Nucleation and core-shell formation mechanism of self-induced $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods grown on sapphire substrates by magnetron sputter epitaxy

Ching-Lien Hsiao, Justinas Palisaitis, Per O A Persson, Muhammad Junaid, Alexandra Serban, Per Sandström, Lars Hultman and Jens Birch

Journal Article

N.B.: When citing this work, cite the original article.

Original Publication:

Ching-Lien Hsiao, Justinas Palisaitis, Per O A Persson, Muhammad Junaid, Alexandra Serban, Per Sandström, Lars Hultman and Jens Birch, Nucleation and core-shell formation mechanism of self-induced $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods grown on sapphire substrates by magnetron sputter epitaxy, Vacuum, 2016. 131, pp.39-43.

<http://dx.doi.org/10.1016/j.vacuum.2016.05.022>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-131902>

Nucleation and core-shell formation mechanism of self-induced $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods grown on sapphire substrates by magnetron sputter epitaxy

Ching-Lien Hsiao*, Justinas Palisaitis, Per O. Å. Persson, Muhammad Junaid, Elena Alexandra Serban, Per Sandström, Lars Hultman, and Jens Birch

Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

Nucleation of self-induced $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorod and core-shell structure formation by surface-induced phase separation have been studied at the initial growth stage. The growth of well-separated core-shell nanorods is only found in a transition temperature region in contrast to the result of thin film growth outside this region. Formation of multiple compositional domains, due to phase separation, after ~20 nm $\text{In}_x\text{Al}_{1-x}\text{N}$ epilayer growth from sapphire substrate promotes the core-shell nanorod growth, showing a modified Stranski-Krastanov growth mode. The use of VN seed layer makes the initial growth of the nanorods directly at the substrate interface, revealing a Volmer-Weber growth mode. Different compositional domains are found on VN template surface to support that the phase separation takes place at the initial nucleation process and forms by a self-patterning effect. The nanorods were grown from In-rich domains and initiated the formation of core-shell nanorods due to spinodal decomposition of the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy with a composition in the miscibility gap.

*E-mail address: hcl@ifm.liu.se

Keywords: InAlN, nanorods, nanostructures, STEM, EDX, sputtering, MSE

Semiconductor core-shell nanorods are regarded as a key building block for novel functional units exhibiting enhanced quantum efficiency (QE) as a result of large junction areas between the cores and shells compared to 2-dimensional (2D) heterojunctions.[1-6] The heterojunctions formed at non-polar sidewalls of *c*-axis oriented wurtzite semiconductor core-shell nanorods are free from the internal electric field, quantum confined Stark effect, which further benefits the QE enhancement. Ternary group III-nitride semiconductors, including $\text{In}_x\text{Ga}_{1-x}\text{N}$, $\text{Al}_x\text{Ga}_{1-x}\text{N}$, and $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods, are highly desired to apply for high-performance nanodevices.[1-6] For instance, high-brightness light-emitting devices, high-responsivity photodetectors, solar cells, and circular polarizer.

The growth of III-nitride semiconductor core-shell nanorods are mostly realized in terms of spontaneous formation of ternary alloys and intentional growth with different combinations of ternary/binary alloys using different growth techniques, such as chemical vapor deposition (CVD), molecular-beam epitaxy (MBE), and magnetron sputter epitaxy (MSE).[1-12] Uniform core and shell thicknesses after a mature nanorod formed are often found in the case of spontaneous formation, which can be of advantage for the device performance. Although the spontaneous formation of III-nitride core-shell nanorods were reported, most of the studies were only focused on the compositional distribution inside the nanorods using different analytical tools.[7-12] Details of how the core-shell nanorod formed from initial nucleation stage to a mature core-shell structure, and a comprehensive morphological and compositional evolutions of ternary alloys, from continuous $\text{In}_x\text{Al}_{1-x}\text{N}$ films, to core-shell nanorods, and to highly Al-rich single-phase $\text{In}_x\text{Al}_{1-x}\text{N}$ film, upon temperature and seed layer were rarely reported and discussed.[7-12] Likewise, the study

of $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods is hitherto very limited in comparison with $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{Al}_x\text{Ga}_{1-x}\text{N}$. [1-12] The development of $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods is very important for fabricating semiconductor nanoscale optoelectronics covering broad-optical range from infrared to ultraviolet. [11-17] Understanding the formation mechanism is needed to further control the growth of core-shell nanostructures.

In this letter, we present a study on the structural evolution of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods from the segregation of In and Al in the early coalescence stage of film formation, epitaxied on sapphire substrates assisted with/without a VN seed layer by ultra-high-vacuum (UHV) MSE. Two different growth modes, Stranski-Krastanov and Volmer-Weber, were clearly observed in a transition temperature region in contrast to the result of thin film growth outside this region. Novel details are revealed for the formation of the self-induced core-shell nanorods at the initial nucleation stage, and their development into well-faceted hexagonal core-shell nanorods. Structural transitions from $\text{In}_x\text{Al}_{1-x}\text{N}$ epilayer or islands to core-shell nanorods predominated by phase separation is clearly presented by mass-contrast scanning transmission electron microscopy (STEM) and elemental line-profile energy dispersive x-ray spectroscopy (EDX). We also discuss effects of growth temperature and the use of seed layer on $\text{In}_x\text{Al}_{1-x}\text{N}$ morphological and compositional evolutions.

The sample growth was performed in an UHV MSE system, equipped with four magnetrons and a reflection high-energy electron diffraction (RHEED). Details of the growth system can be found elsewhere. [11,12] Two series of the $\text{In}_x\text{Al}_{1-x}\text{N}$ growth, 1) no seed layer and 2) with a vanadium nitride (VN) seed layer, on *c*-plane sapphire substrates

were implemented in a temperature range of 500-900 °C, measured from thermal couple in the heater. Before the sample growth, the sapphire substrates were subsequently degreased with trichloroethylene, acetone, and isopropanol in ultrasonic baths for 5 min each and blown dry with pure nitrogen. Afterwards, the substrates were outgassed for 30 min at 1000 °C in the MSE chamber. For the samples with seed layer growth, a ~ 30 nm 111-orientated VN layer was deposited at 800 °C by sputtering from a V target in the same chamber. The $\text{In}_x\text{Al}_{1-x}\text{N}$ growth was cosputtered from aluminum (Al) (99.999%) and indium (In) (99.999%) targets for 20 min. The sputtering processes were carried out in a pure nitrogen (99.999999%) atmosphere at a working pressure of 5 mTorr, with a negative substrate potential of -30 V applied to the rotating substrate. DC-magnetron powers provided for Al/In targets were 300/10 and 350/9 watts for the growth without and with VN seed layer, respectively. The morphology of the as-grown samples were characterized by a LEO-1550 field-emission scanning electron microscopy (FE-SEM). Analyses of structural properties and compositional profiles were performed by $\theta/2\theta$ XRD scan using a Philips 1820 Bragg-Bretano diffractometer as well as scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDX) using a FEI Tecnai G² TF 20 UT 200 kV FEG microscope.[18,19]

Figures 1(a) and 1(b) show the $\theta/2\theta$ XRD scans and FESEM images of the $\text{In}_x\text{Al}_{1-x}\text{N}$ samples directly grown on sapphire substrates, respectively. Obviously, the growth temperature influences not only alloy composition, but also morphology. As increasing the growth temperature, the $\text{In}_x\text{Al}_{1-x}\text{N}$ 0002 reflections show a transition from single peak located at 34.70°, to double peaks at 34.63° and 35.03°, and to single peak at 35.52°, corresponding to the In content, x , of 0.26, 0.28 and 0.20, and 0.10, for samples grown at

700, 800, and 900 °C, respectively. Here, x is denote to the composition of dominant phase in the $\text{In}_x\text{Al}_{1-x}\text{N}$ samples, which is determined by Vegard's rule, $x = (c_{\text{In}_x\text{Al}_{1-x}\text{N}} - c_{\text{AlN}}) / (c_{\text{InN}} - c_{\text{AlN}})$, using the measured c lattice constants of $\text{In}_x\text{Al}_{1-x}\text{N}$ as well as strain-free bulk AlN and InN, without considering strain effect.[15,16] Meanwhile, the morphology changes with increasing temperature from continuous thin films to nanorods, and back to thin films. The corresponding thickness measured from cross-sectional SEM are 204, 273, and 162 nm, respectively. As can be seen in Fig 1, high-temperature film shows smoother surface (appearing atomically flat) than low-temperature film, revealing that lateral growth is enhanced at high temperature because of higher Al adatom mobility and low In incorporation towards one of the miscibility region of $x \leq 0.1$. [20, 21] At intermediate temperature region, 750 – 850 °C, the nanorods formed are well-separated and have a regular hexagonal shape. Since the In content of the film grown at 700 °C is in between two major phase contents of the nanorods grown at 800 °C, it implies that most of the In adatoms were incorporated into the growth not re-desorbed from the surface. This is also supported by the result of a higher growth rate of nanorods, around 133%, than the film, attributed to the effect of morphological change.[14] With increasing temperature to 900 °C, less In incorporated into the growth results in a lower growth rate, around 20 %, than the film grown at 700 °C. The above results indicate that the $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorod sample consists of multi-phases.

Figures 2(a) and 2(b) are the $\theta/2\theta$ XRD patterns and SEM images of the $\text{In}_x\text{Al}_{1-x}\text{N}$ samples grown on VN seed layers, respectively. The trend of In content varied with growth temperature is very similar to those samples which were directly grown on sapphire, but the whole growth window is shifted to low temperature side with an around 200 °C. Almost

no In was incorporated into the growth at 800 °C. The shift of growth temperature window is mainly due to higher sample surface temperatures with the VN seed layer coating. Moreover, there are some differences to the samples grown directly on sapphire substrates. The nanorods were not distributed uniformly on the VN seed layer although they were also grown well-separated with a hexagonal shape. On the other hand, the samples grown at 500 and 800 °C show granular and porous films, respectively. In addition, both $\text{In}_x\text{Al}_{1-x}\text{N}$ films and nanorods reveal lower intensity and broader linewidth of the XRD peaks, as compared to those $\text{In}_x\text{Al}_{1-x}\text{N}$ samples grown without seed layer, indicating a higher degree of misalignment along the c axis, poorer crystalline quality, and/or a wider compositional distribution.

The microstructural and compositional evolution of the $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods were further characterized by STEM and EDX. Fig. 3(a) shows a mass-contrast STEM micrograph of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods grown directly on a sapphire substrate. Apparently, the $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods were not formed directly at the interface. Instead, an initial $\text{In}_x\text{Al}_{1-x}\text{N}$ film was first grown on the substrate surface. Subsequently, the core-shell structure started to form at ~ 20 nm above the substrate surface. The nanorods exhibit a uniform core-shell structure with a higher In content in the core. The core diameter and shell thickness are in the range of 25 – 35 nm and 5 – 10 nm, respectively. Some multilayer-like contrasts shown in the image are related to the Morié fringe originated from the overlap of nanorods. A phase-separation process thus begins at this transition stage. Fig. 3(b) shows a high-resolution (HR) STEM image, revealing a multi-compositional film comprised of In-rich core surrounded with Al-rich shell domains and ultra-thin In-rich domain boundary walls (~ 1 nm), marked as **a**, **b**, and **upward arrow**, respectively. Throughout the phase

separation in the film, all domains retain a preferential growth with the c -axis orientation perpendicular to the substrate surface. At this stage of film-to-rod growth transition, the thickness of In-rich cores and Al-rich shells evolves in opposite way, showing a decrease and increase in the width, respectively. However, the boundary walls keep the same thickness. After this stage, well-separated nanorods with uniform core/shell widths are formed and the In-rich boundary walls disappear.

As to the $\text{In}_x\text{Al}_{1-x}\text{N}$ grown on VN seed layer, initial growth of the nanorods can be seen at a very early stage (< 3 nm) close to the VN surface, shown in the Fig. 4(a). It seems that highly Al-rich $\text{In}_x\text{Al}_{1-x}\text{N}$ ($x \leq 0.1$) islands, marked as **a**, were formed isolated on the VN surface. In-rich domains, marked as **b**, were grown between the islands and eventually formed the cores of the nanorods. Besides, the cores show a clean superlattice-structural mass contrast with an around 2-nm period along the rod growth direction and inclined ultra-thin In-rich domains, 1 - 2 nm, embedded in the shell. Similar compositional modulations but with a wider period of ~ 6 nm presented in the core of $\text{In}_x\text{Ga}_{1-x}\text{N}$ core-shell nanorods grown by molecular-beam epitaxy (MBE) was recently reported by D. Chern *et al.*, which was attributed to spinodal decomposition[12] also along the growth direction. Figs. 4(b) and 4(c) are elemental line profiles scanned through EDX nano-probe in the regions **a** and **b** from the interface, respectively. The line profile-**a** shows no In incorporation with around 5 nm from interface, indicating that the islands consist of almost pure AlN. In the region **b**, In signal was detected at a very early stage and intensity increased monotonically in the first 15-nm growth region, but Al profile behaved oppositely. The reason might be due to the small In-rich domain surrounded by AlN islands, giving strong Al and weak In signals, given the cross-sectional projection used. The

increase of the In signal along the growth direction can be correlated to the broadening of the rod core. After a 15-nm growth, the Al and In intensity profiles do not change too much, which is in consistent with the uniform core/shell widths and a low degree of rod diameter broadening.

All above results indicate that formation of the $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods grown by MSE is originated from phase separation starting at the initial growth stage and continuously during steady-state growth. We ascribe their formation to spinodal decomposition[16,17,20,21] of the $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy due to the wide-range immiscibility, $0.1 < x < 0.9$, and the low dissociation temperature of InN (550 °C).[22,23] In addition, catalyst-assisted vapor-liquid-solid (VLS) or VLS-like growth mechanism can be excluded in the nanorod growth because no transition metal or transition metal nitride cluster was found at the rod top.[24-26] The entire nanorod growth process is likely a catalyst-free vapor-solid (VS)[25,26] growth initiated by the phase separation and leading to the formation of the observed core-shell structure.

Several factors can be considered to discuss the $\text{In}_x\text{Al}_{1-x}\text{N}$ growth, including the alloy solubility (miscibility), interface and strain energy, surface energy, and kinetic energy of adatoms. Since MSE is a non-equilibrium growth process owning high sticking ability of reactant species and has an advantage of kinetic energy enhancement with low-energy ion assistance, metastable single-phase $\text{In}_x\text{Al}_{1-x}\text{N}$ can be maintained within miscibility gap at low-temperature growth.[15,16] With reducing interface energy using isostructural templates, same crystal structure as the deposited material, the growth of single-crystal $\text{In}_x\text{Al}_{1-x}\text{N}$ epitaxial films was demonstrated even at room temperature.[15] Although the crystal of used sapphires is rhombohedral not wurtzite structure, the c planes are still

constituted of hexagonal lattice. The stacking of hexagonal-on-hexagonal lattice remain preferable to lower interface energy for promoting laterally epitaxial growth of metastable single-phase $\text{In}_x\text{Al}_{1-x}\text{N}$ film accompanying with dislocations generated by mismatched lattices. When adatoms obtain more energy from thermal heating in the transition temperature region, stronger adatom diffusion encourages multi-phases formation within miscibility gap, induced by spinodal decomposition on the growth surface, in order to toward to a low-energy stable state.[20,21] Although an $\text{In}_x\text{Al}_{1-x}\text{N}$ epitaxial film was still grown on sapphire at initial stage (see Fig. 3), phase separation was triggered to release more energies accommodated with increasing layer thickness. When multi-compositional domains were formed, the domains contained highly In-rich $\text{In}_x\text{Al}_{1-x}\text{N}$ ultrathin nanowalls dissociated to In adatoms and re-desorbed. Then, well-separated nanorods were formed with the structure of In-rich core surrounded with Al-rich shell. Similar results were observed in the growth of $\text{In}_{0.18}\text{Al}_{0.82}\text{N}$ films on lattice-matched GaN templates, showing a structure of lateral compositional modulations, but the films did not develop to well-separated nanorods.[27,28] This phenomenon is very similar to the Stranski-Krastanov (SK) growth mode, [29,30] a morphological transformation from two-dimensional (2D) film to 3D islands during growth, which is often seen in the case of quantum dot formation.[30] In the high temperature region, less In can be incorporated into the growth, thanks to a high desorption-to-adsorption rate ratio of In and negligible desorption of Al, resulted in single-phase single-crystalline $\text{In}_x\text{Al}_{1-x}\text{N}$ film formation outside miscibility gap ($x \leq 0.1$). This result further implies that phase separation predominately operated by spinodal decomposition, which has the major role in the formation of the present core-shell nanorods.

When a VN seed layer is used in the growth experiments, the morphology of $\text{In}_x\text{Al}_{1-x}\text{N}$ changes to 3D island-like structure throughout entire temperature region. The Volmer-Weber growth mode,[27,28] 3D island growth, becomes dominant regardless of compositional region. Since VN has high surface energy and the seed layer contains twinning domains, observed by RHEED (not shown here), the formation of granular $\text{In}_x\text{Al}_{1-x}\text{N}$ film and highly Al-rich $\text{In}_x\text{Al}_{1-x}\text{N}$ ($x \leq 0.1$) porous film at low and high temperature regions, respectively, is reasonable. The effects further drive the phase separation to take place directly at initial nucleation stage on the VN surface to form domains with different compositions in the transition temperature region, see Fig. 4. The core-shell structure was developed on these domains assisted with spinodal decomposition during growth, self-patterning induced by oblique incoming fluxes, as well as different surface diffusion ability and residential time between Al and In adatoms.

In conclusion, we find that $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorod formation onto $\text{Al}_2\text{O}_3(0001)$ substrates is by a self-induced process, initiated by phase separation at initial growth stage, regardless of the use of a VN seed layer. The formation mechanism of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods on sapphire substrate and VN seed layer shows similarity to SK and VW growth modes, respectively. The SK-like growth mode reveals a three-step growth transition from a single-phase $\text{In}_x\text{Al}_{1-x}\text{N}$ continuous film layer, to a multi-compositional domain layer, and to well-separated core-shell nanorods. The VW-like growth mode shows a two-step growth transition from Al- and In-rich $\text{In}_x\text{Al}_{1-x}\text{N}$ island domains to well-separated core-shell nanorods. In addition, the growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ alloy is highly sensitive to temperature, showing a variation from continuous $\text{In}_x\text{Al}_{1-x}\text{N}$ films, to core-shell nanorods, and to highly Al-rich single-phase $\text{In}_x\text{Al}_{1-x}\text{N}$ film with increasing temperature.

This temperature dependence of morphological and compositional evolutions further supports that the phase separation is triggered by spinodal decomposition, within the miscibility gap, on the growth surface front during deposition.

COMPETING INTERESTS

The authors declare that they have no competing interests.

ACKNOWLEDGMENT

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 Ultra Electron Microscopy Laboratory.

Figure captions

Figure 1 (a) Temperature dependence of $\theta/2\theta$ scan XRD patterns of $\text{In}_x\text{Al}_{1-x}\text{N}$ directly grown on Al_2O_3 substrate. (b), (c), and (d) Plan-view images of the $\text{In}_x\text{Al}_{1-x}\text{N}$ grown at 900 °C, 800 °C, and 700 °C, respectively.

Figure 2 (a) Temperature dependence of $\theta/2\theta$ scan XRD patterns of $\text{In}_x\text{Al}_{1-x}\text{N}$ grown on VN(111) seed layers. (b), (c), and (d) Plan-view images of the $\text{In}_x\text{Al}_{1-x}\text{N}$ grown at 800 °C, 700 °C, and 500 °C, respectively.

Figure 3 (a) STEM image of core-shell $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods directly grown on Al_2O_3 substrate. (b) HR-STEM image taken at $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods/ Al_2O_3 interface.

Figure 4 (a) STEM image taken at $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods/VN(111) interface. (b) and (c) EDX line- profiles scanned at **a** and **b** areas, respectively, marked in the Fig. 4(a).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Reference

- [1] S. Li and A. Waag, GaN based nanorods for solid state lighting, *J. Appl. Phys.* **111**, 071101 (2012).
- [2] B. O. Jung, S.-Y. Bae, S.Y. Kim, S. Lee, J. Y. Lee, D.-S. Lee, Y. Kato, Y. Honda, H. Amano, Highly ordered catalyst-free InGaN/GaN core-shell architecture arrays with expanded active area region, *Nano Energy* **11**, 294-303(2015).
- [3] C. Durand, C. Bougerol, J. F. Carlin, G. Rossbach, F. Godel, J. Eymery, P. H. Jouneau, A. Mukhtarova, R. Butté and N. Grandjean, M-plane GaN/InAlN multiple quantum wells in core-shell wire structure for UV emission, *ACS Photonics* **1**, 38-46 (2014).
- [4] R.-S. Chen, C.-C. Tang, C.-L. Hsiao, P. O. Holtz and J. Birch, Electronic transport properties in aluminum indium nitride nanorods grown by magnetron sputter epitaxy, *Appl. Surf. Sci.* **285**, 625–628 (2013).
- [5] S. L. Howell, S. Padalkar, K. H. Yoon, Q. Li, D. D. Koleske, J. J. Wierer, G. T. Wang, L. J. Lauhon, Spatial Mapping of Efficiency of GaN/InGaN Nanowire Array Solar Cells Using Scanning Photocurrent Microscopy, *Nano Lett.* **13**, 5123-5128 (2013).
- [6] C. L. Hsiao, R. Magnusson, J. Palisaitis, P. Sandström, P. O. Å. Persson, S. Valyukh, L. Hultman, K. Järrendahl, and J. Birch, Curved-lattice epitaxial growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanospirals with tailored chirality, *Nano Lett.* **15**, 294-300 (2015).
- [7] R. F. Allah, T. Ben, R. Songmuang, and David González, Imaging and Analysis by Transmission Electron Microscopy of the Spontaneous Formation of Al-Rich Shell Structure in $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ Nanowires, *Appl. Phys. Exp.* **5**, 045002 (2012).
- [8] J. Segura-Ruiz G. Martínez-Criado, C. Denker, J. Malindretos, and A. Rizzi, Phase separation in single $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires revealed through a hard X-ray synchrotron nanoprobe, *Nano Lett.* **14**, 1300-1305, (2014).

- [9] C. Leclere, N. A. Katcho, G. Tourbot, B. Daudin, M. G. Proietti, and H. Renevier, Anisotropic In distribution in InGaN core-shell nanowires, *J. Appl. Phys.* **116**, 013517 (2014).
- [10] D. Cherns, R. F. Webster, S. V. Novikov, C. T. Foxon, A. M. Fischer, F. A. Ponce, and S. J. Haigh, Compositional variations in $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ nanorods grown by molecular beam epitaxy, *Nanotechnology*, **25**, 215705 (2014).
- [11] C. L. Hsiao, J. Palisaitis, M. Junaid, R.-S. Chen, P. O. A. Persson, P. Sandström, P.-O. Holtz, L. Hultman, and J. Birch, Spontaneous formation of AlInN core-shell nanorod arrays by ultrahigh-vacuum magnetron sputter epitaxy, *Appl. Phys. Exp.* **4**, 115002 (2011).
- [12] E. A. Serban, P. O. Å. Persson, I. Poenaru, M. Junaid, L. Hultman, J. Birch and C.-L. Hsiao, 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, *Nanotechnology* **26**, 215602 (2015).
- [13] L. Du, Q. Wu, X. Pei, T. Sun, Y. Zhang, L. Yang, X. Wang, and Z. Hu, Morphology and composition evolution of one dimensional $\text{In}_x\text{Al}_{1-x}\text{N}$ nanostructures induced by the vapour pressure ratio, *CrystEngComm.* **18**, 213 (2016).
- [14] H. Li, G. Zhao, S. Kong, D. Han, H. Wei, L. Wang, Z. Chen, and S. Yang, Morphology and composition controlled growth of polar c-axis and nonpolar m-axis well-aligned ternary III-nitride nanotube arrays, *Nanoscale* **7**, 16481 (2015).
- [15] C.-L. Hsiao et al, Room-temperature heteroepitaxy of single-phase $\text{Al}_{1-x}\text{In}_x\text{N}$ films with full composition range on isostructural wurtzite templates, *Thin Solid Films* **524**, 113–120 (2012).

- [16] T. Seppänen, P. O. Å. Persson, L. Hultman, J. Birch, and G. Z. Radnóczy, Magnetron sputter epitaxy of wurtzite $\text{Al}_{1-x}\text{In}_x\text{N}$ ($0.1 < x < 0.9$) by dual reactive dc magnetron sputter deposition, *J. Appl. Phys.* **97**, 083503 (2005).
- [17] R. Butté, J. -F. Carlin, E. Feltin, M. Gonschorek, S. Nicolay, G. Christmann, D. Simeonov, A. Castiglia, J. Dorsaz, H. J. Buehlmann, S. Christopoulos, G. Baldassarri, H. von Högersthal, A. J. D. Grundy, M. Mosca, C. Pinquier, M. A. Py, and F. Demangeot, Current status of AlInN layers lattice-matched to GaN for photonics and electronics, *J. Phys. D: Appl. Phys.* **40**, 6328-6344 (2007).
- [18] J. Palisaitis, C. L. Hsiao, M. Junaid, M. Xie, V. Darakchieva, J. Carlin, N. Grandjean, J. Birch, L. Hultman, and P. O. Å. Persson, Standard-free composition measurements of $\text{Al}_x\text{In}_{1-x}\text{N}$ by low-loss electron energy loss spectroscopy, *Phys. Status Solidi: Rapid Res. Lett.* **5**, 50-52 (2011).
- [19] J. Palisaitis, C.-L. Hsiao, L. Hultman, J. Birch and P.O.Å. Persson, 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, *Acta Materialia* **61**, 4683–4688 (2013).
- [20] M. Ferhat and F. Bechstedt, First-principles calculations of gap bowing in $\text{In}_x\text{Ga}_{1-x}\text{N}$ and $\text{In}_x\text{Al}_{1-x}\text{N}$ alloys: Relation to structural and thermodynamic properties, *Phys. Rev. B* **65**, 075213 (2002).
- [21] C. Hums, J. Bläsing, A. Dadgar, A. Diez, T. Hempel, J. Christen, A. Krost, K. Lorenz, and E. Alves, Anisotropic structural and optical properties of a-plane (11 $\bar{2}$ 0) AlInN nearly-lattice-matched to GaN, *Appl. Phys. Lett.* **90**, 022105 (2011).
- [22] C. L. Hsiao, L. W. Tu, M. Chen, Z. W. Jiang, N. W. Fan, Y. J. Tu, and K. R. Wang,

Polycrystalline to Single-Crystalline InN Grown on Si(111) Substrates by Plasma-Assisted Molecular-Beam Epitaxy, *Jpn. J. Appl. Phys.* **44**, L1076-L1079 (2005).

- [23] J. Wu, When group-III nitrides go infrared: New properties and perspectives, *J. Appl. Phys.* **106**, 011101 (2009).
- [24] Morales, A. M. and Lieber, C. M., A laser ablation method for the synthesis of crystalline semiconductor nanowires. *Science* **279**, 208–211 (1998).
- [25] C. Chèze, L. Geelhaar, O. Brandt, W. M. Weber, H. Riechert, S. Münch, R. Rothmund, S. Reitzenstein, A. Forchel, T. Kehagias, P. Komninou, G. P. Dimitrakopoulos, T. Karakostas, Direct comparison of catalyst-free and catalyst-induced GaN nanowires, *Nano Research* **3**, 528-536 (2010).
- [26] V. Consonni, Self-induced growth of GaN nanowires by molecular beam epitaxy, *Phys. Status Solidi RRL* **7**, 699–712 (2013).
- [27] L. Zhou, D. J. Smith, M. R. McCartney, D. S. Katzer, and D. F. Storm, Observation of vertical honeycomb structure in InAlN/GaN heterostructures due to lateral phase separation, *Appl. Phys. Lett.* **90**, 081917 (2007).
- [28] S. Choi, F. Wu, R. Shivaraman, E. C. Young, and J. S. Speck, Observation of columnar microstructure in lattice-matched InAlN/GaN grown by plasma assisted molecular beam epitaxy, *Appl. Phys. Lett.* **100**, 232102 (2012).
- [29] J. A. Venables, G. D. T. Spiller and M. Hanbücken, Nucleation and growth of thin films, *Rep. Prog. Phys.* **47**, 399-459, (1984).
- [30] D. Huang, M. A. Reshchikov, and H. Morkoç, Growth, structure, and optical properties of III-nitride semiconductor quantum dots, *International Journal of High Speed Electronics and Systems* **12**, 79-110 (2002).