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III-nitride core-shell nanowire arrayed solar cells

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Abstract

A solar cell based on a III-nitride hybrid nanowire-film architecture is demonstrated. It consists of a vertically-aligned array of InGa_N/Ga_N multi-quantum well core-shell nanowires, electrically connected by a coalesced p-type InGa_N canopy layer. This hybrid structure allows for standard planar device processing, solving an important challenge with nanowire device integration. It also enables various advantages such as higher indium composition InGa_N layers via elastic strain relief, efficient carrier collection through thin layers, and enhanced light trapping. This proof-of-concept nanowire-based device presents a path forward for high-efficiency III-nitride solar cells. Fabricated III-nitride nanowire solar cells exhibit a photoresponse out to 2.1 eV and short circuit current density of $\sim 1 \text{ mA/cm}^2$ (1 sun AM1.5G).

ACKNOWLEDGMENTS

CONTENTS

1. Introduction.....	7
2. Experimental Details.....	9
3. Results and Discussion	13
4. Conclusion	15
5. References.....	17
Distribution [can go on an even or an odd page]	20

FIGURES

Figure 1. Schematic illustrating (a) the steps to form the hybrid nanowire film solar cell, and (b) a cross-section of the final structure.....	9
Figure 2. Scanning electron microscope images showing (a) the nanowire template, (b) the nanowires after MQW growth, (c) the structure after p-InGaN canopy growth, and (d) the canopy layer from the top.....	10
Figure 3. STEM images of (a) a row of nanowires, (b) a single nanowire illustrating the MQW, and p-type GaN layers, and (c) a close up of the MQWs on different facets.....	11
Figure 4. A (a) top view of a simple solar cell, and (a) a schematic cross-section of the completed device.....	12
Figure 5. EQE of the III-nitride nanowire solar cell. Inset is a close-up at lower energies.....	13
Figure 6. JV characteristic under dark and 1 sun conditions.....	14

NOMENCLATURE

Å	angstroms
µm	micrometer
A	amps
Al	aluminum
AM1.5G	average solar spectrum on earth
Au	gold
cm	centimeters
DOE	Department of Energy
EDS	dispersive x-ray spectroscopy
EQE	external quantum efficiency
eV	electron volts
GaN	gallium nitride
ICP	inductively coupled plasma
InGaN	indium gallium nitride
In _x Ga _{1-x} N	indium gallium nitride
IQE	internal quantum efficiency
JV	current density versus voltage
J _{sc}	short circuit current density
LED	light-emitting diode
mA	milliamps
Mg	magnesium
MOCVD	metal-organic chemical vapor deposition
mm	millimeter
MQW	multiple quantum well
nm	nanometers
Ni	nickel
PCE	power conversion efficiency
PL	photoluminescence
SEM	scanning electron microscope
STEM	scanning transmission electron microscopy
Si	silicon
SNL	Sandia National Laboratories
x	indium composition

1. INTRODUCTION

III-nitride semiconductors are normally used in blue and green light-emitting diodes (LEDs) [1], but their unique properties also make them interesting for photovoltaics. These properties include the ability to tune the bandgap of InGaN across nearly the entire solar spectrum (0.7eV-3.4eV) [2], high absorption coefficient ($\sim 10^5 \text{cm}^{-1}$) [3], and high radiation resistance [4]. In theory these properties, could translate into solar cells with high efficiency, in thin layers, and with long lifetimes. Tuning the InGaN bandgap to lower energies has proven difficult, because traditionally InGaN is grown on GaN, and the lattice-mismatch strain limits the InGaN composition and layer thickness. Thin-films of $\text{In}_x\text{Ga}_{1-x}\text{N}$ can be grown over the entire compositional range with traditional growth methods, but InGaN with indium compositions $x > 0.1$ at a thickness $> 100 \text{ nm}$ are highly defective and are not useful for photovoltaic devices [5]. Therefore $\text{In}_x\text{Ga}_{1-x}\text{N}$ -based solar cells have been limited to indium compositions of $x \sim 0.1$ for layers 100-200 nm thick [6, 7]. Additionally, InGaN is formed at low growth temperatures to incorporate sufficient indium. This results in increased incorporation of impurities [8] or other point and V-defect related non-radiative recombination centers [9]. Instead of thick layers, multiple quantum well (MQW) absorption layers can be used, leading to increases the indium composition ($x \sim 0.25-0.3$) [10, 11], and higher internal quantum efficiencies ($> 70\%$) at high energies ($\sim 3\text{eV}$) [11]. These energies though are not near the optimum bandgap energies necessary for an efficient single gap solar cell in power conversion efficiencies (PCE) below 3% [10]. If InGaN materials are going to gain serious consideration for photovoltaics, a new approach is required.

One potential way to overcome lattice-mismatch strain limitations and achieve higher indium composition InGaN is to use nanowire structures. Nanowires come in many configurations but for photovoltaics core-shell (or radial) structures [12] consisting of GaN nanowire cores covered by InGaN shells layers [13, 14] are interesting. The high aspect ratio and the small diameter of the GaN nanowire core GaN allows for the InGaN shell to partially relax the epitaxial strain through purely elastic deformation of the nanowire; a relaxation mode not available via planar growth because of the absence of

lateral free surfaces within the continuous layer. Because of the elastic strain relief enabled by the nanowire geometry, $\text{In}_x\text{Ga}_{1-x}\text{N}$ shells grown on GaN cores have achieved higher indium compositions (up to $x \sim 0.4$) in thick shell layers with low defect densities [14]. Other benefits of the nanowire core-shell architecture are the decoupling of charge collection and light absorption [15], and the enhanced absorption occurring via nanophotonic light scattering [16, 17]. These benefits should help with the diffusion limited carriers and thickness limited InGaN layers in III-nitrides.

Nanowire arrayed solar cells constructed from other material systems have been demonstrated [18, 19]. For III-nitrides the only demonstration of a core-shell (coaxial) nanowire solar cell used a single nanowire [13]. Here, for the first time, a III-nitride nanowire solar cell consisting of a vertically aligned and integrated array of GaN-InGaN core-shell nanowires is shown. It employs a unique hybrid nanowire-film architecture. The nanowires are connected at the tops by a continuous p-InGaN “canopy” layer. This structure allows for standard device fabrication techniques while maintaining the benefits enabled by the nanowires. The embedded air void structure and a rough entrance surface also aids in light collection and absorption [16, 17]. The structure is created with standard growth and fabrication technologies that can be easily scaled to large areas. The III-nitride nanowire solar cell demonstrated here has a PCE of $\sim 0.3\%$, a photo-response out to 2.1 eV, and a short circuit current density (J_{sc}) of $\sim 1 \text{ mA/cm}^2$. Even though the performance of this device is modest, this nanowire architecture shows a potential path forward for higher efficiency III-nitride solar cells.

2. EXPERIMENTAL DETAILS

Figure 1 is a schematic representing the steps taken to form the hybrid nanowire-film solar cell structure. The core GaN nanowires are created by a “top-down” fabrication scheme. It uses a colloidal silica mask [20] and wet and dry etching steps to create a semi-periodic array with an average pitch of ~ 500 nm (left grouping in Fig. 1(a)) and ~ 900 nm height. The cylindrically shaped nanowires have straight micro-faceted sidewalls with preferred [20] *m*-plane exposed facets, and a top (0001) *c*-plane facet. Next radial growth of the InGa_N/Ga_N MQW absorbing shell layers (middle grouping of nanowires in Fig. 1(a)) is performed and the shell layers changes the nanowire morphology into *m*-plane hexagonally faceted sidewalls and new semi-polar facets at the nanowire tip and base. The last step is a p-type InGa_N “canopy” layer (right grouping of Fig. 1(a)) that initially grows on all facets of the nanowires, shown in the cross-section schematic in Fig 1(b), and then coalesces and grows only on the top. This forms a continuous film, and electrically connects the tops and sides of all the nanowires.

Construction of the nanowire template layer begins with growing a ~ 4 μm thick GaN layer on *c*-plane sapphire substrate by metal-organic chemical vapor deposition (MOCVD) using a two-step approach and a delayed-recovery technique [8]. This yields GaN with a threading dislocation density of $\sim 7 \times 10^8 \text{ cm}^{-2}$. This GaN layer is coated with a masking layer consisting of a hexagonally close-packed monolayer of self-assembled colloidal silica spheres formed in a Langmuir-Blodgett trough [21]. Next the sample is etched in an inductively coupled plasma (ICP) etcher using a Cl-based chemistry. This forms the semi-periodic array of vertically-aligned nanowires that are tapered with wider diameters at the base, have an average pitch of ~ 500 nm determined by the diameter of the colloidal silica spheres, and

Figure 1. Schematic illustrating (a) the steps to form the hybrid nanowire film solar cell, and (b) a cross-section of the final structure.

are uniform in height (~ 900 nm). The sample is then etched in an anisotropic KOH-based (AZ400K photoresist developer) wet etch that removes surface damage from the ICP etch [20] and forms ~ 100 nm diameter cylindrically shaped nanowires. A nanowire template made this way, but using a colloidal silica sphere diameter of ~ 1 μm , is shown in the scanning electron microscope (SEM) image in Fig 2(a). Planes perpendicular to the Ga polar (0001) top facet etch faster resulting in micro-faceted sidewalls with preferred *m*-plane exposed facets and a (0001) *c*-plane top facet. This fabrication technique [20] has several advantages including all the nanowires of the same height, the sidewalls have defined crystal facets, and dry etch damage is removed.

The sample is then returned to the MOCVD reactor and shell layers are grown starting with a ~ 80 nm thick n-type GaN layer. Then an absorbing shell layers consisting of a 15 nm thick $\text{In}_{0.015}\text{Ga}_{0.985}\text{N}$ layer and an eight period multiple quantum well (MQW) structure is grown. The MQW thicknesses depends on which facet they grow on but the targets were ~ 4 nm thick $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum wells, and ~ 10 nm thick Si-doped n-type GaN barriers. The MQW is capped with ~ 8 nm of undoped GaN. During shell layer growth the formation of new semi-polar facets occurs at the nanowire tip and base, resulting in the extinction of the top *c*-plane facet and creating nanowires with a pointed apex (shown in Fig. 2(b)). Growth is completed with a p-type $\text{In}_{0.015}\text{Ga}_{0.985}\text{N}$ “canopy” layer. This layer initially grows on all facets of the nanowires, and then coalesces and grows only on the top, to form a continuous film that electrically connects the tops and sides of all the nanowires.

Figure 2. Scanning electron microscope images showing (a) the nanowire template, (b) the nanowires after MQW growth, (c) the structure after p-InGaN canopy growth, and (d) the canopy layer from the top.

Figure 2(c) shows a cross-sectional SEM image of the completed structure. The p-type InGaN layer coalesces the structure, leaving embedded air voids between nanowires which enhance light scattering and absorption within the structure. A top view of the surface is shown in the SEM image of Fig. 2(d). It is off-white in appearance, consisting of a dense array of V-defects formed by the intersection of the top $\{10\bar{1}1\}$ facets of the nanowires after coalescence. This is typical of thick, lower temperature growth of III-nitrides [22]. The nanowire array has some short range hexagonal ordering and manifests in the regular hexagonal shaped features of the surface seen in some areas, most notably at the upper right in Fig. 2(d). The nanowires are centered below the apexes of the faceted surface.

Cross-sectional scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS) were also performed. The STEM sample was cross-sectioned so that the m -plane facets oriented perpendicular to the page in Fig. 3. The STEM images in Fig. 3(a) and (b) show the nanowires with a diameter of ~ 400 nm at a point halfway up the height of the nanowire, leaving ~ 100 nm spaces between nanowires. The shell growth tapers the nanowire. The MQWs grow on all of the exposed facets with growth on the m -plane facets faster than on the $\{10\bar{1}1\}$ facets. This is shown in the close-up image in Fig. 3(c). On the $\{10\bar{1}1\}$ facets the wells and barriers are each ~ 1.5 nm thick. The MQW thickness on the m -plane facets varies along the height of the tapered nanowire. The MQW also has non-uniform growth on the m -plane because the growth products differing along the height of the nanowire.

Figure 3. STEM images of (a) a row of nanowires, (b) a single nanowire illustrating the MQW, and p-type GaN layers, and (c) a close up of the MQWs on different facets.

This creates faster growth at the top of the nanowire sidewalls compared to the bottom. At the top the well and barrier thicknesses are $\sim 2.5\text{nm}$ and $\sim 9\text{nm}$ respectively. At the bottom of the MQW is thinner, and the innermost wells and barriers are thicker than the outermost wells and barriers. The innermost well and barrier is $\sim 2.5\text{ nm}$ and $\sim 5.5\text{ nm}$ thick respectively while the outermost well and barrier is $\sim 1.8\text{nm}$ and $\sim 3\text{nm}$ thick respectively. This change in MQW thickness is due to reduced transport of gas phase reactants as the opening between nanowires is pinched off during growth. EDS reveals the indium incorporation in quantum wells is also different on the sidewall and $\{10\text{-}11\}$ facets with $x \sim 0.33 (\pm 5\%)$ on the m -planes compared to $x \sim 0.22 (\pm 5\%)$ on the $\{10\text{-}11\}$ planes. The difference in indium composition on the two different planes has also been observed in planar material [25]. Lastly, the p-type InGaN layer extends down along the nanowire sidewalls, allowing for the capture carriers generated by light absorption in the m -plane MQWs.

The wafer is processed into simple solar cells and tested. Fig. 4 shows a top-view image (a) and a cross-sectional schematic (b) of the completed device. A Ni/Au ($150\text{\AA}/150\text{\AA}$) contact patterned on the p-

Figure 4. A (a) top view of a simple solar cell, and (a) a schematic cross-section of the completed device.

type layer, with contact pattern defining a uncovered 0.25 mm diameter circular aperture to collect light. The contact is annealed and then covered with an identically patterned Al to facilitate electrical probing. The outermost periphery the device is ICP etched down to the n-type GaN layer and an Al n-type contact is made. The devices are tested by probing in wafer form on top of an Al reflector. The external quantum efficiency (EQE) is measured by shining monochromatic light on the device scanned versus wavelength and measuring J_{sc} . The PCE of the device is measured under 1 sun of AM1.5G solar spectrum and dark conditions while measuring the current density versus voltage (JV) characteristic.

3. RESULTS AND DISCUSSION

Figure 5 shows the measured EQE of the III-nitride nanowire solar cell. The EQE has a peak of ~23% at ~3eV, and as the energy decreases the EQE also decreases down to the lowest energies at 2.1eV. This gradual decrease with decreased energy is also observed in the absorption (data not shown). The low-energy absorption tail extends out to very small energies for III-nitrides. This is observed not only in our MQW nanowire shells but also in other planar MQW solar cells [11], showing it is primarily a signature of the MQW structure and not the nanowire device architecture. In MQW-based solar cell devices, both planar and nanowire-based, carrier collection should become more difficult as the carriers are created deeper in the quantum wells. These deep carriers require additional energy to escape over the barriers and contribute to the current, contributing to the decrease in EQE with decreased energy. The energy where the measured EQE (photo-response) of the solar cell begins to significantly rise is ~2.1eV (Fig.5 inset), indicating the device's spectral absorption extends out to 2.1 eV. The combined EQE results are evidence of the smallest bandgap demonstrated in any III-nitride solar cell to date. This bandgap energy is consistent with the $x \sim 0.33$ indium composition measured for the *m*-plane quantum wells, while it is much too low for the $x \sim 0.22$ semipolar facets, suggesting that current generated in the *m*-plane MQWs is the most likely cause of the lowest energy photoresponse. While the observed EQE is promising, further work is required to improve the EQE in these nanowire MQW structures.

Figure 6 shows the JV characteristic under dark and 1 sun conditions. At 1 sun the J_{sc} is $\sim 1 \text{ mA/cm}^2$, the fill factor is $\sim 54 \%$, and the open circuit voltage is $\sim 0.5 \text{ V}$. The resulting PCE is modest ($\sim 0.3\%$), but it does represent the highest recorded in a III-nitride nanowire solar cell. The open circuit voltage is lower

Figure 5. EQE of the III-nitride nanowire solar cell. Inset is a close-up at lower energies.

given the fairly high bandgap (2.1eV). This is a result of electrical shorting in some areas of the device. It is most likely due to two different occurrences. The first potential problem is p-InGaN growth occurring on pattern defect areas with no nanowires. In the absence of nanowires, planar growth occurs resulting in highly defective InGaN layers containing a high concentration of indium metal, providing a shorting path when contacted by the subsequent p-type InGaN growth. The p-type InGaN layer fails to form a canopy and slumps onto the planar, defective InGaN domains. The second occurrence is incomplete coalescence of the p-type InGaN canopy layer in a few areas that are observed in SEM analysis. These areas allow the p-contact metal layers to directly contact the n-type layers creating an electrical short.

Figure 6. JV characteristic under dark and 1 sun conditions.

4. CONCLUSION

For the first time solar cells consisting of a vertically integrated array of core-shell III-nitride nanowires are demonstrated. The novel hybrid nanowire-film structure is created by radial growth on an n-type array of GaN nanowires formed by simple wet and dry etching. The p-type InGaN canopy layer electrically connects the nanowires and allows for simple fabrication techniques. The nanowire structure has benefits such as higher indium composition InGaN layers and more efficient carrier collection and enhanced light trapping. The solar cell exhibits a photoresponse out to 2.1 eV, the lowest bandgap of any III-nitride solar cell so far, and the power conversion efficiency is the highest recorded for a III-nitride nanowire solar cell.

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