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Group III-nitride radial heterojunction nanowire light emitters

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Heterojunction nanowires were fabricated via a vapor-liquid-solid growth mechanism in a metal organic chemical vapor deposition system. The structure consisted of a n-type GaN:Si core surrounding by a distinct p-type AlGaN:Mg shell. Transmission electron microscopy revealed that the nanowires were free of extended defects. Photoluminescence measured a strong UV emission peak. Additionally, sources of mid-gap transitions are linked to surface states on the nanowire surface.

Key words: III-nitride, Nanowire, Defect.

Introduction

The technological advancements made in conjunction with the societal impact of the semiconductor light emitting diode and laser diode can not be overstated. Beyond the early prototypes, incredible performance gains were made by precisely controlling the fabrication process at the nano-scale, *i.e.,* less than 200 nm, to enhance quantum confinement, control electromagnetic wave propagation, and, overall, boost device efficiency. Despite the nano-scale design, these devices are primarily integrated at the macro-scale systems level. Electrically driven nano-wire optoelectronics offer considerable potential for integration and interaction with nano-scale electronic devices in silicon CMOS technology or, potentially, an all-optical processor as well as other applications such as near field scanning optical microscopy. The vapor-liquid-solid (VLS) growth approach, presented in the article, allows lithographic arrangement of the catalyst for direct placement of single or multiple nanowires[1-4].

Experimental

In this study, III-nitride crystals were grown via a nickel nitrate seed on a-plane sapphire, 4H-SiC, Si (111) and Si (100) wafers. A nickel nitrate 0.05 M solution was either dripped or spun onto the substrate. The substrate was heated to approximately 60 °C to drive off excess water then loaded into a modified vertical impinging flow, metal organic chemical vapor deposition reactor. A 50-Torr (6670 Pa), N_2/H_2 mixed atmosphere was used during the ramp to the growth temperature. Trimethylgallium was flowed for 2 s prior to the onset of NH_3 flow to prevent nitridation of the nickel seeds. The core structures with a 20-nm width were deposited in a H_2 ambient at a temperature of 725 °C, a pressure of 50 Torr (6670 Pa) and a V/III ratio of 50. Nano-wires with larger width, *e.g.,* 80 nm, could be produced by increasing the growth temperature to 775 °C and increasing the V/III ratio to 80. The non-uniform thickness of the dispersed seed led to a distribution in the growth rate across the wafer. Nevertheless, beyond the initial stages of growth, an average growth rate of 50 nm/minute was constant for growth times of 0.5 to 90 minute. A radial (Al)GaN:Mg sheath was produced by increasing the growth conditions to a temperature of 850 °C and a V/III ratio of 500, resulting in a horizontal growth rate of 40 nm/minute. The p-n junctions were created by switching the dopant source between SiH_4 for n-type and bis (cyclopentadienyl)magnesium (Cp_2Mg) for p-type. The samples were cooled from the growth temperature in pure nitrogen ambient to avoid rapid decomposition in hydrogen and, in the case of the p-type samples, to activate the acceptor dopant (Mg).

Structural characterization was performed with a Panalytical X'pert X-ray diffraction (XRD) system as well as a LEO Field Emission Scanning Electron Microscope (SEM) and a FEI NOVA 200 Focused-Ion Beam(FIB) with energy dispersive X-ray (EDX) analysis was used to mill and analyze GaN:Si / (Al)GaN:Mg (core/sheath) radial nano-wires. A Ga-ion beam was used to characterize the cross-section of the AlGaN/GaN nanowires.

The photoluminescence system employed the 351.0 nm line (3.41 eV) of a Coherent Innova 90-5 argon ion laser directed into the microscope through an optical inlet, with an optical output of approximately 2.5 mW at the sample.

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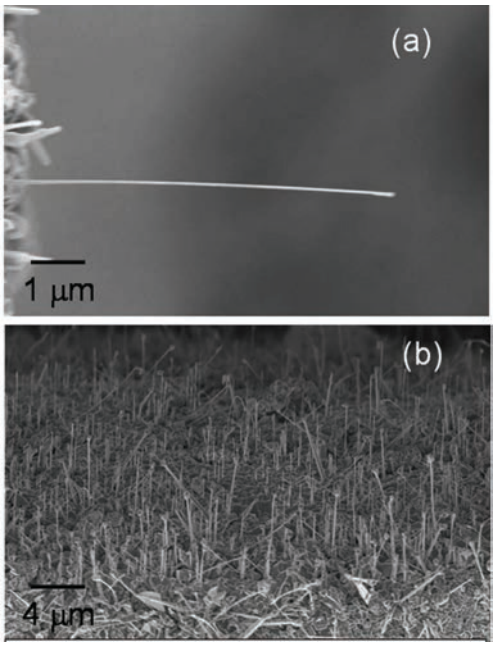

Fig. 1. Electron micrograph of (a) a 80-nm width, 10-um long GaN nano-wire and (b) 10-um long AlGaN:Mg (20-nm outer-width sheath) / GaN:Si (80 nm width core) nano-wires deposited on a Si substrate from a nickel seed. The sphere at the tip of the wires is the nickel seed, which provides verification of the VLS growth mechanism.

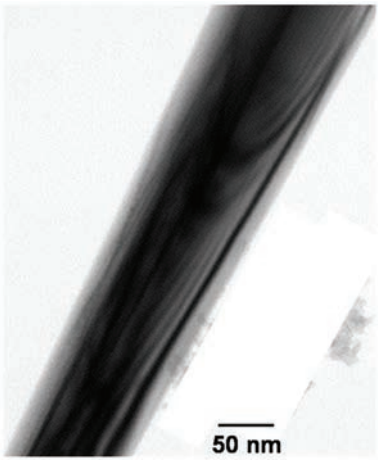

Fig. 2. Transmission electron micrograph of an AlGaN (shell) surrounding a GaN core nanowire. This bright field image reveals that the nanowire is free of threading dislocations as expected for the unconstrained VLS growth mode [7].

Results

We have produced various GaN:Si / (Al)GaN:Mg (core /sheath) radial nano-wires by metal organic chemical vapor deposition. The vertical (axial) and horizontal (radial) growth rates were controlled by controlling the growth temperature and reactant V/III ratio. Fig. 1 shows that wires maintain their 80 nm width over a 10-um length for a growth temperature of 775 ºC.

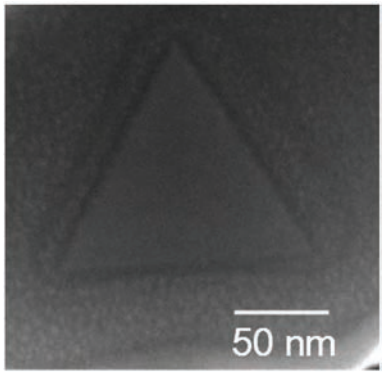

Fig. 3. Cross-sectional electron micrograph of an AlGaN/GaN nanowire. Focused ion beam milling was employed to cut across AlGaN/GaN nanowires. Pt was coated to protect the surface of AlGaN/GaN nanowires. The isosceles triangle cross-section is characteristic of unrestricted growth of a III-nitride crystal along the m-plane. The nanowire imaged down the [11-20] zone axis reveals that the nanowire has a triangular cross section that consists of a (0001) facet and two {-110-1} facets.

A radial core/sheath structure has been fabricated in a two-step process [5]. In VLS growth, the metal seed initially forms a solution with the GaN matrix. Beyond the eutectic point, the liquid metal seed phase segregates from the solid GaN matrix. Under proper growth conditions, this metal-catalyst perpetually enhances the growth rate perpendicular to the substrate, thus creating semiconductor wires with extremely high aspect ratios [6]. The inner core (80 nm width) was deposited at the growth conditions that encourage the VLS growth mechanism. Subsequently, an outer AlGaN:Mg sheath was deposited at growth conditions approaching that used for a thin film with a high horizontal growth rate. The width of the sheath was directly proportional to growth time indicating controlled lateral growth.

A low magnification transmission electron micrograph, in Fig. 2, provides an overview of an as-grown nanowire. This image showed that the wires are free of extended defects. Fig. 3 presents a cross-sectional view of a nanowire that was milled with a focused ion beam to expose the internal structure. A distinct AlGaN shell matched to the inner triangular GaN core is observable.

The photoluminescence (PL) spectra taken at room temperature in Fig. 4 provide a comparison of bulk GaN to AlGaN(sheath)/GaN(core) nano-wires deposited on various substrates. A number of radiative transitions are deconvoluted from the spectrum in Fig. 4(a). The band-edge of the GaN nano-was measured at 361.56 nm. Also, the mid-gap transitions, blue/violet and green transitions as well as the well-known GaN yellow band, are stronger in the nanowires than in the bulk sample.

Discussion

Although these mid-gap transitions are radiative, for practical applications they detract from the desired band

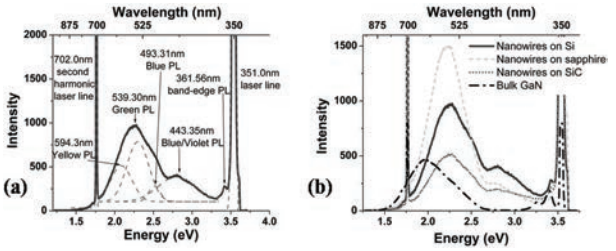

Fig. 4. (Color Online) Room temperature PL spectra of AlGaN: Mg (sheath) / GaN:Si (core) nano-wires grown from a nickel seed on (a) a Si(111) substrate and (b) Si(111), on-axis 4H-SiC and a-plane sapphire substrates with a comparison to bulk GaN. The spectrum in (a) is deconvoluted to show the multiple radiative transitions in the nano-wires.

-edge emission mechanism. Typically, the defects related to these luminescent transitions are engineered out of commercial thin film devices by optimization of growth parameters [8-10] However, as a fundamental study, the presence of these mid-gap states in nanowires gives an insight into the nature of the defects in III-nitrides.

The various defect bands in GaN are linked to Ga and N vacancies as well as intentional and unintentional oxygen impurities. In certain studies, a clear relation is observed, such as the work of Hautakangas, *et al.*, which showed that increasing levels of Mg acceptor doping in GaN create N vacancies that appear as V_N-Mg_{Ga} pairs and vacancy clusters [11]. This mechanism creates highly compensated material with a V_N-Mg_{Ga} pair luminescence transition that shifts deeper into the gap with increasing doping concentration.

Nevertheless, a luminescence study of a GaN thin film reveals a multitude of transitions that are challenging to assign [12]. These film-dependent studies are exacerbated by the natural interplay of bulk point and surface defects with extended dislocations in GaN. For example, Leung *et al.* [13]. calculated that vacancies tend to cluster near dislocations and Liliental-Weber *et al*. [14] used high resolution electron microscopy coupled with exit surface wave analysis to show that Mg and O impurities as well as N vacancies accumulate at structural defects in GaN. This link was further confirmed by Glaser *et al.* who used optically-detected magnetic resonance to show that Mg atoms in defective GaN were perturbed by in-plane strain and electric field distortion [15].

This is relevant as the characterization presented in Fig. 2 and, in general, the free-forming nature of VLS growth suggests that the nanowires can be described as a single grain that is free of extended dislocations and strain. Additionally, the Mg doping levels in these nanowires were not at a concentration to generate a significant amount of vacancies as suggested by Hautakangas, *et al.* [11].

A relatively new understanding of defect formation in semiconductors has been developed based on the Fermi stabilization level concept [16]. In essence, any damage to the semiconductor, including irradiation, severed bonds on a surface, dislocations, high doping levels, and implant damage, drives an equilibrium process to generate defects [17]. The Fermi level trends with increasing damage to the Fermi stabilization level at approximately 4.9 eV from the vacuum level[18]. This native defect system has a wave function independent of the semiconductor host [19]. In GaN, this Fermi stabilization level is predicted to exist near 2.4 eV [20].

The surface of a semiconductor intrinsically possesses severed bonds that reconstruct to minimize the free energy of the local system. A nanowire is particularly interesting since its properties are dominated by its surface due to its extremely large surface-to-volume ratio. For example, Simpkins *et al.* recently found that the surface states of a GaN nanowire create a depletion region that encompasses the conductive interior of the wire with an insulating shell [21]. In this study, Fig. 4 revealed a strong luminescence transition near 2.4 eV in the nanowires as predicted by the Fermi stabilization level theory. Similar surface-related luminescence at the Fermi stabilization level has also been observed in other wide bandgap nanowires including ZnO [22, 23].

Clearly, a GaN nanowire provides an interesting test-bed to study states generated at the surface of the semiconductor. Beyond, isolating the effects of defects on the surface, this approach allows a deeper understanding into the formation of defect-related complexes in GaN. For example, a III-nitride thin film often grows as a high density of aligned grains that are delineated by screw and edge dislocations from the particularly tilt and twist, respectively. The surface of the nanowire can simulate the atomic structure on a grain surface. Conceptually, a GaN grain prior to coalescence is structurally similar to a GaN nanowire.

Conclusion

Heterojunction pn III-nitride nanowires were grown and shown to display strong UV luminescence. Analysis of mid-gap emission suggests a band of surface states to which the Fermi level is pinned [24]: these states participate one of multiple complexes with vacancy-related defects in GaN [25].

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