Structural and optical characteristics of GaN/ZnO coaxial nanotube heterostructure arrays for light-emitting device applications

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\textit{New Journal of Physics} 11 (2009) 125021 (13pp)
Received 1 June 2009
Published 17 December 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/12/125021

Abstract. We report on the structural and optical characteristics of position-controlled GaN/ZnO coaxial nanotube heterostructure and GaN/In\textsubscript{x}Ga\textsubscript{1−x}N coaxial nanotube quantum structure arrays for light-emitting diode (LED) applications. The GaN/ZnO nanotube heterostructures were fabricated by growing a GaN layer on the entire surface of position-controlled ZnO nanotube arrays using low-pressure metal-organic vapour-phase epitaxy. As determined by transmission-electron microscopy (TEM), an abrupt and coherent interface between the core ZnO and the GaN overlayer was observed. The optical characteristics of heteroepitaxial GaN/ZnO nanotube heterostructures were also investigated using cathodoluminescence (CL) spectroscopy. This position-controlled growth of high-quality single crystalline GaN/ZnO coaxial nanotube heterostructures allowed the fabrication of artificial arrays of

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high-quality GaN-based coaxial quantum structures by the heteroepitaxial growth of GaN/In$_x$Ga$_{1-x}$N multiple quantum wells along the circumference of the GaN/ZnO nanotubes. The optical and structural characteristics of the position-controlled GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structures were investigated by using CL spectroscopy and TEM analysis, respectively. The green LED microarrays were successfully fabricated by the controlled heteroepitaxial coaxial coatings of GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structures and the outermost Mg-doped p-type GaN layer onto the GaN/ZnO coaxial nanotube heterostructures, presumably implying that the position-controlled growth of high-quality GaN/ZnO coaxial nanotube heterostructure arrays provides a general and rational route of integrating vertical nanodevices for nanoscale electronics and optoelectronics.

Contents

1. Introduction .......................... 2
2. Experimental ......................... 3
3. Structural and optical characteristics of GaN/ZnO coaxial nanotube heterostructures ....................... 5
4. Structural and optical characteristics of GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structures ....................... 8
5. Coaxial nanotube LED microarrays consist of GaN-based p–n homojunction heterostructures with GaN/In$_x$Ga$_{1-x}$N coaxial multiple QWs ................................. 10
6. Summary and conclusions ............... 11
Acknowledgments .......................... 12
References ................................ 12

1. Introduction

For the past several decades, monolithically integrated devices have been fabricated using a top-down process consisting of thin film deposition, lithography and etching [1]. Preparing high-quality thin films by heteroepitaxy [2]–[4] is the first step in fabricating high-quality nanodevices using the top-down method. However, even a small mismatch in lattice constant or thermal-expansion coefficient between the thin film and substrate leads to film quality deterioration through the formation of structural defects and cracks [4, 5]. In addition, films can easily be contaminated and damaged during the lithography and etching processes [6]. These difficulties resulting from material incompatibility between film and substrate in the top-down approach may be circumvented by selectively growing nanostructures on nano-scale sites. Nanoscale devices, such as light-emitting diodes (LEDs), have also been fabricated using the bottom-up method [7]–[10], where various one-dimensional (1D) semiconductor nanomaterials, including nanorods, nanowires, nanobelts and nanotubes, have been synthesized for device fabrications [11]–[15]. However, despite extensive research on bottom-up methods, it is still very difficult to control the positioning of nanomaterials for nanodevice integration.
Accordingly, in growing 1D nanostructures, using both top-down and bottom-up processes, the development of a method for precisely controlling the position and dimension is crucial.

Position control of nanostructures has been achieved by the selective growth of 1D nanostructures on specifically patterned sites using either metal catalyst-assisted [16] or catalyst-free methods [15, 17, 18]. The next challenge is to fabricate position-controlled 1D nanomaterial heterostructures with compositional modulations along either the axial or radial directions [19, 20]. These heterostructures could greatly increase the versatility in designing novel electronic and optoelectronic nanodevices [7, 21, 22]. For 1D heterostructured nanodevice applications, nanomaterial heterostructures must have a clean, abrupt interface with a very low interfacial defect concentration as the effects of interfacial defects on nanomaterial properties and nanodevice characteristics become more significant with a high interface-to-volume ratio of the nanomaterial heterostructure. However, the structural and optical characteristics of position-controlled 1D nanomaterial heterostructures have rarely been studied [19, 23].

Here, we report on the structural and optical characteristics of position-controlled ZnO/GaN coaxial nanotube heterostructure arrays for LED applications. Among numerous semiconductor nanomaterials, ZnO nanostructures with high crystallinity and optical qualities have been widely studied for optoelectronic nanodevice applications. Very recently, both the position and dimension of ZnO nanotubes have been precisely controlled using conventional lithography and selective area metal-organic vapour-phase epitaxy (MOVPE) [15, 24]. However, since reliable and reproducible growth of p-type ZnO is still a formidable task [25], realization of high-brightness ZnO-based p–n homojunction LEDs has yet to be obtained [26, 27]. Conversely, in III-nitride semiconductor heterostructures, controlled n- and p-type dopings and compositions have been achieved, which yielded high-brightness blue LEDs and even short-wavelength laser diodes [28]. Meanwhile, nanostructure LEDs can be fabricated using the epitaxial coating of nitride LED structures on well position-controlled ZnO nanostructures [7]. In this paper, the structural defects and optical characteristics of GaN/ZnO coaxial nanotube heterostructures and GaN/In\textsubscript{x}Ga\textsubscript{1-x}N coaxial nanotube quantum structures, which were investigated using electron microscopy and cathodoluminescence (CL) spectroscopy, respectively, are described.

2. Experimental

GaN/ZnO coaxial nanotube heterostructure arrays were grown on GaN/c-Al\textsubscript{2}O\textsubscript{3} substrates using catalyst-free, low-pressure MOVPE. Figure 1 depicts schematics of the overall procedure for fabricating these position-controlled coaxial nanotube heterostructures. The position-controlled nanostructures were fabricated by selectively growing the ZnO nanotubes only on the hole patterns of the substrates. First, ZnO nanotube arrays were prepared on c-Al\textsubscript{2}O\textsubscript{3} substrates with a GaN seed layer and a hole array-patterned 50-nm-thick amorphous SiO\textsubscript{2} thin film as a growth-mask layer (figures 1(a) and (b)); details of the selective growth are described elsewhere [15]. Immediately following the ZnO nanotube array preparation, GaN layers were grown along the circumferences of the nanotube arrays using MOVPE (figure 1(c)). For the reactants of GaN, trimethylgallium and ammonia, with typical flow rates of 1.5 and 1000 sccm, respectively, were used. The typical GaN growth temperature was 600 °C. The typical thickness of the GaN layer grown for 30 min was ~200 nm. After the preparation of GaN/ZnO coaxial nanotube heterostructure arrays, three-period GaN/In\textsubscript{0.24}Ga\textsubscript{0.76}N multiple quantum wells (MQWs) were heteroepitaxially deposited on the circumferential surface of
Figure 1. Schematic representation of the fabrication process for position-controlled selective growth of GaN/ZnO coaxial nanotube heterostructure and GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structure arrays. (a) Hole pattern formation of a SiO$_2$ growth-mask layer on a GaN/c-Al$_2$O$_3$ substrate by selective etching of SiO$_2$ thin layer deposition using e-beam lithography and chemical etching processes. (b) Position-controlled selective MOVPE growth of ZnO nanotubes on a hole-patterned substrate. (c) MOVPE coating of GaN on ZnO nanotubes. The schematic of the GaN/ZnO coaxial nanotube heterostructure is also shown. (d) Heteroepitaxial growth of GaN/In$_x$Ga$_{1-x}$N MQW layers on GaN/ZnO nanotube arrays. The schematic of the GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structure is also shown.

GaN/ZnO coaxial nanotube heterostructure arrays using a commercial nitride MOVPE system (figure 1(d)) [7]. For GaN/In$_{0.24}$Ga$_{0.76}$N MQWs, the 3-nm-thick quantum well (QW) and 13-nm-thick quantum barrier (QB) were grown at 720 and 820°C, respectively, with the expectation of green colour emission. For In$_x$Ga$_{1-x}$N QW layers, trimethylindium and trimethylgallium as well as ammonia were employed as reactants. Subsequently, an Mg-doped p-GaN layer with a thickness of 120 nm was deposited on top of the last GaN QB at 950°C using a commercial nitride MOVPE system. For p-type doping of GaN, biscyclopentadienyl magnesium was employed.

Coaxial nanotube heterostructure LED microarrays were fabricated by making Ohmic contacts on both the p-GaN surface of the coaxial nanotube heterostructures and the heavily doped n-GaN seed layer. To fabricate metal contacts on the n-GaN seed layer, a Ti/Au (50/100 nm) layer was first evaporated onto an n-GaN layer. Next, in order to fill the gaps between individual nanotubes and isolate two different metal electrodes, a spin-on-glass (SOG)
layer was coated by the spin coating method and cured at 425 °C. For metal contacts on p-GaN, wet chemical etching of the SOG layer was performed in a buffered-oxide etchant to expose the tip surface of the nanotubes; then an Ni/Au (10/10 nm) layer was deposited on the exposed p-GaN surface by using electron-beam evaporation. It should be noted that the conformal coating of continuous contact layers allowed the occurrence of uniform current injection in the entire nanotubes surface.

The morphology and structural characteristics of GaN/ZnO coaxial nanotube heterostructures and GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structures were investigated using field-emission scanning-electron microscopy (FE-SEM; Philips XL30SFEG) and high-resolution transmission-electron microscopy (HR-TEM; FEI Tecnai G$^2$ F20). For TEM imaging and electron diffraction analysis of the GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structure, samples were milled cross-sectionally with 30 kV-accelerated Ga ions using a focused ion beam machine (NOVA 200 Nanolab, FEI Company) in the dual beam mode. The acceleration voltage of Ga ions was decreased from 30 to 5 kV at the finishing stage in order to reduce the damage of the sample and inevitable contamination with Ga ions. The compositional line profile of the GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structure along its radial direction was obtained from energy-dispersive x-ray spectroscopy (EDX) in the scanning-TEM (STEM) mode of the TEM facility.

CL measurements were performed to investigate the optical characteristics of nanotube heterostructures. A CL facility (Gatan MonoCL3+) attached to the SEM (Hitachi S-4300) was employed. CL images and spectra were measured at 80 K and room temperature using a 10-kV electron beam. The spectral resolution of the employed high-resolution CL measurement system was as accurate as ±8 meV. Details of the CL measurements are described elsewhere.[19]

3. Structural and optical characteristics of GaN/ZnO coaxial nanotube heterostructures

Figure 2 shows the FE-SEM images of position-controlled ZnO nanotube and GaN/ZnO nanotube heterostructure arrays, which reveal the general morphology of nanostructures after the procedures shown in figures 1(b) and (c), respectively. As depicted in figure 2(a), the ZnO nanotube dimensions were quite uniform, with a mean diameter of 400 ± 40 nm and a length
Figure 3. (a) HR-TEM image of a GaN/ZnO coaxial nanotube heterostructure at the GaN/ZnO layer interface, (b) the corresponding diffraction pattern obtained from an FFT and (c) its filtered inverse FFT image. (d) HR-TEM image of a GaN layer in the GaN/ZnO coaxial nanotube heterostructure.

of 4.0 ± 0.1 µm. A typical growth rate for the ZnO nanotubes was 2 µm h⁻¹. The diameters of the nanotubes, the distances between nanotubes and the area density of the arrays can easily be controlled by changing the geometric parameters of the hole-patterned SiO₂ growth-mask layer. The FE-SEM image of GaN/ZnO nanotube heterostructures in figure 2(b) indicates that, after the heteroepitaxial growth of a GaN layer for 30 min, the nanotube wall thickness increased from 15 to 200 nm, although the general morphology of a nanotube was not significantly changed. This increase in wall thickness indicates successful coating of a GaN layer onto the circumferential surface of ZnO nanotubes.

The microscopic crystal structure of GaN/ZnO coaxial nanotube heterostructures was investigated using HR-TEM. In figure 3(a), an HR-TEM image of a GaN/ZnO nanotube heterostructure coated for 1 min shows that the heterostructure consisted of an approximately 7-nm-thick GaN layer. The typical GaN growth rate on the ZnO nanotube side walls was therefore estimated to be ∼7 nm min⁻¹. The low growth rate makes it possible to accurately control GaN layer thickness with growth time.

Further investigation of possible defect formation in the nanotube heterostructures was carried out. Figure 3(b) shows the diffraction pattern of a GaN/ZnO coaxial nanotube heterostructure obtained through the fast Fourier transform (FFT) of the HR-TEM image in
The FFT of HR-TEM image is indexed as a [1\bar{2}10] zone axis of hexagonal wurzite ZnO and GaN, where the two diffraction spots that make a right angle correspond to the (0002) and (1010) planes shown in figure 3(b). This indicates that a single crystalline wurzite GaN layer was epitaxially coated onto the ZnO nanotube. In figure 3(c), the inverse FFT image of the diffraction pattern also confirms the defect-free single crystallinity of the nanotube heterostructure. Figure 3(d) displays an enlarged image of the selected GaN area from the HR-TEM image of a GaN/ZnO nanotube heterostructure in figure 3(a), indicating a highly ordered lattice structure of the outer GaN layer. From this image, the lattice spacing between adjacent planes was measured as \( \sim 0.26 \) nm, corresponding to the d-spacing of GaN(0001) planes.

The inset of figure 3(b) shows two peaks corresponding to the (10\bar{1}2) diffraction planes of ZnO and GaN, which are resolved through the difference in lattice constants along the radial direction. However, the (0002) reflection along the growth direction does not show peak splitting. These results indicate that strain exists at the GaN/ZnO interface, although the atomic configurations are not under any constraint in the radial direction. Similar behaviour was observed for GaN/ZnO coaxial nanorod heterostructures, where a GaN layer was coated on solid ZnO nanorods [29]. As reported for GaN/ZnO core–shell nanorods [29], stress due to the lattice mismatch in the axial direction may cause edge dislocations with a Burgers vector. Hence, interfaces of the hollow nanotube heterostructures were thoroughly investigated in the long length scale of several hundred nanometres from the HR-TEM images of several nanotube heterostructures. However, no structural defect was found. The different behaviour in the defect formation in nanorods and nanotube heterostructures is presumably attributed to the hollow structure of GaN/ZnO nanotube heterostructures. In comparison with a solid ZnO core nanorod in the nanorod heterostructures, nanotubes offer a larger circumference, so the strain induced at the interface should be reduced.

The optical characteristics of GaN/ZnO coaxial nanotube heterostructure arrays were individually investigated at high spatial resolution. Figure 4 shows the CL spectra of a single GaN/ZnO coaxial nanotube heterostructure. As shown in the inset of figure 4(a), the room temperature CL spectrum shows strong ultraviolet emission consisting of two distinct CL peaks at 3.28 and 3.39 eV that are attributed to near-band-edge (NBE) emissions from ZnO and GaN, respectively. Also, no deep-level green or yellow emission from either ZnO or GaN was observed in the room temperature CL spectrum, indicating the high optical quality of the GaN/ZnO coaxial nanotube heterostructures (figure 4(a)). Additionally, the CL spectrum measured at 80 K shown in figure 4(b) presents dominant CL peaks at 3.35 and 3.44 eV that are ascribed to excitonic emissions from the core ZnO nanotube and outer GaN layer, respectively. A further high-resolution CL spectrum measured in the range of 3.0–3.6 eV shows an additional CL emission at 3.21 eV with an energy difference of \( \sim 40 \) meV from the excitonic emission of ZnO, similar to the two-electron satellite (TES) separation energy for excitons in ZnO [19, 30].

The spatially resolved CL characteristics of individual GaN/ZnO coaxial nanotube heterostructure were investigated by measuring monochromatic CL images at room temperature. Figure 4(c) presents a SEM image showing surface morphology and figures 4(d) and (e) present monochromatic CL images measured at photon energies of 3.28 \pm 0.01 and 3.39 \pm 0.01 eV, corresponding to CL peak energies from the NBE emission of ZnO and GaN, respectively. These CL images show that NBE emission of GaN originated from the nanotube structure, which strongly suggests that the GaN layer was deposited mainly on the outer surface of the core ZnO nanotubes. It is also notable that the CL spectra measured in different tubes
did not show any peak shift within a spectral resolution of the CL measurement system, indicating that the optical characteristics of each GaN/ZnO nanotube heterostructure are almost uniform.

4. Structural and optical characteristics of GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structures

The catalyst-free MOVPE of nanostructures enables the control of both the composition and the layer thickness of nanotube heterostructures. As shown in figure 1(d), GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structures were deposited along the circumference of GaN/ZnO coaxial nanotube heterostructure arrays. The tilted-view SEM image in figure 5(a) shows the morphology of a hexagon-faceted GaN/In$_{0.24}$Ga$_{0.76}$N coaxial nanotube quantum structure array with a typical diameter of 1.0 ± 0.1 µm and a length of 4.0 ± 0.2 µm. Figure 5(b) presents the cross-sectional STEM image and the corresponding FFT image of a GaN/In$_{0.24}$Ga$_{0.76}$N coaxial nanotube quantum structure. The high magnification STEM image of figure 5(b) obviously reveals that MQW layers were radially coated on the GaN/ZnO nanotube heterostructures. Three bright lines corresponding to In$_{0.24}$Ga$_{0.76}$N QW layers were observed alternating with clearly discriminated GaN QB layers. The corresponding FFT image of the coaxial nanotube quantum structure reveals single crystallinity with six-fold rotational symmetry in the $\{10\bar{1}0\}$ plane (inset of figure 5(b)).

Further TEM analysis was carried out to confirm the indium composition in In$_x$Ga$_{1-x}$N MQWs and to investigate interfacial defects. The compositional line profile along the radial direction of the GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structure was obtained by
employing EDX in the TEM facility. Figure 5(b) shows the EDX line profiles of gallium and indium, from which the indium concentration in In$_x$Ga$_{1-x}$N QWs was estimated at $x = 0.24$ by averaging the integrated EDX profile within the QW thicknesses. Moreover, composition analysis by EDX confirmed the formation of three-period GaN/In$_x$Ga$_{1-x}$N MQW layers on the GaN/ZnO nanotube heterostructures. Figure 5(c) displays the enlarged image of selected area from the HR-TEM image of a GaN/In$_{0.24}$Ga$_{0.76}$N QW in figure 5(b). The interface between GaN and In$_{0.24}$Ga$_{0.76}$N is clearly visible, indicating the formation of an abrupt interface. Structural defects, such as dislocations at the interface, were rarely observed.

The optical characteristics of position-controlled GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structure arrays were individually investigated by measuring CL spectra. Figure 6 shows the CL spectra of a single GaN/In$_{0.24}$Ga$_{0.76}$N coaxial nanotube quantum structure measured at temperatures of 80 and 297 K. As shown in figure 6, four dominant CL peaks at 2.58, 3.0, 3.29 and 3.48 eV were observed at 80 K. Among them, the CL peak at 3.48 eV is ascribed to the neutral-donor-bound excitons from the core GaN layer. The broad CL emission peaks at 3.0 and 3.29 eV are attributed to band to acceptor and Mg-related donor–acceptor pair (DAP) transition from the outermost Mg-doped p-GaN layer, respectively [31]. The most dominant CL emission at 2.58 eV is assigned to GaN/In$_{0.24}$Ga$_{0.76}$N MQW emissions. At 297 K, three CL peaks were observed at 2.46, 2.9 and 3.41 eV. The CL peak at 3.41 eV is attributed to NBE emission of the core GaN layer. The very broad CL peak at 2.46 eV is ascribed to the band to acceptor emission of the outermost Mg-doped p-GaN layer. The most dominant CL peak centred at 2.46 eV is assigned to GaN/In$_{0.24}$Ga$_{0.76}$N MQW emissions, which appeared
Figure 6. CL spectra of an individual GaN/In$_x$Ga$_{1-x}$N coaxial nanotube quantum structure measured at room temperature and 80 K.

after the coaxial coating of GaN/In$_{0.24}$Ga$_{0.76}$N MQWs on GaN/ZnO nanotube heterostructures. The intensity of the 80 K CL emission at 2.58 eV decreased much more slowly while the CL peak at 3.48 eV decreased rapidly on increasing the temperature. This strongly suggests that the room temperature CL emission centred at 2.58 eV originated from GaN/In$_{0.24}$Ga$_{0.76}$N coaxial MQWs. It is also noted that the full-width at half-maximum (FWHM) value of the CL peak of 2.46 eV was estimated to be as broad as 0.24 eV, presumably due to the broad distributions in thickness of In$_{0.24}$Ga$_{0.76}$N QW layers deposited on the six sidewalls of the GaN/ZnO coaxial nanotubes.

5. Coaxial nanotube LED microarrays consist of GaN-based p–n homojunction heterostructures with GaN/In$_x$Ga$_{1-x}$N coaxial multiple QWs

The controlled formation of GaN/In$_x$Ga$_{1-x}$N MQWs onto position-controlled GaN/ZnO nanotube heterostructures enabled the fabrication of coaxial nanotube LED microarrays by coating of the outermost p-type GaN layer. Electrical characteristics of the nanotube LEDs were investigated by measuring current–voltage ($I$–$V$) characteristic curves on the LEDs. The $I$–$V$ curve shown in figure 7(a) clearly exhibited nonlinear and typical rectifying behaviour with a turn-on voltage of $\sim$3 V and a leakage current of $\sim$4 $\times$ 10$^{-4}$ mA at $-4$ V. Above the turn-on voltage, the current began to increase rapidly with bias voltage, resulting in an increase in light emission intensity. Figure 7(b) exhibits the electroluminescence (EL) spectra of nanotube LED microarrays measured at an applied current of 90 mA. The EL spectra clearly exhibited a dominant peak centred at $\sim$2.4 eV. Moreover, the EL emission of 2.4 eV is closely matched to the CL peak at $\sim$2.4 eV. Since we expected and designed the coaxial QW structures to observe green colour emission from MQW thickness and composition, the EL peak of $\sim$2.4 eV results from GaN/In$_{0.24}$Ga$_{0.76}$N MQWs. Figure 7(c) shows the microscopic magnified photographs of light emission from the coaxial nanotube LED microarrays at current levels of 40 and 120 mA. At zero applied current, no light emission was observed (not shown). Upon increasing the applied current, while most individual nanotube LEDs started to emit clear light, some individual LEDs did not emit light, presumably due to non-uniform distributions in the turn-on voltage of individual coaxial nanotube LEDs. At a high current level above 100 mA, most
nanotube LEDs emitted light. The EL colour was mostly green and partly blue, and the light emission was so strong that it was clearly observed with the naked eye even under normal room-illumination conditions. Although some local areas did not emit light, presumably due to failure of the contact layers, nearly the entire patterned area of nanotube LED microarrays clearly emitted light. The number of turned-on LEDs increased with increasing applied current, indicating that the turn-on voltages of individual LEDs were different from each other. The observed non-uniformities of the turn-on voltage and light intensity of individual nanotube LEDs presumably resulted from non-uniform light extraction, current injection through the metal contact layer, or both.

6. Summary and conclusions

Position-controlled GaN/ZnO coaxial nanotube heterostructures arrays were fabricated by the catalyst-free MOVPE method. HR-TEM analysis revealed that GaN/ZnO nanotube heterostructures were single crystalline without any significant formation of structural defects. Furthermore, the position-controlled nanotube heterostructures exhibited excellent CL characteristics. The high-quality heteroepitaxial GaN/ZnO nanotube heterostructures enabled greater tunability in the thickness and composition of the QW as well as GaN-based p–n homojunction diodes in the heterostructures, which will significantly enhance the versatility of the components for nanoscale electronics and photonics. This simple,
precise, well-controlled ‘bottom-up’ method for fabricating high-quality, position-controlled coaxial nanotube heterostructures provides a general and rational route of integrating vertical nanodevices for nanometre-scale electronics and optoelectronics.

Acknowledgments

This work was financially supported by the National Creative Research Initiative Project (R16-2004-004-01001-0) of the Korea Science and Engineering Foundations (KOSEF). The work by M Kim was supported by a KOSEF grant funded by the Korean Ministry of Engineering and Science Technology (MEST) (R0A-2007-000-10014-0). The work of S-RJ was supported by the IT R&D program of MKE/KEIT (2009-F-021-01).

References

[1] Sze S M 1981 Physics of Semiconductor Devices (New York: Wiley)
[2] Chang L L, Esaki L and Tsu R 1974 Resonant tunneling in semiconductor double barriers Appl. Phys. Lett. 24 593
[3] Dingle R, Wiegmann W and Henry C H 1974 Quantum states of confined carriers in very thin AlGaAs/GaAs/AlGaAs heterostructures Phys. Rev. Lett. 33 827
[4] Ayers J E 2007 Heteroepitaxy of Semiconductors: Theory, Growth, and Characterization (Boca Raton, FL: CRC Press)
[5] Chen Y and Washburn J 1996 Structural transition in large-lattice-mismatch heteroepitaxy Phys. Rev. Lett. 77 4046
[6] Lin M E, Fan Z F, Ma Z, Allen L H and Morkoc H 1994 Reactive ion etching of GaN using BCl₃ Appl. Phys. Lett. 64 887
[7] Lee C-H, Yoo Y J, Cho J, Kim Y-J, Jeon S-R, Baek J H and Yi G-C 2009 GaN/In₁₋ₓGaxN/GaN/ZnO nanoarchitecture light emitting diode microarrays Appl. Phys. Lett. 94 213101
[8] Duan X F, Huang Y, Cui Y, Wang J F and Lieber C M 2001 Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices Nature 409 66
[9] Kikuchi A, Kawai M, Tada M and Kishino K 2004 InGaN/GaN multiple quantum disk nanocolumn light-emitting diodes grown on (111)Si substrate Japan. J. Appl. Phys. 2 43 L1524
[10] Svensson C P T, Martensson T, Tragardh J, Larsson C, Rask M, Hessman D, Samuelson L and Ohlsson J 2008 Monolithic GaAs/InGaP nanowire light emitting diodes on silicon Nanotechnology 19 305201
[11] Morales A M and Lieber C M 1998 A laser ablation method for the synthesis of crystalline semiconductor nanowires Science 279 208
[12] Pan Z W, Dai Z R and Wang Z L 2001 Nanobelts of semiconductor oxides Science 291 1947
[13] Park W I, Kim D H, Jung S-W and Yi G-C 2002 Metalorganic vapor-phase epitaxial growth of vertically well-aligned ZnO nanorods Appl. Phys. Lett. 80 4232
[14] Goldberger J, He R R, Zhang Y F, Lee S W, Yan H Q, Choi H J and Yang P D 2003 Single-crystal gallium nitride nanotubes Nature 422 599
[15] Hong Y J, Jung H S, Yoo J, Kim Y-J, Lee C-H, Kim M and Yi G-C 2009 Shape-controlled nanoarchitectures using nanowalls Adv. Mater. 21 222
[16] Jensen L E, Björk M T, Jeppesen S, Persson A I, Ohlsson B J and Samuelson L 2004 Role of surface diffusion in chemical beam epitaxy of InAs nanowires Nano Lett. 4 1961
[17] Hong Y J, An S J, Jung H S, Lee C-H and Yi G-C 2007 Position-controlled selective growth of ZnO nanorods on Si substrates using facet-controlled GaN micropatterns Adv. Mater. 19 4416
[18] Noborisaka J, Motohisa J and Fukui T 2005 Catalyst-free growth of GaAs nanowires by selective-area metalorganic vapor-phase epitaxy Appl. Phys. Lett. 86 213102

New Journal of Physics 11 (2009) 125021 (http://www.njp.org/)
[19] Yoo J, Hong Y J, Jung H S, Kim Y-J, Lee C-H, Cho J, Doh Y-J, Dang L S, Park K H and Yi G-C 2009 Fabrication and optical characteristics of position-controlled ZnO Nanotubes and ZnO/Zn0.8Mg0.2O coaxial nanotube quantum structure arrays Adv. Funct. Mater. 19 1601
[20] Motohisa J, Takeda J, Inari M, Noborisaka J and Fukui T 2004 Growth of GaAs/AlGaAs hexagonal pillars on GaAs (111)B surfaces by selective-area MOVPE Physica E 23 298
[21] Hersee S D, Fairchild M, Rishinaramangalam A K, Ferdous M S, Zhang L, Varangis P M, Swartzentruber B S and Talin A A 2009 GaN nanowire light emitting diodes based on templated and scalable nanowire growth process Electron. Lett. 45 75-U24
[22] Yi G-C 2009 Nanophotonics and Nanofabrication ed M Ohtsu (Weinheim: Wiley-VCH) pp 105–46
[23] Mohan P, Motohisa J and Fukui T 2006 Realization of conductive InAs nanotubes based on lattice-mismatched InP/InAs core-shell nanowires Appl. Phys. Lett. 88 013110
[24] Hong Y J, Yoo J, Doh Y-J, Kang S H, Kong K-j, Kim M, Lee D R, Oh K H and Yi G-C 2009 Controlled epitaxial growth modes of ZnO nanostructures using different substrate crystal planes J. Mater. Chem. 19 941
[25] Klingshirn C 2007 ZnO: from basics towards applications Phys. Status Solidi b 244 3027
[26] Tsukazaki A et al 2005 Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO Nat. Mater. 4 42
[27] Lim J-H, Kang C-K, Kim K-K, Park I-K, Hwang D-K and Park S-J 2006 UV electroluminescence emission from ZnO light-emitting diodes grown by high-temperature radiofrequency sputtering Adv. Mater. 18 2720
[28] Nakamura S, Pearton S and Fasol G 2000 The Blue Laser Diode: The Complete Story (Berlin: Springer)
[29] An S J, Park W I, Yi G-C, Kim Y-J, Kang H-B and Kim M 2004 Heteroepitaxial fabrication and structural characterizations of ultraline GaN/ZnO coaxial nanorod heterostructures Appl. Phys. Lett. 84 3612
[30] Meyer B K et al 2004 Bound exciton and donor-acceptor pair recombinations in ZnO Phys. Status Solidi b 241 231
[31] Viswanath A K, Shin E J, Lee J I, Yu S, Kim D, Kim B, Choi Y and Hong C H 1998 Magnesium acceptor levels in GaN studied by photoluminescence J. Appl. Phys. 83 2272