eV. Finally, Al-rich $\text{Al}_{1-x}\text{In}_x\text{N}$ ($x=0.18$ and $x=0.29$) layers were found to resist the thermal annealing, although initial stages of decomposition were observed for the $\text{Al}_{0.71}\text{In}_{0.29}\text{N}$ layer.

1. INTRODUCTION

Group III-nitride semiconductor ternary alloys pose a significant potential for contemporary optoelectronic applications in light emitting diodes (LEDs), laser diodes (LDs), photonic devices, high efficiency solar cells, and Bragg mirrors [1-5]. The demonstrated technology is attainable through a tunable direct bandgap ranging from near infrared (InN ~ 0.64 eV) to ultraviolet (AlN ~ 6.2 eV) [6]. While AlInN exhibits the most extensive range, the InGaN and AlGaN alloys have received the most attention, which can be explained by challenges in growing single-phase AlInN, exhibiting low defect density throughout the whole compositional range. AlInN, like many other nitride semiconductor compounds, poses a significant miscibility gap [7-8], which complicates growth throughout the compositional range. The realization of AlInN films was demonstrated by a number of growth techniques such as magnetron sputter epitaxy (MSE) [9], metal organic chemical vapor phase deposition (MOCVD) [10], and molecular beam epitaxy (MBE) [11]. MSE has the advantage of enabling growth of epitaxial AlInN films at low temperatures, covering the whole compositional range including compositions inside the miscibility gap, without the onset of phase separation [12].

The thermal stability of AlInN is a key property if the material will be implemented into high-temperature applications such as in AlInN/GaN HEMT structures, also grown at high temperature. AlInN can be grown lattice matched to GaN when the In composition is around 17-18% [13] and has been shown to be stable up to 1000 °C at this composition [14]. Recently, an AlInN/GaN HEMT structure was also shown to operate successfully at 1000 °C [15]. So far, there are few reports on the thermal stability of

AlInN with In concentrations above those lattice matched to GaN [16,17], hence little is known, particularly for material from within inside the miscibility gap.

In this paper, we present results from a thermal annealing study, as performed *in-situ* in a scanning transmission electron microscope (STEM). The thermal stability and decomposition mechanism of $\text{Al}_{1-x}\text{In}_x\text{N}$ layers with In content throughout the compositional range ($0 \leq x \leq 1$), including compositions inside the miscibility gap, are investigated. The stages of the annealing process, from 750 °C to 950 °C, were monitored *in-situ* by a combination of STEM imaging and bulk plasmon energy (E_p) mapping. Finally, the activation energies of the decomposition processes were extracted from Arrhenius plots.

2. EXPERIMENTAL DETAILS

A multilayer $\text{Al}_{1-x}\text{In}_x\text{N}$ sample was grown by ultra-high vacuum magnetron sputter epitaxy (MSE) at room temperature on a $\text{Al}_2\text{O}_3(0001)$ substrate. The multilayer consist of six layers covering the whole compositional range starting from a AlN layer, followed by $\text{Al}_{1-x}\text{In}_x\text{N}$ layers where the In content increases with each layer and ended with InN. The compositional variation of the respective $\text{Al}_{1-x}\text{In}_x\text{N}$ layers were achieved by tailoring the magnetron power of the In and Al targets. A detailed description of the growth conditions used for this and similar structures can be found elsewhere [12].

For high resolution reciprocal space mapping, over (0002) and $(10\bar{1}5)$ reciprocal lattice points, the beam of pure $\text{CuK}\alpha_1$ radiation, produced through a parabolically curved graded multilayer mirror followed by a two-bounce symmetric channel-cut Ge(220)

monochromator, was used as the primary optics. A 1° receiving slit as analyzer was used for reciprocal space mapping (RSMs) to collect the diffracted beam.

An electron transparent cross-sectional sample for the *in-situ* annealing experiments was prepared from the as-grown material the structure using the traditional ‘sandwich’ approach. First the sample was cut, mounted in a titanium grind and glued with a high temperature glue (Gatan G-1 epoxy), followed by mechanical polishing to $\sim 50\text{ }\mu\text{m}$ thickness. Ar^+ ion milling at 5 keV and 5° from both sides was performed in a Gatan precision ion polishing system (PIPS) while cooled by liquid nitrogen. The Ar^+ ion energy was gradually reduced to 2 keV during the final step of milling for minimizing the surface damage on the sample.

The *in-situ* annealing experiment was performed in the doubly-corrected Linköping FEI Titan³ 60-300, by using a furnace type double tilt heating holder (Gatan Model 652). The sample was heated up to 950°C . *In-situ* annealing at higher temperature was not possible due to the limitation of the annealing holder and the degradation of the vacuum inside the microscope. The *in-situ* annealing experiment started by pre-heating the sample at 500°C for 0.1 h and then continuously annealing from 750°C to 950°C by increasing the temperature by 50°C steps and holding the condition for 1 h at the given temperature. For the maximum applied temperature (950°C), the sample was subject to an additional 5 h (6 h total).

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging as well as monochromated valence electron energy loss spectroscopy (VEELS) spectrum imaging (SI) was performed at 300 kV. SI was performed throughout the VEELS measurements using an energy spread of the primary electron

beam of 0.2 eV, optimized for beam current, as defined by the full width at half maximum (FWHM) of the zero loss peak. The convergence semi-angle in monochromated mode was set to 20 mrad, providing a sub-Ångström probe with 0.3 nA of current. VEELS spectrum images, of $150 \times 150 \text{ px}^2$, were recorded using a 0.025 eV/channel energy dispersion, a collection semi-angle of 6 mrad, 0.005 s dwell time for each pixel and a total of 3 minutes for recording the complete SI. Furthermore, the SI was further recorded for higher signal-to-noise ratios, according to the method proposed by Bosman [18]. The peak energy position of the bulk plasmon, E_p , was mapped across the structure, and obtained by an initial zero loss peak fitting and re-alignment of the spectrum image for energy drift. This was followed by Fourier-log deconvolution for plural scattering removal. Finally, applying a single Gaussian (2 eV FWHM) to the low-loss spectrum, the VEELS spectrum was fitted by a nonlinear least-squares (NLLS) curve-fitting method centered around the most intense part of the bulk plasmon peak for extracting the energy of the bulk plasmon (E_p) peak with a fitting accuracy of $\pm 0.01 \text{ eV}$ [19,20].

3. RESULTS AND DISCUSSION

The crystal quality and lattice parameters of the as-grown $\text{Al}_{1-x}\text{In}_x\text{N}$ multilayer sample were examined by using RSMs. Figure 1 shows RSMs around the symmetric (0002) and asymmetric ($10\bar{1}5$) reflections of the as-grown multilayer structure grown on Al_2O_3 (0001). All symmetric and asymmetric maps show well distinguishable and aligned contours along $2\theta/\omega$ scan direction which are attributed to the different composition $\text{Al}_{1-x}\text{In}_x\text{N}$ layers. The presented RSMs prove the successful growth of single-phase $\text{Al}_{1-x}\text{In}_x\text{N}$ ($0 \leq x \leq 1$) layers with epitaxial relation to the substrate. Further, full width at half maximum (FWHM) values for the layers was estimated from the x-ray rocking curves. The high temperature AlN layer exhibit a very narrow FWHM of 72 arc sec, while the room temperature layers have FWHM changing from 2160 arc sec for $\text{Al}_{0.82}\text{In}_{0.18}\text{N}$ to 4430 arc sec for InN indicating degrading crystal quality. A more detailed analysis of the RSM can be found elsewhere [12].

STEM overview images of the as-grown and as-annealed $\text{Al}_{1-x}\text{In}_x\text{N}$ multilayer sample viewed along the $[1\bar{1}00]$ zone axis with corresponding diffraction patterns are shown in Fig. 2a and c, as well as Fig. 2b and d, respectively. The STEM images were acquired by employing strong Z contrast, thus the $\text{Al}_{1-x}\text{In}_x\text{N}$ layers exhibit an increasing contrast with an increasing amount of incorporated In. The as-grown sample contains six layers starting with AlN (dark, closest to the substrate), followed by alloys of $\text{Al}_{1-x}\text{In}_x\text{N}$ with increasing In content and finally InN (bright) at the top. As can be seen from the STEM image, the individual layers of the as-grown ML sample exhibit a columnar structure and moderately rough layer interfaces. There is no indication of phase separation in the as-grown sample. The compositions of the individual $\text{Al}_{1-x}\text{In}_x\text{N}$ layers were determined using the E_p value, which was shown to give an reliable measurement of the

composition [21, 22]. The $\text{Al}_{1-x}\text{In}_x\text{N}$ layer thicknesses and compositions in the sample were determined to be ~ 40 nm for AlN, ~ 90 nm – $\text{Al}_{0.82}\text{In}_{0.18}\text{N}$, ~ 75 nm – $\text{Al}_{0.71}\text{In}_{0.29}\text{N}$, ~ 60 nm – $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$, ~ 75 nm – $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and ~ 100 nm – InN. The total thickness of the as-grown $\text{Al}_{1-x}\text{In}_x\text{N}$ multilayer sample was ~ 440 nm.

The diffraction pattern obtained along the $[1\bar{1}00]$ zone axis from the as-grown sample, as shown in the inset of Fig. 2c, reveal six discrete (0002), $(11\bar{2}0)$, and $(11\bar{2}2)$ diffraction spots (higher orders not shown), which are attributed to the varying lattice parameters of the respective $\text{Al}_{1-x}\text{In}_x\text{N}$ single layers as a consequence of the different compositions. In the diffraction pattern the (0002) reflections of the $\text{Al}_{1-x}\text{In}_x\text{N}$ single layers and the (0006) of Al_2O_3 are indicated. Other allowed and forbidden reflections are also visible, but are not indicated. The observed variations are in agreement with the lattice parameter change obtained by X-ray reciprocal space mapping (not shown) [12].

The STEM overview image of the $\text{Al}_{1-x}\text{In}_x\text{N}$ multilayer sample after completing full prolonged annealing cycle is shown in Fig. 2b with the corresponding diffraction pattern, Fig. 2d. As can be seen, the top InN layer has vanished and the two top $\text{Al}_{1-x}\text{In}_x\text{N}$ layers (originally $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$) have undergone extensive decomposition. It is well known that InN is stable up to 550°C [23,24], above which it decomposes. The present *in-situ* annealing experiment was performed at much higher temperature, hence the InN decomposed shortly after reaching 750°C annealing temperature into N_2 and liquid In, which was completely evaporated in few minutes. The contrast from the as-annealed sample indicates that the In-rich $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layers have suffered a pronounced loss of In and altered microstructure. Loss of In is most pronounced in the $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layer. The diffraction pattern from

the as-annealed structure shows three diffraction spots corresponding to the first three individual layers (AlN , $\text{Al}_{0.82}\text{In}_{0.18}\text{N}$, and $\text{Al}_{0.71}\text{In}_{0.29}\text{N}$). Diffraction from the In-deficient $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layers is considerably weaker and is partly overlapping with the remaining discrete pattern.

The STEM images and superpositioned bulk plasmon energy E_p maps in combination with associated diffraction patterns, reveal the critical events in the thermal stability of the $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layers, and are displayed in Figs. 3 and 4, respectively. Initially, elemental In is observed to segregate and cluster at grain boundaries along in the $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layer after annealing the sample for 0.5 h at 750 °C (Fig. 3a). The average lateral size of the In clusters was estimated to be 3-5 nm. The E_p map, superimposed on the STEM image, confirms the In clustering, where the green color indicates the presence of a sharp peak at 11.4 eV as observed from the 0.5 h spectrum in Fig. 5a. This peak is a fingerprint of In [25]. A second resonance around 17.7 eV is observed from the remaining, In-reduced matrix, which corresponds to a $\text{Al}_{0.39}\text{In}_{0.61}\text{N}$ composition. The arc-shaped spots found in the corresponding diffraction pattern, obtained exclusively from this layer, indicates the formation of In particles.

Upon continued annealing, the In clusters are removed from the layer after 1 h at 750 °C (Fig. 3b). The E_p map, superimposed on the STEM image, shows a more homogeneous composition although local residual In particles remain. From the STEM image, the remaining structure can be described as porous and appears to be composed from nanoparticles. The pores are a direct consequence of the void, which remain after the In is ejected from the structure. The electron diffraction pattern also exhibits this transformation, where the In-related arcs disappear and the initially discrete

$\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ diffraction pattern becomes broadened and weaker as a result of In loss and the appearance of the nanostructured particles.

The spatially averaged VEELS spectrum evolution during annealing from the $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layer is shown in Fig. 5a. Initially, E_p was situated at 17.1 eV with a second smaller peak around 20.8 eV, which is attributed to interband transitions. During annealing at 750 °C the main peak exhibits a significant shape change due to the segregation of the In, which is gone after 1 h at 750 °C (Fig. 3b). The remaining spectrum contains only a blunt peak, which is expected from the here observed disordered nanoparticles, which most likely have a range of compositions. Upon prolonged annealing, the E_p is additionally shifted to 20.35 eV indicating further loss of In.

From the results shown in Fig. 3, it is concluded that the decomposition of the In-rich single-phase $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layer begins at ~750 °C. The other layers (AlN , $\text{Al}_{0.82}\text{In}_{0.18}\text{N}$, $\text{Al}_{0.71}\text{In}_{0.29}\text{N}$, and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$) were seemingly unaffected after the present thermal annealing (1 h at 750 °C).

To study the thermal stability of the remaining layers the temperature was increased to 800 °C, which resulted in the first observable changes in the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer. Figure 4a shows the STEM image with superimposed E_p map and corresponding diffraction pattern from the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer after annealing for 1 h at 800 °C. It is evident from the STEM image that the layer, particularly at grain boundaries, exhibit a less dense appearance, and the E_p map reveals a corresponding increase in energy (green color along grain boundaries) as a result of local loss of In. The averaged bulk plasmon peak from the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer, shown in Fig. 5b, shows a slight smoothening and shift towards higher energies after the 800 °C anneal, although the diffraction patterns exhibit

sharp diffraction spots. After the complete annealing cycle (Fig. 4b), the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer suffered further loss of In, which is mostly removed from the near surface region. The STEM image as well as the E_p maps exhibit inhomogeneous contrast owing to the nanocrystalline condition, where the particles may be more or less decomposed. During annealing, no In clustering was observed in this layer, in contrast to the $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layer. The diffraction spots are broadened and have assumed an arc-like appearance, similar to the structure of the In-deficient $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ indicating that the structure holds its orientation with some disorder. The averaged E_p is 19.25 eV, indicating loss of In after prolonged annealing. From the results shown in Fig. 4, the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer undergoes a slow and continuous loss of In while developing a nanocrystalline and porous structure, which retains the epitaxial crystallographic orientation.

Figure 6 reveals the average E_p evolution of the different $\text{Al}_{1-x}\text{In}_x\text{N}$ layers as a function of annealing temperature and time. E_p remains stable for the bottom three layers, AlN, $\text{Al}_{0.82}\text{In}_{0.18}\text{N}$, and $\text{Al}_{0.71}\text{In}_{0.29}\text{N}$, although a minor shift towards lower energies with annealing of these two layers is observed, which can be attributed to defect annihilation during the annealing. It is well established that low-temperature deposition by MSE generates residual point defects [26]. AlN is known to be stable up to 1250 °C [27] and the thermal stability of $\text{Al}_{1-x}\text{In}_x\text{N}$ layers pseudomorphically grown on GaN/Si was previously shown for In concentrations $x=0.18$ at a temperature of 960 °C [16]. The constant E_p suggests that these layers are thermally stable under the investigated conditions. However, it can be seen in the image of the fully annealed sample (Fig. 2b) that a shallow channel has been opened into the $\text{Al}_{0.71}\text{In}_{0.29}\text{N}$ layer, aligned with a channel leading directly from the top surface and through the two In-deficient layers. Hence, decomposition of this layer has been initiated at 950 °C. The E_p continuously

shifts towards higher energy with increasing annealing temperature and time for the two top In-rich $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ and $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layers indicating a continued loss of In. The thermal annealing resulted in an initial rapid depletion of In from the $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layer, manifested as a sharp increase of the average E_p . E_p continues to increase in this layer, though more slowly, after the In ejection (Fig. 3). In contrast, the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer required higher temperature in order to accelerate the loss of In. High temperature (950 °C) prolonged annealing (6 h) continuously reduced the In content, even after the average In composition has reached a level below or near that of the two stable $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layers, respectively. The reason for this is suggested to be the degraded nanocrystalline/nanoporous structure, which exhibits a significantly larger surface area from which the In atoms may desorb.

Finally, the activation energy for the decomposition processes was estimated by utilizing Arrhenius plots where the rate of compositional change was extracted from the E_p for the individual layers. In Fig. 7, the activation energies for the two In-rich layers is shown and found to be ~0.62 eV and ~1.95 eV for $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$, respectively. The activation energy of the top and In-richest layer is not surprisingly the lowest, as it decomposed more rapidly and with an onset at the lower temperature. With more Al, the layers become increasingly stable, and the activation energy of AlN has been shown to be 5.4 eV (in vacuum) and 4.14 eV while flowing H_2 across the surface [28]. As the layers are more InN like the activation energy is reduced. An activation energy of 1.74 eV and 1.11 eV was reported for N and In polarities in vacuum [29] as well as 1.15 eV for N polarity in vacuum [30]. Here, the observed activation energy is lower than previously reported, which is suggested to occur as a consequence of the low

temperature growth of the structure, incorporating more point defects, as it has been observed for GaAs [31].

4. CONCLUSIONS

The thermal stability of $\text{Al}_{1-x}\text{In}_x\text{N}(0001)$ layers for $0 \leq x \leq 1$ can be investigated by *in-situ* thermal annealing up to 950 °C in a STEM. The In content of $\text{Al}_{1-x}\text{In}_x\text{N}$ layers directly affects the thermal stability, such that the In-richest layer ($\text{Al}_{0.28}\text{In}_{0.72}\text{N}$) decomposes at 750 °C, and where the decomposition process is initiated by forming In at grain boundaries. For the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer, In desorption was initiated at 800 °C through continuous desorption of In, while no In clustering was observed. Both In-rich layers ($\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$) were significantly decomposed and transformed into In-deficient, nanocrystalline and porous structures. The In content in these decomposed layers was reduced to and even below the In content of the originally Al-rich $\text{Al}_{1-x}\text{In}_x\text{N}$ layers ($\text{Al}_{0.71}\text{In}_{0.29}\text{N}$ and $\text{Al}_{0.82}\text{In}_{0.18}\text{N}$). These Al-rich layers showed few signs of decomposition, which is shown by the intact structure and retained In content of these layers as compared to the porous nanocrystalline appearance of the decomposed layers. Finally, the activation energy of the thermal decomposition was estimated to be 0.62 eV and 1.95 eV for $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layers, respectively.

FIGURES and FIGURE CAPTIONS

Figure 1. RSMs around (0002) and (10 $\bar{1}$ 5) reflections of as-grown $\text{Al}_{1-x}\text{In}_x\text{N}$ ($0 \leq x \leq 1$) multilayer structure grown on Al_2O_3 (0001).

Figure 2. Overview STEM images and corresponding diffractions patterns in the $[1\bar{1}00]$ zone axis of the (a, c) as-grown and (b, d) annealed $\text{Al}_{1-x}\text{In}_x\text{N}$ ($0 \leq x \leq 1$) multilayer structure grown on $\text{Al}_2\text{O}_3(0001)$.

Figure 3. STEM images, bulk plasmon energy maps, and diffraction patterns from the $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ layer after annealing for (a) 0.5 h at 750 °C and (b) 1 h at 750 °C.

Figure 4. STEM images, bulk plasmon energy maps, and diffraction patterns from the $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layer during annealing for (a) 1 h at 750 °C + 1 h 800 °C and (b) fully annealed.

Figure 5. Average bulk plasmon peak evolution for the (a) $\text{Al}_{0.28}\text{In}_{0.72}\text{N}$ and (b) $\text{Al}_{0.41}\text{In}_{0.59}\text{N}$ layers at different stages during annealing.

Figure 6. Average bulk plasmon energy and AlInN compositional correlation as a function of annealing temperature and time for the individual AlInN layers as obtained from VEELS mapping. AlN and InN bulk plasmon energies are indicated for reference.

Figure 7. Arrhenius plots showing relative normalized amounts of layer composition changes obtained from bulk plasmon energies during isochronal (1 h) annealing from 750 °C to 950 °C in 50 °C steps.

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