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Magnetron Sputter Epitaxy of Group III-Nitride Semiconductor Nanorods

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Abstract

The III-nitride semiconductors family includes gallium nitride (GaN), aluminum nitride (AlN), indium nitride (InN), and related ternary and quaternary alloys. The research interest on this group of materials is sparked by the direct bandgaps, and excellent physical and chemical properties. Moreover, the ternary alloys (InGaN, InAlN and AlGaN) present the advantage of bandgap tuning, giving access to the whole visible spectrum, from near infrared into deep ultraviolet wavelengths. The intrinsic properties of III-nitride materials can be combined with characteristic features of nanodimension and geometry in nanorod structures. Moreover, nanorods offer the advantage of avoiding problems arising from the lack of native substrates, like lattice and thermal expansion, film – substrate mismatch.

The growth and characterization of group III-nitride semiconductors nanorods, namely InAlN and GaN nanorods, is presented in this thesis. All the nanostructures were grown by employing direct-current reactive magnetron sputter epitaxy. $\text{In}_x\text{Al}_{1-x}\text{N}$ self-assembled, core-shell nanorods on Si(111) substrates were demonstrated. A comprehensive study of temperature effect upon the morphology and composition of the nanorods was realized. The radial nanorod heterostructure consists of In-rich cores surrounded by Al-rich shells with different thicknesses. The spontaneous formation of core-shell nanorods is suggested to originate from phase separation due to spinodal decomposition. As the growth temperature increase, In desorption is favored, resulting in thicker Al-rich shells and larger nanorod diameters.

Both self-assembled and selective-area grown GaN nanorods are presented.

Self-assembled growth of GaN nanorods on cost-effective substrates offers a cheaper alternative and simplifies device processing. Successful growth of high-quality GaN (exhibiting strong bandedge emission and high crystalline quality) on conductive templates/substrates such as Si, SiC, TiN/Si, ZrB₂/Si, ZrB₂/SiC, Mo, and Ti is supported by the possibility to be used as electrodes when integrated in optoelectronic devices.

The self-assembled growth leads to mainly random nucleation, resulting in nanorods with large varieties of diameters, heights and densities within a single growth run. This translates into non-uniform properties and complicates device processing. These problems can be circumvented by employing selective-area growth. Pre-patterned substrates by nano-sphere lithography resulted in GaN nanorods with controlled length, diameter, shape, and density. Well-faceted *c*-axis oriented GaN nanorods were grown directly onto the native SiO_x layer inside nano-opening areas, exhibiting strong bandedge emission at room-temperature and single-mode lasing. Our studies on the growth mechanism revealed a different growth behavior when compared with selective-area grown GaN nanorods by MBE and MOCVD. The time-dependent growth series helped define a comprehensive growth mechanism from the initial thin wetting layer formed inside the openings, to the well-defined, uniform, hexagonal NRs resulted from the coalescence of multiple initial nuclei.

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Included papers

I. 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

Elena Alexandra Serban, Per Ola Åke Persson, Iuliana Poenaru, Muhammad Junaid, Lars Hultman, Jens Birch and Ching-Lien Hsiao
Nanotechnology 26, 215602 – 215610 (2015)

II. Magnetron sputter epitaxy of high-quality GaN nanorods on functional and cost-effective templates/substrates

Elena Alexandra Serban, Justinas Palisaitis, Muhammad Junaid, Lina Tengdelius, Hans Högberg, Lars Hultman, Per Ola Åke Persson, Jens Birch and Ching-Lien Hsiao
Energies 10(9), 1322 - 1334 (2017)

III. Selective-area growth of single-crystal wurtzite GaN nanorods on $\text{SiO}_x/\text{Si}(001)$ substrates by reactive magnetron sputter epitaxy exhibiting single-mode lasing

Elena Alexandra Serban, Justinas Palisaitis, Chia-Cheng Yeh, Hsu-Cheng Hsu, Yu-Lin Tsai, Hao-Chung Kuo, Muhammad Junaid, Lars Hultman, Per Ola Åke Persson, Jens Birch and Ching-Lien Hsiao
Submitted

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1. Introduction

The semiconductor market is currently evaluated at approximately US\$ 400 billion, and prognosis supports a rapid expansion in the future. The optoelectronics segment, currently dominates the global semiconductor industry, as the fastest growing segment with around 10% of the total market share. [1] III-nitride semiconductors, gallium nitride (GaN), aluminum nitride (AlN), indium nitride (InN), and related alloys, present the advantage of direct tunable bandgaps [0.7 eV (InN) – 3.4 eV (GaN) – 6.1 eV (AlN)], and bandgap bowing (non-linear variation of the alloy bandgap with composition) imprinting properties that open up new applications for ternary and quaternary alloys. [2] In particular, introduction of high-brightness blue light-emitting diodes (LEDs) with InGaN as the active layer [3] and violet blue laser diode based on InGaN multiple-quantum-well structure [4] sandwiched in p-/n-doped GaN epilayers in the 1990s, revolutionized and marked the rapid development of solid state lighting technology.

The first ones who investigated deeply the properties of this group of materials were Maruska and Pankove in the seventies. [5] However, these research programs were abandoned because of the inability to grow high-quality materials by heteroepitaxy and achieve p-type doping. The major breakthrough came in 1986, when Amano et al. succeeded growing high-quality GaN films on sapphire, using AlN buffer layers. [6] AlN layer was deposited at low temperature on sapphire before the growth of GaN, to compensate the strain induced by GaN layer - sapphire substrate lattice mismatch. The same group reported low resistivity p-type in 1989, by using low-energy electron beam

annealing to activate Mg-doped GaN. [7] However, good p-type group III-nitrides are still difficult to achieve. The difficulties arise from the ionization energies of acceptor dopants which are relatively high in III-nitrides, low dopant solubility, and hydrogen passivation. [8] This affects the performance of nitride-based devices for electronics, such as field-effect transistors and also conducts to the so-called efficiency droop in LEDs (efficiency reduction at high current density injection). [9]

The emergence of group III-nitride semiconductors nanostructures saw intense research activity, combining the intrinsic properties of III-nitride materials with unique properties induced by the nanorod geometry. The distinctive features that nanodimensionality offers like quantum confinement, high crystal quality, and strain relaxation promise significant advances in modern devices, and especially for optoelectronics. [10] Group III-nitride nanorods were first reported in 1998, obtained through self-assembly processes by molecular beam epitaxy (MBE). [11, 12]

The Thin Film Physics Division at Linköping University has a long history of employing and developing magnetron sputter epitaxy (MSE) technique, being one among only a few groups that use it successfully for the growth of group III-nitrides semiconductors. This knowledge gained by years of researching sputtering processes in ultrahigh vacuum (UHV) systems, conducted to the development of wurtzite III-nitrides semiconductors which include thin films, [13-15] but also nanostructures like: nanorods, [16, 17] nanospirals, [18] or nanograss. [19]

2. Group III-nitride semiconductors

Group III-nitride semiconductors, including AlN, GaN, InN, and their alloys form a group of materials with high perspectives because of their good properties, such as: high iconicity, low compressibility, high melting point, high thermal conductivity, chemical inertness, high breakdown voltages, and ability to sustain high-temperature and high-power operation. [2] They are direct bandgap materials and can crystallize in both wurtzite and zincblende polytypes (Figure 2.1). The difference between the polytypes consists in the stacking sequence: for the wurtzite phase ...ABAB... along the [0001] axis and ...ABCABC... along the [111] axis for the zincblende phase.

Figure 2.1. Wurtzite and zincblende unit cells for group III-nitride materials.

The atoms are tetrahedrally coordinated in both crystal structures. The Bravais lattice consists of two hexagonal close-packed sublattices shifted by $3/8$ [0001] for wurtzite, while for zincblende the structure consists of two face-centered cubic sublattices shifted in respect with each other by $1/4$ [111]. A sublattice consists of four atoms per unit cell where every group III atom is tetrahedrally coordinated by four atoms of nitrogen, and vice versa. For the growth of III-

nitride semiconductors, it is important to mention that the wurtzite structure represents the thermodynamically stable phase. [20]

Properties and growth behaviors of these wurtzite materials are also strongly related to the polarity. The directions $[0001]$ and $[000\bar{1}]$ are not equivalent because of the lack of inversion symmetry as it can be seen in Figure 2.2. The wurtzite III-nitrides can have a metal (Ga, Al, In)-face polarity if the group III atoms are facing towards the sample surface and vice versa for N-face polarity.

Figure 2.2. Group III- and N-polarity for wurtzite group III-nitride crystals.

The polarity of the grown structure can be influenced by the growth technique and conditions but also by the substrate and buffer layer used as templates during the growing process. It has been noticed that GaN films grown on sapphire by metalorganic chemical vapor deposition (MOCVD) [21] or hydride vapor phase epitaxy (HVPE) [22] usually present a Ga-face polarity, while, using molecular beam epitaxy (MBE) and a low-temperature AlN buffer layer, usually lead to N-face surfaces. [23] Besides the differences that appear in structure and morphology, the polarity also influences the electronic properties. Samples with different polarities have different Schottky barrier heights. [24]

Wurtzite ternary III-nitride alloys, $\text{In}_x\text{Ga}_{1-x}\text{N}$, $\text{In}_x\text{Al}_{1-x}\text{N}$, and $\text{Al}_x\text{Ga}_{1-x}\text{N}$, are all direct bandgap semiconductors, and the bandgap spans from ≈ 0.7 eV for InN,

to 3.4 eV for GaN, and to 6.2 eV for AlN. By tuning the bandgap of the ternaries, the whole visible spectrum can be covered from near IR into deep ultraviolet (UV) region. The bandgap energies exhibit bowing with composition, characterized by a bowing parameter, deviating from the linearity of Vegard's law according to Equation 2.1.

$$E_g^{InAlN}(x) = E_g^{AlN} \cdot x + E_g^{InN} \cdot (1 - x) - b \cdot x \cdot (1 - x), \quad (2.1)$$

where E_g is the bandgap, x is the Al fraction, and b is the bowing parameter.

This deviation is presented in Figure 2.3, where the bandgap energy is plotted as a function of lattice constant, considering the following bowing parameters: 1.6, 0.7, and 3.4 for $In_xGa_{1-x}N$, $Al_xGa_{1-x}N$, and $In_xAl_{1-x}N$, respectively. [25]

Figure 2.3. Bandgap energies as a function of lattice parameter of group III-nitrides. The following bowing parameters: 1.6, 0.7, and 3.4 for $In_xGa_{1-x}N$, $Al_xGa_{1-x}N$ and $In_xAl_{1-x}N$, respectively were considered. [25]

Of particular interest can be $\text{In}_x\text{Al}_{1-x}\text{N}$, due to the wide range of bandgap energies accessible, but also because it can be grown lattice-matched to GaN at a composition of 18% In, suitable for strain-free barrier and capping layer. Despite these perspectives, not many reports exist on the growth of $\text{In}_x\text{Al}_{1-x}\text{N}$, a lot of problems arising from the high immiscibility in the range $0.1 < x < 0.9$ and lattice mismatch between AlN and InN, of $\sim 13\%$. These problems can be easily surpassed by using non-equilibrium growth techniques such as MSE, and full-composition range was demonstrated. [14, 17, 18]

3. *One-dimensional nanostructures*

One-dimensional (1D) nanostructured materials, such as nanorods, nanowires, nanocolumns, which have one dimension of the order of 10^{-9} m gained attention because of their possible applications, being adequate for the fabrication of both nanoscale devices and interconnections owing to their size, morphology and properties. Numerous works report the use of III-nitride semiconductor nanorods as building blocks in nanodevices. Such devices include: nanolasers, [26] LEDs, [27] high electron mobility transistors (HEMTs), [28] nanosensors, [29] solar cells, [30] and nanogenerators. [31] These advances supported the intensive research dedicated to growth and development of III-nitride semiconductor nanorods in the past years. Various techniques were employed for the growth of 1D nanostructures, such as chemical vapor deposition, [32] laser ablation, [33] MOCVD, [34] MBE, [35] HVPE, [36] and MSE. [16, 17]

At this scale, quantum confinement effects can be exploited in terms of tailoring geometry. For example, there is a dependence between size of the nanostructures and bandgap. Theoretical calculations show the bandgap increase with size decrease. [37] This bandgap energy variation (ΔE_g) depending on geometrical confinement (thickness or diameter – d^{-2}) with the slope (S) line variation in dots (0D), rods (1D), and wells (2D) is presented in Figure 3.1. The calculated line slope ratios were: $S_{\text{well}}:S_{\text{rod}}:S_{\text{dot}} = 1.00:2.34:4.00$. [38] This result points out that modifying the geometry and size offers the possibility of tuning of the optical and electrical properties of nanostructured semiconductors.

Figure 3.1. Theoretically calculated slope relationships for GaAs material representing the size dependence of the effective bandgaps in dots (0D), rods (1D) and wells (2D). [38]

Group III-nitrides can be grown both homoepitaxially and heteroepitaxially. Homoepitaxy means the substrate is the same material as the grown material, while in heteroepitaxy, the substrate and grown material are different. Heteroepitaxy is commonly used for the growth of group III-nitride due to difficulties in achieving bulk group III-nitride substrates.

The lack of native substrates represents a major problem for the growth of III-nitride films, resulting in a high density of dislocations induced by the film – substrate mismatch. Dislocation act as non-radiative centers, decreasing luminescence efficiency and leading to degradation of optoelectronic devices. [39] The nanorod’s geometry, with the characteristic small cross-sections, allows them to accommodate much higher levels of strain induced by lattice mismatch. The crystal structure can elastically relax for a wider range of mismatches, and dislocations are either confined to the interface or are likely to bend to the sidewalls, enabling the growth of defect-free nanorods on a wide range of substrates. Besides, the small footprint of the nanorods contributes to avoidance of crack generation by relieving the strain induced by thermal expansion mismatch with the substrate.

3.1 Nanorod structures

Nanorods can be obtained as single phase or heterostructured nanorods (Figure 3.2). The heterostructures offer the possibilities of combining two or more materials, and so take advantage of the properties and characteristics of both. Owing to the small footprint, the structure degradation due to mismatch in lattice is avoided. Depending on the direction the materials are inserted, we can have radial nanorod heterostructure (termed as core-shell structure), or axial nanorod heterostructure.

Figure 3.2. Representation of single-phase and heterostructured nanorods.

Axial nanorod heterostructures simplify the production of devices such as LEDs, and lead to improved size dependent properties but also offer an easy way of incorporating quantum wells and dots in the active regions. [40, 41]

Radial nanorod heterostructures consist of a nanorod core region surrounded by coaxial shell layers. There are two ways of obtaining core-shell nanorods. One is a two steps method consisting in growing a single nanorod (core), which is then coated with another material (shell), usually with a larger bandgap. [42] Another method consists of a single step growth and refers to the spontaneous formation of core-shell nanorods consisting of two phases with different

concentrations. [43, 17] In a ternary III-nitride, a complete phase separation can occur, resulting in nanorods where the core and the shell are each composed of a binary compound. An incomplete phase separation results in compositional fluctuation, and both the shell and core of the nanorods are composed of ternary material, but with a different concentrations x .

3.2 Synthesis of group III-nitride nanorods

3.2.1 Top-down synthesis

Fabrication of nanorods can be approached by top-down or bottom-up methods. Top-down methods offers the advantage of patterning with better reproducibility, and dimension control accuracy. However, top-down fabrication includes several processing steps in order to reach to the final nanorod shape: epitaxy, patterning and etching. The starting point is a bulk material or a film which can be obtained by different epitaxy methods, and from which material is carved away until nanorods with the desired size are obtained. Heterostructured nanorods can be obtained from multilayers. Next, the patterning is applied by the use of a lithographic technique such as: photolithography, electron-beam lithography, nanoimprint lithography or colloidal lithography. The desired pattern is transferred either with the help of a photo- or electro-sensitive polymer called resist or by coating the surface with a solution of dispersed nano-spheres (colloidal lithography). The uncovered areas are afterwards etched away by a dry or wet etching procedure. A typical process of obtaining axial nanorod heterostructures by electron-beam lithography is presented in Figure 3.3.

Figure 3.3. Typical processing steps for obtaining nanorods from thin films by a top-down method

3.2.2 Bottom-up synthesis

Bottom-up methods require less effort and result in a better crystalline quality of nanorods and smoother side surfaces since no nanorod etching step is involved. The growth process can be catalyst-assisted, also termed as vapor-liquid-solid (VLS) growth, or catalyst-free leading to the self-assembled nanorods.

Catalyst-assisted growth

The catalyst-assisted VLS growth process was first proposed by Wagner and Ellis in 1964, for the growth of Si whiskers, using gold catalyst. [44] The growth mechanism describes unidirectional growth resulted from the impinging of the vapor phase precursor of the nanorod material on a liquid phase seed droplet. The commonly used catalysts for GaN nanorod growth, are Au, Ni, a mixture of both, or Ta. The catalyst is either coated on the substrate and thermally annealed to result in metallic droplets, or deposited as particles on the substrates' surface. Catalyst/III-nitride precursor alloying takes place, resulting in

supersaturation of the liquid alloy and precipitation at the liquid/solid interface. The precipitation leads to nanorod growth, which continues as long as the vapor-phase reactants are supplied (Figure 3.4).

Figure 3.4. Catalyst-assisted growth of III-nitride nanorods.

Position-controlled growth can be applied by patterning of the catalyst, employing lithography methods. However, the crystal quality is often affected by the incorporation of the catalyst material into the nanorod. The presence of Ni catalyst was reported to affect the structural and optical properties of the GaN nanorods, being connected to stacking fault formation or stabilization of zincblende structure. [45]

Catalyst-free growth

Catalyst-free growth, also termed as self-assembled or self-induced growth, denotes the spontaneous formation of nanorods during growth. Spontaneous formation was proved using different methods, such as MBE, MOVPE, HVPE or MSE. Growth is not determined anymore by the catalyst presence, but surface diffusion and adatom mobility control more on the process and resultant morphology. [46] Spontaneous III-nitride nanorod growth can be divided into

two steps: nucleation and growth. Processes as adsorption, diffusion, and desorption are essential for understanding the nucleation and growth in this case. During the nucleation, adatoms migrate on the surface of the substrate and are adsorbed, leading to the formation of stable clusters. The coarsening of these clusters results in the nanorods nuclei formation and kinetics determine the elongation and final nanorod growth. [35, 47] The general rule is that nanorods grow in the direction of minimizing the total surface energy of the crystal. [48] III-nitride nanorods, usually grow preferentially along *c*-axis, since the average surface energies of the polar and semipolar planes are higher than those of nonpolar planes. [49] Adatoms tend to migrate along the substrate surface and the lateral nonpolar planes of nanorods, being incorporated primarily in the nanorod top polar planes. The diffusion-induced growth means that nucleation of nanorods is mainly random resulting in a large varieties of diameters, heights, and densities within a single growth run.

3.2.3 Selective-area growth

The randomness specific to self-assembled nanorods leads to non-uniform properties and hinders device processing. Selective-area growth (SAG) of nanorods was introduced to circumvent these problems, since it offers precise control on size (length and diameter), shape, position, density and orientation of the nanorods. [50, 51] Pre-patterned substrates, with mask layers that limit the growth to specific areas are employed for SAG of uniform nanorod arrays. The commonly used mask materials are: TiN_x, [52] SiN_x [53] or SiO₂. [54] After the deposition of the mask layer, lithographic methods are used to define the growth area, such as: photolithography, electron-beam lithography, laser interferometric lithography, nanoimprint lithography or nano-sphere lithography.

4. Growth of group III-nitrides

4.1 Metalorganic Chemical Vapor Deposition

MOCVD is a technique where growth takes place in thermodynamic equilibrium conditions by chemical reactions. [55] The metalorganic precursor molecules are carried away by a gas from a stainless steel container to an epitaxial growth chamber. The precursor can be either in solid or liquid form and must exhibit an appropriate volatility and reactivity to thermally decompose inside the chamber. The most common precursors used for the growth of group III-nitrides are: trimethylgallium (TMGa), triethylgallium (TEGa), trimethylaluminum (TMAI), and trimethylindium (TMIn), while ammonia is used as the source material for nitrogen. The general reaction that takes place can be described by:

where R represents the organic radical and III-M the group III-metal.

The growth process take place in four steps: gas input, pyrolysis, diffusion, and surface reaction. The by-products that result are then pumped away with the carrier gases. The precursors used, and the resulted residual gases, can have a negative impact for human health and environment. For dealing with this, a variety of exhaust systems are now available like scrubbing systems (which capture, isolate and convert pollutants before releasing into the environment) and burnboxes (where the unreacted gases are cracked and oxidised at high temperatures). [56]

4.2 Molecular beam epitaxy

MBE is a non-equilibrium growth method that employs the usage of Knudsen effusion cells or electron-beam evaporators for heating and evaporating/sublimating source material under UVH conditions. For III-nitride semiconductor growth, typically the source material for nitrogen is ammonia or a nitrogen plasma and the compound is formed through the reaction between the group III-metal and nitrogen at the substrate's surface. In this case, the reaction is kinetically driven by the surface processes, and is not a reaction taking place at thermodynamic equilibrium unlike MOCVD. [57] The resulting growth rates are relatively low compared to MOCVD.

4.3 Magnetron sputtering

Sputtering is a physical vapor deposition, taking place in a vacuum environment, and consists in ejecting atoms from a target material by bombarding it with high energetic ions, and condensing these ejected atoms onto a substrate. Plasma is generated by introducing a working gas into the vacuum chamber and applying a negative potential on the target. The energy transferred to the target atoms by the colliding positive ions is described in equation 4.2. [58]

$$\Lambda = \frac{4M_i M_t}{(M_i + M_t)^2}, \quad (4.2)$$

where Λ is the transferred energy, and M_i and M_t are the mass of the incident ion and target atom, respectively.

The interaction between the bombarding ions and target material generates not only sputtered atoms, but also secondary electrons which are important for

maintaining the plasma. A limitation of MBE and MOCVD growth consist in the high temperatures needed for obtaining high quality III-nitride materials. Due to the ion assisted growth which enhances adatom mobility, MSE allows for the growth of single-crystal, high-quality films even at room-temperature. [14] In MSE, the ionization process is enhanced by using a magnetic field. Reactive sputtering is when a reactive gas, like oxygen or nitrogen, is introduced into the sputtering chamber. The sputtered particles can undergo a chemical reaction with the reactive gas particles both before condensing onto the substrate and on substrate surface. Therefore, the deposited material can be a compound, different from the metallic target material. The chemically reactive gas can react not only with the ejected atoms from the target, but also with the target surface. This phenomenon is called target poisoning and can cause instability to the process, if the hysteresis effect occurs. [59]

MSE has developed rapidly becoming the main sputtering process for obtaining a wide range of industrially important coatings. The applications include: hard, wear-resistant coatings, low friction coatings, corrosion-resistant coatings, decorative coatings, and coatings with special optical or electrical properties. [60] An important step was represented by the introduction of balanced magnetrons in the early 1970s. However, the process limitations were truly overcome with the development of the unbalanced magnetron in the late 1980s.

Depending on their magnetic field configuration three types of magnetrons can be defined (Figure 4.1).

- Balanced magnetron (center and outer poles have equal strength)
- Unbalanced magnetron type I (center pole is stronger than the outer pole)
- Unbalanced magnetron type II (outer pole is stronger than the inner pole).

[61]

Figure 4.1. Schematic illustration of magnetron types and their magnetic field configuration.

The stronger magnets on the outside of an unbalanced magnetron result in an expanded plasma away from the surface of the target towards the substrate. The secondary electrons that escape the target's surface produce a greater number of ions closer to the substrate, increasing the ion bombardment.

In DC sputtering, a potential difference is applied between target and substrate, leading to the acceleration of the gas ions towards the target's surface. Atoms are ejected from the target's surface and travel to the substrate surface where they are deposited.

Recently, high quality III-nitrides were grown by reactive magnetron sputtering from metallic targets under pure or diluted N_2 sputtering gas. Argon or other inert gases are used to avoid the formation of a nitride layer on the target's surface that can cause problems during deposition. The process of nitride formation consists in breaking the strong N-N bonds that can be stimulated by proper methods, such as increasing the substrate temperature and/or applying a negative potential to the substrate. Recently LEDs with sputtered GaN/InGaN/GaN active layers on glass substrates were demonstrated. GaN layers with clear p-type conductivity were grown at low temperature. These results cannot be obtained by classical MBE and MOCVD methods at such low

temperatures, confirming MSE as a very promising technique for industrial integration. [62, 63]

4.3.1 System description

GaN was grown in a UVH growth chamber connected, with the chamber used for $\text{In}_x\text{Al}_{1-x}\text{N}$ growth through a common load lock and transfer tube system. This makes possible the future growth of nanorod heterostructures, without the need to vent the chamber every time during loading and unloading, and exposing the sample to air. The scheme of the system is presented in figure 4.2. The base pressure inside the growth chamber is 1×10^{-8} Torr. A liquid Ga target (99.99999% pure) is placed in a stainless steel crucible, in vertical position to avoid spilling. An enhanced ionization is achieved through the usage of a water cooled, type II unbalanced magnetron. [64]

Figure 4.2. Schematic drawing of the growth chamber used for MSE of GaN.

The sputtering system used for the growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods is represented in figure 4.3, also with a base pressure of 1×10^{-8} Torr. The system is equipped

with 4 type II unbalanced magnetrons, corresponding to 4 metallic targets (Al, In, Ti and Sc), situated at approximately 13 cm from the substrate position with an inclination of 30°. [65]

Figure 4.3. Schematic drawing of the growth chamber used for MSE of InAlN.

5. Characterization techniques

5.1 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive structural characterization technique. With the help of this technique, the most studied factors are: internal structure, chemical composition, stress, crystal orientation, crystal quality, crystal size, texture, lattice parameters, and surface and interface roughness.

X-rays typically have wavelengths similar to the spacing of lattice in crystals in the range of a few Å. They are generated by decelerating highly energetic electrons shoot onto a target material (typically Cu). The resulted characteristic x-rays, typical Cu-K α and Cu-K β line, are used as the light source in XRD measurement. Normally, Cu-K β line is filtered out by a Ni plate. The incident x-ray scatters by the electron cloud surrounding each atom in the crystal, and constructive interference occurs between the scattered x-rays only if the path difference is an even number of wavelengths (Figure 5.1).

Figure 5.1. X-ray interaction with a crystal structure.

The diffraction of x-rays by different crystallographic planes in a crystal can be described using Bragg's law:

$$n\lambda = 2d_{hkl} \sin\theta, \quad (5.1)$$

where, n is the diffraction order as an integer, λ is the x-ray wavelength, d_{hkl} is the spacing between adjacent crystallographic planes with Miller indices hkl , and θ is the Bragg angle between incident beam and crystal planes. In typical $\theta/2\theta$ scan, the angle between the incident beam and scattered beam is always kept as 2θ .

The parameter d_{hkl} is defined differently for each Bravais lattice, providing correlations between specific planes and Bragg angles for the wavelength of x-ray, λ . For a hexagonal Bravais lattice the d spacing is described by the equation:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + k^2 + l^2}{a^2} \right) + \frac{1}{c^2}, \quad (5.2)$$

5.1.1 $\theta/2\theta$ scan

In a symmetric scan, i.e. $\theta/2\theta$ scan, the reflected angle, 2θ , is always kept as twice of incident angle, θ , during measurement. Since the scattering vector is perpendicular to the surface, only the crystal planes parallel to the surface will contribute to Bragg's diffraction. A single-crystal sample will produce only one family of peaks in the diffraction pattern when measured in a $\theta/2\theta$ scan configuration. The diffraction pattern will contain a set of plane spacings, shown at various 2θ angles, and the corresponding relative intensities (I). The peak analysis can give the following information: peak position (2θ) - size of the unit

cell, peak intensity (I) – content of the unit cell, and broadening of the peaks - particle size and strain in the sample. A typical $\theta/2\theta$ diffraction pattern for single-crystal GaN nanorods grown on Si(111) substrate is presented in figure 5.2.

Figure 5.2. $\theta/2\theta$ of single-crystal GaN(0001) nanorods grown on Si(111) substrate.

The crystalline structures were characterized by $\theta/2\theta$ scan with a Philips 1820 Bragg- Bretano diffractometer using Cu- K_{α} radiation.

5.1.2 Pole figures

Pole figure XRD is a common technique to obtain texture information. The pole figure is a stereographic projection representing a map of crystal directions with respect to the sample reference frame. The pole figure gives the probability of finding a given (hkl) plane, as a function of the specimen orientation. In a pole figure measurement, the sample reference frame is scanned by varying the ϕ

angle (twist angle around sample's normal direction) and Ψ angle (tilt angle around sample's normal direction) at a fixed 2θ angle.

When the III-nitride associated reflexions join together forming a ring of higher intensity, it indicates that the nanorods have a fiber texture with their c -axes along the growth direction and with random in-plane orientation (Figure 5.3a). When a treatment is applied to the substrate to remove the native oxide layer, such as HF etching or clean sputtering, the in-plane orientation of the III-nitride nanorods changes, exhibiting six distinct peaks, separated by $\varphi = 60^\circ$, and indicating an ordering in the in-plane orientation (Figure 5.3b).

Figure 5.3. 10-15 pole figure of (a) randomly oriented, and (b) in-plane oriented GaN nanorods grown on Si substrate.

For nanorods samples, the elongation along the phi (φ) angle is attributed to a broad in-plane misorientation, meaning that the nanorods exhibits a small-angle twist with respect to each other. The elongation along psi (Ψ) angle is due to the tilted growth of the nanorods in respect to template's surface normal.

5.2 Scanning Electron Microscopy

The scanning electron microscope (SEM) is a powerful tool that utilizes a focused electron beam to obtain information by scanning it over a sample surface. The high-resolution three-dimensional images produced by SEMs can provide topographical, morphological, and compositional information, which makes it invaluable in a variety of science and industry applications. [66]

Electron microscopes work on the same basic principles as optical microscopes, but use a focused beam of energetic electrons rather than photons in order to obtain higher magnified images of an object. The wavelength of the white light limits the resolution of the optical microscope to about 200-250 nm. Electrons have much shorter wavelengths, enabling better spatial resolution. The wavelength of accelerated electrons is based on relativistic theory and is described by the equation:

$$\lambda = \frac{h}{\sqrt{2m_e eV} \sqrt{1 + \frac{eV}{2m_e c^2}}}, \quad (5.3)$$

where h is Planck constant, c is the speed of light in vacuum, e is the electron charge, V is potential difference between anode and cathode, and m_e is the electron mass.

The working principle is that a beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through a vacuum column where electromagnetic lenses focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample which are then analysed by appropriate detectors.

The accelerated electrons carry significant amounts of kinetic energy and a variety of signals are produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (SE), backscattered electrons (BSE), diffracted backscattered electrons (used to determine crystal structures and orientations of minerals), characteristic x-rays (used for elemental analysis), photons (used in cathodoluminescence analysis), and heat. SE and BSE are used for imaging samples. SE are most valuable for showing morphology and topography (Figure 5.4). These emitted SE are detected with the “in-lens” detector. The edges and protruding parts look brighter than the rest of the image since more SE can leave the sample at edges (so-called edge effect).

Figure 5.4. Tilt-view SEM image on SAG GaN nanorods

5.3 Cathodoluminescence spectroscopy

In this technique, the signal consists in cathodoluminescence (CL) emission by a sample on which an electron beam is focused. Photons are emitted due to the radiative recombination resulted from the excitation of the electrons of the material analysed in the conduction band under electron beam irradiation. A detector can produce high-resolution cathodoluminescent images of luminescent materials and it can be attached to a SEM or a transmission electron microscope (TEM). CL is a common technique used for group III-nitride

materials, since they possess high radiative recombination (Figure 5.5), to analyse the bandgap and intermediate band (impurity and/or defect). CL emission can be enhanced with higher beam voltage and current, however, resulting in sample heating and charging effects.

Figure 5.5. A typical room-temperature CL spectrum of GaN nanorods.

In this thesis, sample morphologies were characterized with a Zeiss Leo 1550 field-emission gun SEM. The SEM is equipped with a Gatan MonoCL4 spectroscope, used for performing room-temperature cathodoluminescence (CL) spectroscopy and mapping. The emission from the samples is dispersed by a monochromator with a 150 lines/mm grating blazed at 500 nm and detected by a Peltier-cooled photomultiplier tube.

5.4 Transmission electron microscopy

In a transmission electron microscope, the electrons generated by an electron gun are accelerated and go through the illumination system composed of two or more sets of condenser magnetic lenses. An electron-transparent sample is

irradiated by electrons with energies of the order of 100-300 kV. After the interaction with the sample, the electrons are either transmitted, scattered or reflected. The transmitted and scattered electrons enter the imaging system of the microscope composed of the objective, intermediate and projector magnetic lenses. The resulting image can be visualized on a fluorescent screen and recorded with the help of a CCD-camera. The TEM specimens must be sufficiently thin (~ 100 nm) to allow transmission of electrons. TEM provides information regarding the crystal structure of the specimen, like: microstructure, crystal structure and position of the atoms in the crystal, but also about composition and elemental mapping.

The standard TEM imaging modes are bright-field and dark-field imaging (Figure 5.6). In the bright-field operation mode the objective aperture is placed so that only the transmitted beam is allowed to pass forming the image. This way, the parts of the sample that scatter more have less intensity, appearing darker in the image. Dark-field images are formed when the objective aperture is placed so that only one diffracted beam is allowed to pass. In this case, the parts of the sample that have a high scattering become brighter in the image.

Figure 5.6. Diagram of standard TEM imaging modes.

In high-resolution TEM (HRTEM), an image of the crystal lattice is obtained by interference of transmitted beam and diffracted beams.

Depending on the spot size of the beam, TEM can be operated in the microprobe mode (1-25 nm), i.e. the illumination is parallel on the sample, or nanoprobe mode, i.e. a nanometric spot size (0.1-2 nm) is obtained by a convergent beam illumination. Microprobe is used in TEM and electron diffraction analysis, to illuminate large areas. Nanoprobe is used for spectroscopic techniques: electron energy loss spectroscopy (EELS) and energy-dispersive x-ray spectroscopy (EDX), and in scanning TEM (STEM).

In STEM, a nanoprobe is scanned across the surface of the specimen, and the diffracted electrons are analysed with a detector placed under the column. This way, the contrast in STEM mode is determined by the scattering angle. Electrons scattered at an intermediate angle can be probed with a dark-field detector and will result in a diffraction dominated contrast. Electrons scattered at large angles can be probed with a high-angle annular dark-field (HAADF) detector, and the contrast will be determined by the atomic number of the species in the analysed sample.

Another type of interaction after the samples' irradiation with the electron beam results from the ejection of a core electron and the decay of the excited atom to its ground state by emitting characteristic x-rays. Elemental composition can be probed by measuring the characteristic x-rays by an EDX spectrometer (Figure 5.7).

Figure 5.7. STEM-HAADF image and corresponding EDX elemental mappings of core-shell $\text{In}_x\text{Al}_{1-x}\text{N}$ nanorods.

Microstructural analyses were performed by using the double-corrected Linköping FEI Titan³ 60-300, operated at 300 kV.

6. Summary of the included results

In the *first paper*, I demonstrate the successful growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ radial nanorod heterostructures on Si(111) substrates using direct current reactive MSE. No catalyst was used for the growth of $\text{In}_x\text{Al}_{1-x}\text{N}$ core-shell nanorods. The temperature effect upon the morphology and composition of the nanorods was investigated by SEM, XRD, STEM, and EDX mapping. The spontaneous formation of core-shell nanorods, consisting of In-rich cores surrounded by Al-rich shells with different thicknesses was observed. The nanorod diameter and shell thickness increase with the increase in growth temperature. It was revealed that lower growth temperatures induce the formation of well-separated and uniform core-shell nanorods with high In-content cores (700-800 °C), while a deposition at higher temperature (850 °C) leads to the formation of an Al-rich $\text{In}_x\text{Al}_{1-x}\text{N}$ film resulted from the coalescence of core-shell nanorods. The formation of the nanostructures was traced to the initial growth. Substrate treatment was applied so that the in-plane fiber-textured growth of the nanorods was modified to an epitaxial growth. A correlation between the influence of the substrate treatment upon the formation of the interfacial layer and crystallographic relationship was reported.

The versatility of MSE in achieving high-quality GaN nanorods was demonstrated in *paper 2*. Different substrate/template combinations, specifically Si, SiC, TiN/Si, ZrB_2/Si , ZrB_2/SiC , Mo, and Ti were employed for the growth of self-assembled GaN nanorods. Growth temperature was optimized resulting in increased nanorod aspect ratio. The decrease of the diffusion length with increased temperature was observed, in agreement with established models. High-resolution TEM and CL studies revealed nanorods

with strong bandedge emission resulting from their high purity and quality, especially for GaN nanorods grown on TiN/Si. Non-conventional substrates are not only cost-effective but also eliminate post-processing steps in device fabrication.

Paper 3 presents the first successful SAG of single-crystal wurtzite GaN nanorods by reactive MSE. The Si(001) substrates with un-etched native SiO_x amorphous layer were pre-patterned by NSL, employing a TiN_x mask. The initial growth stages and the time evolution of SAG GaN(0001) nanorods were studied, based on observations from samples grown for different sputtering times. With the help of characterization techniques like SEM, XRD, TEM, STEM, and EDX, a 5-step growth model was defined. The growth mechanism steps are: formation of a polycrystalline wetting layer, predominating *c*-axis oriented nucleation, coarsening and coalescence of multi-islands, single nanorod evolution, and finally quasi-equilibrium crystal shape formation. Our SAG-GaN nanorods possess strong bandedge emission with uniform luminescence as seen by room-temperature CL analysis. Moreover, single-longitudinal-mode lasing, was obtained at room-temperature by optical pumping with a pulsed laser. The lasing characteristics are attributed to well-faceted nanorod geometry forming a Fabry–Pérot cavity, proving the high potential of MSE for fabricating high-performance laser optoelectronics.

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