Study of Charge Transport in Vertically-Aligned Nitride Nanowire Based Core Shell P-I-N Junctions

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July 2016

Grant HDTRA1-14-1-0003

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Study of Charge Transport in Vertically-Aligned Nitride Nanowire Based Core Shell P-I-N Junctions

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We investigated charge transport in large-area arrays of vertically-aligned, gallium nitride (GaN) based core-shell p-i-n (PIN) diodes. The proposed design can potentially produce photodetectors with efficiencies comparable to or better than traditional photomultiplier tubes (PMTs) with significant reduction in Size, Weight, and Power (SWAP). Our approach combines the precision and scalability of top-down processing with the enhanced material quality obtained through selective epitaxy to realize these structures. Vertically-aligned, radial core-shell architecture allows for significant defect reduction, strain engineering, polarity controlled growth, and transformative new device designs.

Gallium Nitride, pin diodes, avalanche diode, radiation detectors
# UNIT CONVERSION TABLE

U.S. customary units to and from international units of measurement

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<th>U.S. Customary Units</th>
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<th>Divide by†</th>
<th>International Units</th>
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<tr>
<td><strong>Length/Area/Volume</strong></td>
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<td></td>
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<tr>
<td>inch (in)</td>
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<td>meter (m)</td>
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<td>meter (m)</td>
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<td>yard (yd)</td>
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<td>meter (m)</td>
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<td>mile (mi, international)</td>
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<td>erg</td>
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<td>pascal (Pa)</td>
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<td>pound force per square inch (psi)</td>
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<td>degree Celsius (°C)</td>
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<td>kelvin (K)</td>
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<td>curie (Ci) [activity of radionuclides]</td>
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<td>per second (s$^{-1}$) [becquerel (Bq)]</td>
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<td>roentgen (R) [air exposure]</td>
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<td>coulomb per kilogram (C kg$^{-1}$)</td>
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<td>rad [absorbed dose]</td>
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<td>joule per kilogram (J kg$^{-1}$) [gray (Gy)]</td>
</tr>
<tr>
<td>rem [equivalent and effective dose]</td>
<td>1 $\times 10^{-2}$</td>
<td></td>
<td>joule per kilogram (J kg$^{-1}$) [sievert (Sv)]</td>
</tr>
</tbody>
</table>

*Specific details regarding the implementation of SI units may be viewed at [http://www.bipm.org/en/si/](http://www.bipm.org/en/si/).
†Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.
Final Report

Study of Charge Transport in Vertically-Aligned Nitride Nanowire Based Core Shell P-I-N Junctions

Grant Number: HDTRA1-14-1-0003

Principal Investigator:
Abhishek Motayed
University of Maryland

DISTRIBUTION A: Public Release
Study of Charge Transport in Vertically-Aligned Nitride Nanowire Based Core-Shell PIN Diodes

I. ABSTRACT.

We have studied charge transport and developed high-efficiency, solid-state photodetectors using large-area arrays of vertically-aligned, gallium nitride (GaN) based core-shell p-i-n (PIN) diodes. The proposed design can potentially produce photodetectors with efficiencies comparable to or better than traditional photomultiplier tubes (PMTs) with significant reduction in Size, Weight, and Power (SWAP). Current C-WMD operational capability is severely limited when utilizing PMTs, given their fragility and performance instabilities when exposed to external stimuli such as vibration, E- or B-fields and high photon fluxes. Nanoengineered nitride-based PIN diodes can completely circumvent these issues and bring to bear an unprecedented level of ruggedness and performance. Through this Fundamental Research program we will demonstrate a pathway to C-WMD detectors with high gain (M ≥ 50,000), low excess noise factor (F<5) and large areas (arrays with 1-10 mm² pixel size), which are insensitive to a battery of external stimuli.

The nitride material system, with tunable direct bandgaps (200 nm for AlN to ~1 μm for InN) and robust material properties, is ideally suited for the development of visible-blind UV photodetectors needed for the next-generation of scintillators in field-deployed radiation detectors. Traditional GaN based thin-film photodetectors suffer from strain, defects, and detrimental polarization effects resulting from heteroepitaxial growth of thin layers on non-native substrates. Although bottom-up growth methods (e.g. catalyst-based nanowire growth) have shown significant promise in terms of realizing defect-free structures, they face insurmountable challenges in scaling up and reproducibility necessary for large-area applications. Our approach combines the precision and scalability of top-down processing with the enhanced material quality obtained through selective epitaxy to realize these structures. Vertically-aligned, radial core-shell architecture allows for significant defect reduction, strain engineering, polarity controlled growth, and transformative new device designs - otherwise not possible in traditional thin-film structures. This project successfully combines University of Maryland team’s unmatched experience in nitride device design and fabrication with Northrop Grumman’s expertise in nitride materials growth and radiological/nuclear detection systems, and National Institute of Standards and Technology’s exceptional nanofabrication and characterization capabilities.

II. SCOPE.

The proposed research aims to investigate novel vertically-aligned nitride core-shell devices as highly-viable replacements for current PMT technologies, with detection efficiency, responsivity, and noise comparable to state-of-the-art PMT-based detectors. The specific objectives include: 1) design and simulation of core-shell structures for realistic estimation of performance metrics achievable from such structures and further refinement of the design, 2) development of growth expertise for control of defects, dopants, and morphology in both thin films and overgrowths with an aim to improve material quality, and 3) fabrication of device structures and their extensive characterization. The emphasis of all the objectives is to investigate the feasibility of operating these structures in the impact ionization field regimes, which would produce avalanche multiplication, hence current gains required for sensitive photodetection. The challenges of operating nitride-based photodetectors at breakdown biases are two folds: materials
and device-related. Both of which, we believe could be resolved by our innovative vertically-aligned core-shell p-i-n structures.

A. OBJECTIVE.
The proposed research will be focused on the demonstration of a working photodetector chip containing integrated arrays of individual core-shell PIN diodes. At the end of this program we will have demonstrated a working nanoengineered nitride-based avalanche photodiode and we will have fully characterized the device level performance of this novel structure. A natural byproduct of this development is evaluating the extent to which such photodetectors can be utilized in C-WMD applications. Significant efforts will be dedicated towards device design, materials development, development and optimization of the fabrication processes, and collection of operational parameters (dark current, quantum efficiency, responsivity, noise power, breakdown voltage) of fabricated devices. We will also consider lab-bench level integration strategies and peripheral interface electronics for future system-level integration.

Our efforts will include:

1) Developing 2-D and 3-D advanced device modeling efforts using industry-standard, high performance device simulator from Silvaco™, allowing for designing high-efficiency devices
2) Developing a strong nitride epitaxial growth program partnering with Northrop Grumman-Electronic Systems, required for the proposed novel device design
3) Wafer-scale nano-patterning with (a) control over shape and morphology, (b) defect free smooth surface of the etched side-walls and base plane, (c) ability to tailor profiles for specific designs, and (d) large-area uniformity and scalability
4) Controlled overgrowth for device structure development with dopant control
5) Complete device fabrication with various process optimization for enhanced detector performance
6) Studying the photodetector performance and reliability (parametric variations and high electric-field induced damage) in design-variants through extensive characterization

The following sections describe the approach and results obtained.
Approach for Efficient Solid State Photon Counting in Near-UV

- GaN (n-type) films will be etched to create "nanopillar" arrays
- The pillar arrays will then undergo two overgrowth stages: i-GaN and p-GaN, in sequence
- This structure—a radial/core-shell PIN junction—could be capable of increased efficiency photodetection
  - Active area will be directly exposed to incident photons—will not have problems with absorption outside the depletion region
- The structure will also provide insight into fundamental charge carrier generation and collection mechanisms in the nitride system
  - Impact of various classes of defects will be apparent
- Coupled to a $^{3}$He scintillator, this structure could be the next generation radiation detection system

SOA: Need Vertical P-N Diode Geometry to Increase Detector Efficiency

Conventional GaN PN Junction
- Losses due to absorption in the p-layer
- Defect density $\sim 10^{10}$ cm$^{-3}$
- Internal E-field due to lattice polarity—juncture exists on polar [0001] plane

Vertical PN Junction Geometry
- Depletion region directly exposed to photons—no p-GaN absorption
- Defect density $< 10^{6}$ cm$^{-3}$
- No internal E-field—juncture exists on non-polar [1100] or [1120] plane
Epitaxial GaN on Si Forms the Basis for Nanopillar PIN Junctions

- **Goal:** Grow high quality, thick (>1 μm) GaN on Si
  - Requires an AlN/AlGaN buffer layer to compensate for lattice mismatch between Si and GaN
  - Buffer layer will negatively impact device performance by changing the amount of active area available in the PIN junction
  - Need to balance material quality (requires large buffer) and device performance (requires smaller buffer)

- **Approach:** Incrementally reduce buffer thickness and measure effect on quality
  - XRD (GaN rocking curve)
  - PL (Band edge intensity, FWHM, defect emission)
  - Electrical (mobility, carrier density, sheet resistance)

**Ultimate Goal:** High Quality GaN Nanopillars

Need Thin Buffer Between Si and GaN Template for Electrical Conductivity

![Diagram of GaN, AlGaN, Si layers with buffer layers and dislocations](image)

- XRD rocking curve shows changes in FWHM with buffer thickness
- FWHM for 1.5 μm films significantly lower than 0.75 μm films
  - More relaxed films
- Band edge position in PL shows very slight red shift with decreasing buffer thickness
- Most PL data do not indicate significant differences with changes in buffer thickness

**High Quality GaN on Si Optimized for Nanopillar Fabrication**
Mask Design Enables Control of GaN Pillar Morphology and NanoAPD Array Properties

- 1st Mask is an array of shapes (7 total)
  - Various diameters (10-0.25\(\mu\)m) and densities (20x20\(\mu\)m to 0.5x0.5\(\mu\)m)
  - Will determine the effect of pillar shape on optical/electrical properties, e.g. charge carrier mobility and collection
  - Varying array densities will allow for optimization of overgrowth process

- Metal chosen as hard mask for RIE processing

- DUV stepper + liftoff to achieve shape arrays

Photolithography Optimization Enables Sub-Micron Array Fidelity

- Some features not present in most cases
  - Features <250nm, with the exception of squares

- Small features found in other locations on the substrate
  - Poor adhesion

- Approach to solve problem with small features:
  - Add Ti adhesion layer
  - Optimize exposure, development and liftoff

*Rounding apparent for smaller features*
Second Mask Design for Very Large NanoAPD Arrays

Dry Etching Process Development Needed for Fabrication of GaN Nanopillars

- Reactive Ion Etching
  - Gas: combination of Cl₂, BCl₃, N₂
  - Pressure: 2-10mTorr
  - ICP Power: 800W
  - RIE Power: 20-90

- Initial Etch Recipe
  - Low power, high pressure, Cl₂/BCl₃
  - Poor sidewall angle: 65-70°
  - Low etch rate and low Al/Ga selectivity

- Modified Recipe
  - High power, low pressure, incorporation of N₂ in process gas
  - Good sidewall angle: >80°
  - Higher etch rate, better Al/Ga selectivity
  - Roughness diminished somewhat

High Power + Incorporation of N₂ Drastically Decreases Sidewall Angle
Optical Emission Spectroscopy (OES): Analysis of Plasma Chemistry for End Point Detection

- Excitation of gaseous species in the plasma facilitates light emission
- Peaks are characteristic of specific atoms and molecules
- Analysis can indicate which species are present and active
- Great for end point detection

OES Analysis as a Function of Time

OES Provides Key Insights into GaN Etching Process vs. Time
MOCVD-Based Shell Growth Shows Promise for n-type and i-type GaN

Benefits of MOCVD Growth

- Atomically smooth surfaces
- Reduced growth rate engenders superior junction thickness control
- Reduced impurity incorporation
- Shell sidewall polarity can be controlled using growth parameters

Future Development

- Develop dopant incorporation control for n-type and insulating GaN
- Calibrate growth parameters for shell thickness and sidewall polarity

Nanoscale GaN Templates Enable Exclusive Crystal Quality

Initial Nucleation and Growth

- Nucleation initiates at multiple points on GaN template
- Most stable nuclei grow rapidly, consume smaller nuclei

Final Morphology

- Shells formed from single grain
- Extremely high quality, smooth surface

- Many grains grow simultaneously
- Large grains merge with significant misregistry, defects
- Rough surfaces

Conventional Feature Sizes Incapable of Producing Necessary Quality
Photoluminescence Studies Show Superior Quality of MOCVD GaN Shells

![Graph showing comparison of signal (mV) vs. wavelength (nm)]

**Peak Ratios: Band Edge/Yellow Defect Emission**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Intensity (cps)</th>
<th>FWHM (°)</th>
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<tbody>
<tr>
<td>As Grown Epi</td>
<td>44.7</td>
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<tr>
<td>i-GaN/n-GaN Shell Growth</td>
<td>129.8</td>
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X-Ray Diffraction Also Shows Significant Improvement Over Original Epi Quality

![Graph showing comparison of intensity (cps) vs. omega (deg)]
Large Area, High Resolution PL Maps Allow In-Depth Growth Uniformity Analysis

GaN Nanopillar Arrays Grown on 100mm Substrates

PL Maps of Full Size 100mm Wafers at 100μm Resolution

*Snapshot of central 20mm

Single Scans Comprise Maps

Wafer-scale Statistics

MOCVD GaN Shell Growth Enables Controlled Morphology Over Large Area
Program Summary

- NanoAPD structure represents a viable solution for current RN detection needs

- Novel GaN Core-Shell diode approach capable of improving collection efficiency by orders of magnitude

- NGES GaN epitaxial design and growth enabled significant improvement in material quality

- Large area GaN shell growth demonstrated via MOCVD

- Further improvements in quality and uniformity will enable unprecedented detector performance
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