Structural and compositional evolutions of $\text{In}_x\text{Al}_{1-x}\text{N}$ core–shell nanorods grown on Si (111) substrates by reactive magnetron sputter epitaxy

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Received 22 January 2015, revised 6 March 2015
Accepted for publication 23 March 2015
Published 6 May 2015

Abstract

Catalystless growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ core–shell nanorods have been realized by reactive magnetron sputter epitaxy onto Si(111) substrates. The samples were characterized by scanning electron microscopy, x-ray diffraction, scanning transmission electron microscopy, and energy dispersive x-ray spectroscopy. The composition and morphology of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods are found to be strongly influenced by the growth temperature. At lower temperatures, the grown materials form well-separated and uniform core–shell nanorods with high In-content cores, while a deposition at higher temperature leads to the formation of an Al-rich $\text{In}_x\text{Al}_{1-x}\text{N}$ film with vertical domains of low In-content as a result of merging Al-rich shells. The thickness and In content of the cores (domains) increase with decreasing growth temperature. The growth of the $\text{In}_x\text{Al}_{1-x}\text{N}$ is traced to the initial stage, showing that the formation of the core–shell nanostructures starts very close to the interface. Phase separation due to spinodal decomposition is suggested as the origin of the resultant structures. Moreover, the in-plane crystallographic relationship of the nanorods and substrate was modified from a fiber textured to an epitaxial growth with an epitaxial relationship of $\text{In}_x\text{Al}_{1-x}\text{N}[0001]/\text{Si}[111]$ and $\text{In}_x\text{Al}_{1-x}\text{N}[11\overline{2}0]/\text{Si}[1\overline{1}0]$ by removing the native SiO$_x$ layer from the substrate.

Keywords: InAlN, core-shell, nanorods, sputtering, MSE, STEM, EDX

(Some figures may appear in colour only in the online journal)
Recently, an increasing number of studies have addressed the growth of III-nitride core–shell nanorods because of the advantage of a large junction area that makes the resultant structures suitable for fabricating high-performance nanodevices, such as high-brightness light-emitting devices, high-sensitive sensors, and 1D HEMTs [4–7]. Normally, the core–shell nanorods can be obtained by growing a semiconductor core, which is then coated with a shell of another material, usually exhibiting a larger bandgap [8–10], or it can spontaneously occur in the form of two phases with different concentrations [11–14]. core–shell nanorods formed spontaneously often show a high-quality crystalline structure and uniform shells along the whole length of the nanorod, which can overcome the shadowing effect caused by directional growth, which leads to the formation of an inverted cone-shaped top with non-uniform shells in the intended grown core–shell nanorods by physical vapor deposition (PVD) [10, 15]. In addition, spontaneously formed core–shell nanostructures can avoid the generation of misfit dislocations between the core and shell, owing to lattice distortions resulting from surface relaxation or reconstruction of the rod core or other materials formed after the core growth [16]. Hence, it is possible to avoid the degradation of the electrical and optical properties of the fabricated devices.

So far, studies on In$_x$Al$_{1-x}$N [11, 14, 15, 17–19], are considerably fewer than for In$_x$Ga$_{1-x}$N and Al$_x$Ga$_{1-x}$N. The reason might be the high difficulty in obtaining high-quality and single-phase In$_x$Al$_{1-x}$N owing to the high immiscibility in the range of 0.1 < x < 0.9 and the large growth temperature difference between AlN and InN [19, 20]. However, the efforts to grow In$_x$Al$_{1-x}$N nanostructures are highly motivated since the material contains unique properties—for instance, wide-range bandgaps from deep ultraviolet (AlN: 6.2 eV) to near infrared (InN: 0.7 eV), giving a wide application region and lattice match to GaN, for x = 0.17–0.18, allowing the use of In$_x$Al$_{1-x}$N as a strain-free barrier and capping layer [21–23].

In this paper, we report the successful growth and characterization of Al-rich In$_x$Al$_{1-x}$N from core–shell nanorods to thin films on Si(111) substrates using direct current (dc) magnetron sputter epitaxy (MSE). Our process is free from catalysts like Au or Ni, otherwise widely used to promote nanorod growth [8, 24, 25]. The effects upon the evolution of morphology and composition of different growth temperatures were investigated by scanning electron microscopy (SEM), x-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and energy dispersive x-ray spectroscopy (EDX) mapping. The formation of the nanostructures was traced to the initial growth. The influence of the substrate treatment upon the formation of the interfacial layer and how this affects the crystallographic relationship was also studied. These results present a considerable potential for large-scale and low-cost production of optoelectronic devices, as well as engagement to integrated circuits (ICs) industrial application in the future.

2. Experimental details

The In$_x$Al$_{1-x}$N samples were grown in an ultra-high vacuum (UHV) magnetron sputtering chamber. The details of the MSE system can be found elsewhere [20, 26, 27]. Prior to the deposition, the Si(111) substrates were degreased with tri-chloroethylene, acetone, and isopropanol in ultrasonic baths for 5 min each and blown dry with pure nitrogen. The substrate was chemically treated in order to remove native SiO$_2$ by dipping into a diluted HF solution for 5 min. Before In$_x$Al$_{1-x}$N growth, the substrates were outgassed for 20 min at 1000 °C to eliminate the remaining contaminants from the substrate surface. The In$_x$Al$_{1-x}$N was deposited by cosputtering aluminum (99.999%) and indium (99.999%) targets at constant powers of 300 W and 10 W, respectively, for 30 min in pure nitrogen (99.9 9999%) at a working pressure of 5 mTorr. The growth temperatures were 700, 750, 800, and 850 °C.

The surface and cross-sectional views of the samples were analyzed using a Zeiss Leo 1550 field-emission gun SEM. The crystalline structures and epitaxial relationship were characterized by θ/2θ scan and pole-figure XRD measured for (1015) plane spacings using a Philips 1820 Bragg-Bretano diffractometer and a Philips X’Pert Materials Research Diffractometer, respectively.

Microstructural analyses were performed by high-resolution STEM, as well as STEM-EDX mapping using the double-corrected Linköping FEI Titan³ 60-300. The transmission electron microscopy (TEM) samples were prepared by mechanical polishing followed by low-angle argon ion milling at 5 keV in a Gatan precision ion polishing system (PIPS). The voltage was decreased to 2 keV during the final stage of the milling to reduce the surface damage.

3. Results and discussion

3.1. Temperature effect on the morphology and composition of In$_x$Al$_{1-x}$N growth

Figure 1 shows side- and top-view SEM micrographs of In$_x$Al$_{1-x}$N nanorods and films grown on Si(111) substrates at 700 °C (a, b), 750 °C (c, d), 800 °C (e, f) and 850 °C (g, h). As it can be seen, the increase in temperature decreases the aspect ratio of the nanorods, and merged rods appear at 800 °C. The In$_x$Al$_{1-x}$N grown at 700 °C shows a high density of well-separated hexagonal nanorods, seen in figure 1(a) and (b). As the growth temperature increases from 700 °C to 750 °C, the nanorods grow shorter and their diameter enlarges (figures 1(c) and (d)). When the growth temperature is raised to 800 °C, the hexagonal shape of the rod cross-section is still visible, but the rods start to coalesce (figures 1(e) and (f)). This process is enhanced at 850 °C, leading to the formation of a continuous film with a thickness of approximately 130 nm (figures 1(g), (h)).

Figure 2 shows the temperature dependence upon the dimensional distribution and the growth rate of the In$_x$Al$_{1-x}$N nanorods. In figure 2(a) it can be seen that the sample grown
at 700 °C exhibits diameter distribution in the range from 25 to 42 nm with a pronounced maximum at 37 nm. A wider diameter distribution is visible for the sample grown at 750 °C in a range of 25 to 55 nm with an average diameter size of 39 nm, while at 800 °C, the distribution becomes even wider, 20 to 60 nm, though with a well-defined maximum of around 45 nm—most of the rods exhibit diameters in the range of 40 to 50 nm. Figure 2(b) shows a comparison between the growth rates of In$_x$Al$_{1-x}$N nanorods and films. The nanorod growth rates are measured from the substrate interface in cross-sectional SEM images. Because the In$_x$Al$_{1-x}$N film, 0.1 < $x$ < 0.9, with a uniform composition is difficult to obtain at temperatures higher than 700 °C, the film growth rates are estimated from the linear interpolation of AlN, 5.00 nm min$^{-1}$, and InN, 2.16 nm min$^{-1}$, films grown at 1000 and 350 °C, respectively, using the same compositions as determined by XRD shown in figure 3. It can be seen that the growth rates of the nanorods are all higher than those of the films at the same compositions. Obviously, the growth rate increment is dominated by the morphology change from two-dimensional (2D) film to 1D nanorods if the total volume of the grown materials does not change. The lateral growth is enhanced at a higher temperature, leading to merged In$_x$Al$_{1-x}$N nanorods.

A semi-logarithmic plot of the XRD θ/2θ scans of the In$_x$Al$_{1-x}$N nanorods and films is shown in figure 3(a). Except for a strong Si 111 peak located at 28.49° and the In$_x$Al$_{1-x}$N 0002 peaks located at 34.75, 35.04, 35.33, and 35.80° for growth temperatures of 700, 750, 800, and 850 °C, respectively, no other distinct peak is found in these scans or in long-range scans (not shown here). The indicating lines plotted at 31.34 and 36.02° are the 0002 reflections of strain-free InN and AlN bulk, respectively.
The lattice parameters and the In content, $x$, of the In$_x$Al$_{1-x}$N nanorods grown on Si(111) substrates at different temperatures are summarized in Table 1. Here, the $x$ is determined by Vegard’s law from strain-free AlN and InN lattice constants.

| Sample | Growth temperature (°C) | HF dipping | $2\theta$ (Degree) | FWHM (Degree) | c-lattice parameter (Å) | $x$   |
|--------|-------------------------|------------|-------------------|---------------|------------------------|------|
| A      | 700                     | No         | 34.75             | 0.59          | 5.16                   | 0.25 |
| B      | 750                     | No         | 35.04             | 0.52          | 5.12                   | 0.18 |
| C      | 800                     | No         | 35.33             | 0.48          | 5.07                   | 0.13 |
| D      | 800                     | Yes        | 35.23             | 0.31          | 5.09                   | 0.15 |
| E      | 850                     | No         | 35.80             | 0.34          | 5.01                   | 0.04 |

The temperature dependence of the full-width-at-half-maximum (FWHM) and 2$\theta$ position are plotted in Figure 3(b). The In$_x$Al$_{1-x}$N 0002 diffraction peaks are shifted to increasing $2\theta$ angles with growth temperature, which indicates a decrease in In content. The dramatic decrement of $x$, from 0.25 to 0.04, when the temperature is varied from 700 to 850 °C, is observed. Since the composition of In$_x$Al$_{1-x}$N is correlated with the incorporation rate of both In and Al, it depends on the residence time and sticking coefficient of In and Al adatoms, as well as thermal stability of the formed In$_x$Al$_{1-x}$N compound [29]. Because the incoming In and Al fluxes are fixed, the growth temperature becomes the decisive factor on the incorporation rate. In this temperature region, 700 to 850 °C, AlN is thermally stable and the growth rate is found to be almost independent of the temperature at a fixed flux using both molecular-beam epitaxy (MBE) and MSE [30, 31], indicating a negligible desorption-to-adsorption rate ratio of the Al adatoms on the surface. Hence, the composition of In$_x$Al$_{1-x}$N is mainly associated with the In incorporation rate. Since InN is thermally unstable at temperatures higher than 550 °C and In has a desorption temperature of 650 °C [29, 32], the incorporation rate of In is expected to decrease with increased growth temperature owing to a incremental desorption rate, i.e., decrement of adatom residence time. If the desorption rate is simply correlated with the equilibrium vapor pressure of In, an estimation of vapor pressures around 0.02 to 2 mtorr from 700 to 850 °C is found. This is close with the working pressure of 5 mtorr used in the growth [33], implying a high desorption rate. Instead, the vapor pressure of Al is three orders lower than that of In at the same temperature, revealing a negligible desorption, which is in agreement with the constant growth rate of AlN in this temperature region. On the other hand, although the desorption rate of In is very high in the temperature range, In$_x$Al$_{1-x}$N with $x<0.5$, is thermally stable below 1000 °C, according to our previous study [20]. Once In is incorporated into the growth before desorption, it would not segregate from the In$_x$Al$_{1-x}$N. Therefore, the trend of compositional decrement monotonically with increasing temperature can be correlated to the dependence of the In desorption rate at high temperatures. Another characteristic is the decrease of the FWHM with growth temperature, indicating an increased crystal quality and/or a narrower compositional distribution. Splitting of the peaks can be seen for samples grown at 750 and 800 °C. Here, the peak splitting is attributed to the formation of a second phase, with a higher In content indicating phase separation [26].

The growth temperature is thus a decisive factor that determines the morphological and compositional evolutions of the In$_x$Al$_{1-x}$N. With increasing In incorporation, the growing structure is subject to phase separation and promotes 1D nanorod growth.

Figure 3. (a) XRD θ/2θ scans of the In$_x$Al$_{1-x}$N grown at different temperatures, and (b) temperature dependence of the 2$\theta$ peak position and FWHM.
Figure 4. STEM-EDX mappings of the core–shell In$_x$Al$_{1-x}$N nanostructures grown at different temperatures: (a)–(d) STEM images, (e)–(h) In (yellow) and Al (blue) elemental mappings, and (i)–(l) N (pink) mappings.

3.2. Temperature effect on the compositional distribution inside the In$_x$Al$_{1-x}$N nanostructures and initial growth

To gain more insights into the evolution of the In$_x$Al$_{1-x}$N nanostructures with temperature, STEM-EDX mapping was employed to determine the elemental distribution and crystalline structure. Figure 4 shows In$_x$Al$_{1-x}$N core–shell structures in side view, exhibiting In-rich cores surrounded by Al-rich shells with different thicknesses. Corresponding nitrogen mappings, shown in figures 4(i)–(j), reveal that nitrogen is uniformly distributed throughout the entire length of the nanostructures. In addition, no segregation of metallic In or Al clusters is observed, which is in agreement with XRD results that the nanostructures are constituted of ternary III nitride compounds. As observed by SEM, the diameter of the rods increases with temperature, correlated with the expansion of the Al-rich shells. Samples grown at 700 and 750 °C present In-rich cores of around 25 and 20 nm surrounded by thin Al-rich shells of approximately 5 and 8 nm, respectively. In addition, a more intense In signal is obtained towards the rod tip. Similar results have been seen in MBE-grown In$_x$Ga$_{1-x}$N nanorods as a consequence of a higher growth rate along the c-axis orientation, i.e., the rod growth direction, than on the sidewalls [12, 13]. At 800 °C, the core–shell nanorod structure is maintained. The In-rich compositional domains, characteristic to the core, are still present, but the thickness of the shell increases. These results in the coalescence of the rods so that adjacent cores share joined shells explain the morphology seen in the SEM images. The domains are protruding above the matrix, ~18 nm, surrounded by diminishing shells. Some inclined In-rich domains, ~4 nm, had developed also in the shells. Because the part of the core–shell rods protruding above the matrix is short, the hexagonal nanorods are clearly seen in the top-view but not side-view SEM image. At 850 °C, the In-rich domains are still visible but become weaker and thinner. The film mainly consists of an almost pure AlN matrix. Hence, 4% of the In incorporation calculated from the XRD peak located at 35.8° should be referred to the shell, and a very weak shoulder located at around 34.8° might be from the characteristic core domains (see figure 3).

The result clearly demonstrates that these domains were formed during the growth. Similar results, but with opposite elemental profile in a honeycomb-like structure consisting of Al-rich domains surrounded with a few nanometer-thick In-rich boundaries, were reported in the MBE-grown lattice-matched In$_x$Al$_{1-x}$N films on GaN templates [34, 35]. There the formation mechanism was attributed to the phase separation due to the wide-range spinodal decomposition and/or the trigger of accommodating In between the boundaries of three-dimensionally (3D) AlN nuclei owing to the strain [36, 37]. Formation of core–shell nitride nanorods is commonly explained by different surface diffusion lengths and residence times of the adatoms [12, 13]. Since the In adatoms have the highest mobility and the shortest residence time at growth temperatures higher than 650 °C, the In adatoms may diffuse from the nanorod sidewalls or desorb if not incorporated into the growing material. A higher incoming In flux than re-desorption on the nanorod tops supports the growth continuously. However, the shadowing effect reduces the incoming flux to the sidewalls. Hence, the core–shell nanorod structure is maintained with In-rich cores during the growth.

Although the previous arguments can partly support the In$_x$Al$_{1-x}$N core–shell nanorod growth, the initial nucleation and In-rich domains embedded in the Al-rich matrix cannot be explained only by the ability of adatom surface diffusion and shadowing effects. Phase separation owing to spinodal decomposition of the In$_x$Al$_{1-x}$N, originating from the large lattice mismatch between InN and AlN has to be considered as the primary origin for the core–shell structures. In a previous annealing study [20], it was clearly shown that spinodal decomposition of In-rich In$_x$Al$_{1-x}$N occurred at temperatures above 700 °C. From the previous results, the formation of different compositional domains due to phase separation is seen not only at an initial stage, but also during the subsequent growth, through inclined small In-rich domains grown in the Al-rich shell at 800 °C. The result of the embedded In-rich domains in the Al-rich matrix grown vertically to the substrate at 850 °C further supports that the growth is dominated by the spinodal decomposition rather than the adatom surface diffusion.
3.3. The effect of interfacial layer on the in-plane ordering of the In$_x$Al$_{1-x}$N growth

In order to determine the influence of the interfacial layer upon the In$_x$Al$_{1-x}$N growth, an additional HF dipping after the degreasing procedure was applied to the sample grown at 800 °C. From the SEM image, the sample shows almost no difference to the one grown without HF dipping in the morphology (not shown here). However, the FWHM of the In$_x$Al$_{1-x}$N 0002 peak is much narrower for the HF dipped sample, as shown in table 1, indicating improved crystallinity. The influence of the substrate treatment on the epitaxial relationship of the In$_x$Al$_{1-x}$N nanorods and substrates was investigated by pole-figure XRD. The recorded [1015] pole figures for the two samples are presented in figures 6(a) and (b), respectively. Three strong reflections, shown in both pole figures, located at $\phi \sim 30, 150 \text{ and } 270^\circ$, correspond to the [440] of Si, characteristic of the Si(111) three-fold symmetry. The ring located at $\psi \sim 20^\circ$ shown in figure 6(a) indicates that the nanorods have a fiber texture with their c-axes along the growth direction and with the a-axes randomly oriented along the surface plane. Because the nanorods were grown randomly in the in-plane crystal orientation, only part of the nanorods in the sample can contribute to the diffraction intensity with respect to their $\phi$ angles. This results in a low diffraction intensity and may cause some unexpected peaks shown in the figure because of the low signal-to-noise ratio. The in-plane orientation and diffraction intensity of the nanorods changes drastically when an HF etched substrate is used, as shown in figure 6(b). The pole figure exhibits six distinct peaks, separated by $\phi = 60^\circ$ aligned with the three Si peaks, indicating an ordering in the in-plane orientation of the nanorods on the substrate with an epitaxial relationship of In$_x$Al$_{1-x}$N[0001]/Si [111] and In$_x$Al$_{1-x}$N[11\overline{2}0]/Si[1\overline{1}0]. In addition, the peaks exhibit much stronger intensity than the ring shown in figure 6(b) because the peak intensity results from the contribution from all nanorods with respect to one of the six 10\overline{1}5 planes.

To further investigate the interfacial layers, these two samples were characterized by high-resolution annular bright
field (ABF) STEM and EDX mapping. Lattice-resolved STEM images (figures 6(c) and (d)) confirm the epitaxial relationship in the HF dipped sample and the random in-plane orientation in the sample without HF dipping, as deduced from the pole-figure XRD results. In addition, both samples show a ~2 nm amorphous interfacial layer presented in between nanorods and substrate. The corresponding EDX maps of the interface are shown in figures 6(e) and (f). Clearly, the chemical composition of these two interfacial layers is very different. The sample grown on the substrate without HF dipping presents a SiO\textsubscript{x} interfacial layer, which acts as a nitridation barrier and determines the fiber textured growth of the rods. When using the HF dipped substrate, an amorphous SiN\textsubscript{x} layer can be observed at the interface.

The formation of an amorphous SiN\textsubscript{x} layer was previously reported on the growth of GaN and InN on Si by MBE and MSE [38–40], but it did not often show in the case of AlN grown on Si [41]. As for the epitaxial growth on intermediate amorphous SiN\textsubscript{x}, some mechanisms were proposed in the case of MBE-grown GaN nanorods on Si substrates [40, 42]. For instance, for the growth of GaN on crystalline SiN\textsubscript{x} formed due to the strong Si–N affinity and that was subsequently amorphized [43], and for the GaN epitaxial growth on partial crystalline SiN\textsubscript{x} layer [44]. In addition, the MSE growth mechanism is different from MBE, although the results of MSE-grown In\textsubscript{x}Al\textsubscript{1-x}N nanorods are similar to the MBE-GaN nanorods. Further investigation on the formation of the interfacial layer is necessary to clarify the mechanism.

4. Conclusions

A comprehensive study was reported on the nanostructural evolution and internal elemental distribution of In\textsubscript{x}Al\textsubscript{1-x}N nanorods grown at 800 °C on Si(111) substrates (a), (c), (e) without and (b), (d), (f) with HF etching: (a), (b) 1015 pole-figure XRD measurements of the samples, (c), (d) lattice-resolved images taken at the interface between the nanorods and the substrate, and (e), (f) EDX compositional mappings of the interface (where pink represents Si, orange N and blue O).

Figure 6. Interface study of In\textsubscript{x}Al\textsubscript{1-x}N nanorods grown at 800 °C on Si(111) substrates (a), (c), (e) without and (b), (d), (f) with HF etching: (a), (b) 1015 pole-figure XRD measurements of the samples, (c), (d) lattice-resolved images taken at the interface between the nanorods and the substrate, and (e), (f) EDX compositional mappings of the interface (where pink represents Si, orange N and blue O).
semiconductor nanorods grown on Si(111) substrates by MSE in a process free from catalysts. The growth temperature influences both the morphology and the elemental distribution in the nanostructures and their eventual coalescence into continuous thin films. The amount of In incorporated in the structures is of paramount importance for the morphological evolution determining the thickness of the core in the characteristic core–shell structures. The In$_{1-x}$Al$_x$N evolved sequentially from core–shell nanorods to a thin film, while the In content decreased from 0.25 to 0.04 when the growth temperature increased from 700 to 850 °C, respectively. The thickness of the In-rich cores of nanorods is diminished with rising temperature, while the growth of the Al-rich shell is extended, resulting in coalesced rods with shared shells. The compositional segregation is the factor that determines the initial growth and morphology of the obtained samples. Subsequently, the core–shell nanorods or the matrix were developed on the nuclei of different elemental domains along the growth direction throughout the entire growth. In addition, a native amorphous SiO$_x$ layer formed on the substrate surface determines the fiber-textured growth of the rods. When removing the oxide layer by an HF solution, a preferential in-plane orientation of the nanorods with epitaxial relationships to the substrate is obtained, although an amorphous SiN$_x$ interfacial layer is formed between the In$_{1-x}$Al$_x$N and the substrate.

Acknowledgments

This work was supported by the Swedish Research Council (VR) under grant No.621-2012-4420 and the Swedish Governmental Agency for Innovation Systems (VINNOVA) under the VINNMER international qualification program. Additionally, the authors would like to thank the Knut and Alice Wallenberg Foundation for support of the Linköping Electron Microscopy Laboratory.

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