Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Monolithically Integrated Thin-Film/Silicon Tandem Photoelectrodes for High Efficiency and Stable PEC Water Splitting

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Project ID # PD163

NREL | BERKELEY LAB | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

Project Overview

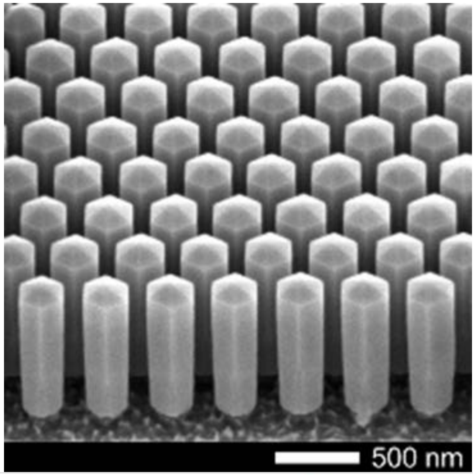
Award #	EE0008086
Start Date Yr 1 End Date Project End Date	10/01/2017 09/30/2018 TBD
Total DOE Share Total Cost Share Year 1 DOE Funding*	$1,000,000 $292,401 $250,000

Project Partners

Zetian Mi, University of Michigan, Ann Arbor
Thomas Hamann, Michigan State University
Dunwei Wang, Boston College
Yanfa Yan, University of Toledo

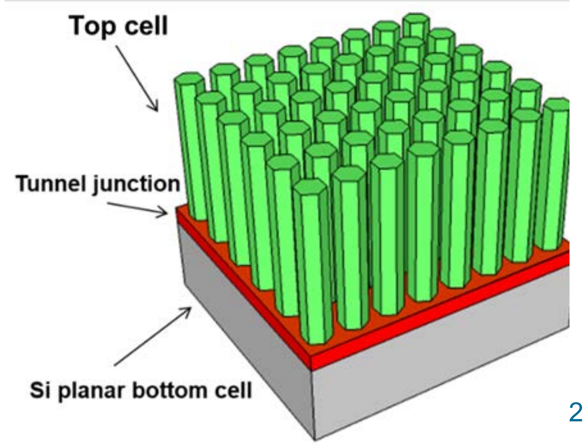
Project Vision

We propose to develop monolithically integrated tandem photoelectrodes on low cost, large area Si wafer to achieve both high efficiency (>15%) and stable (>1,000 hrs) water splitting systems.



Project Impact

Success of the project will help meet the DOE 2020 target (20% solar-to-hydrogen efficiency and $5.70 per kg H_2) and pave the way for widespread commercialization of solar hydrogen production technologies.



** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach- Summary

Project motivation

We aim to tackle the challenges of achieving efficient, cost-effective PEC water splitting devices by developing tandem photoelectrodes, which consist of a bottom Si light absorber and a 1.7-2 eV top light absorber (Ta_3N_5, BCTSSe, or InGaN). We have previously developed:

- ***Ta_3N_5, BCTSSe, or InGaN top photoelectrodes.***
- ***Low resistivity nanowire tunnel junction, which will be used to fabricate top photoelectrode.***
- ***N-terminated GaN, which can protect against photocorrosion and oxidation.***

Barriers

- **Materials Durability – Bulk and Interface:** Identify intrinsically durable and efficient materials for PEC H_2 generation.
- **Integrated Device Configurations:** Develop efficient and stable integrated devices to meet the ultimate targets in PEC H_2 generation.
- **Synthesis and Manufacturing:** Scalable manufacturing of PEC materials and devices.

Key Impact

Metric	State of the Art	Expected Advance
Stability/ Efficiency	*~1 hr @ 16%*	*>1,000 hrs @15%*
Cost/ scalability	*~$150 for 4" GaAs wafers*	*~$100 for 12" Si wafers, i.e. ~10 times reduction in wafer cost*

Partnerships

Co-PIs

- **Dunwei Wang, Boston College:** Cocatalyst deposition, surface protection
- **Thomas Hamann, Michigan State Univ.:** Ta_3N_5, PEC characterization
- **Yanfa Yan, Univ. Toledo:** Sputtering deposition and characterization of BCTSSe

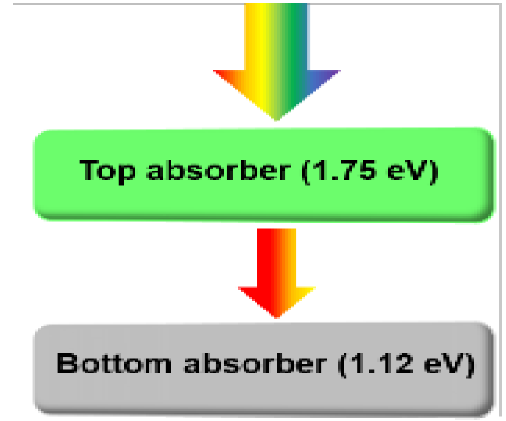
HydroGEN nodes

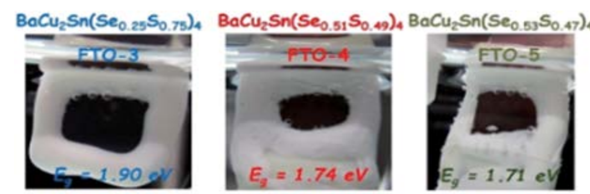
- **Glenn Teeter, NREL:** Surface analysis cluster tool, surface measurements
- **Francesca Toma, LBNL:** Photoelectrochemical AFM and STM
- **Tadashi Ogitsu, LLNL:** Ab initio modeling of electrochemical interfaces
- **Todd Deutsch, NREL:** Surface modifications and protection

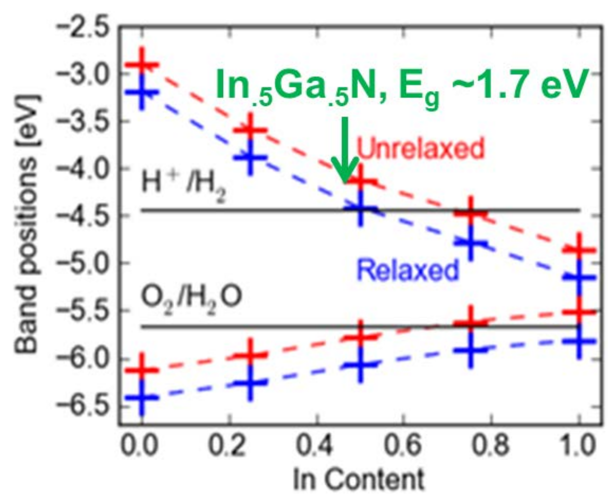
Adv. Ener. Mater., 7, 1600952, 2017. *Adv. Mater.* 28, 8388, 2016. *Nano Lett.*, 15, 2721, 2016.

Approach- Innovation

- The use of Si as the bottom light absorber to reduce the cost of tandem water splitting devices.
- The use of recently developed low cost Ta_3N_5, BCTSSe, and $In_{0.5}Ga_{0.5}N$ photoelectrodes as the top light absorber.
  - Direct bandgap ~1.7-2.0 eV.
  - Controlled n or p-type doping.
  - Straddle water splitting potentials.
- Si and GaN are the two most produced semiconductors in the world.
  - Scalable, low cost manufacturing.



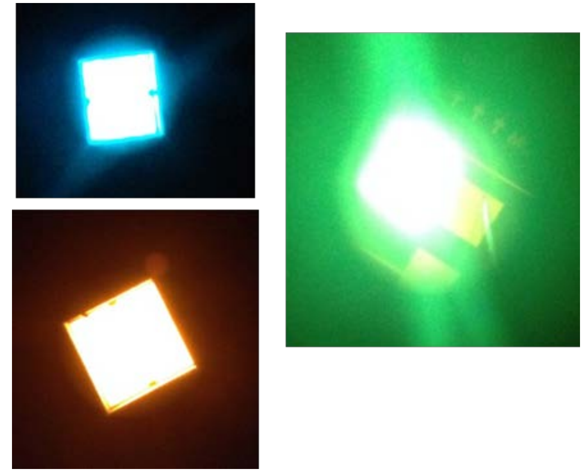




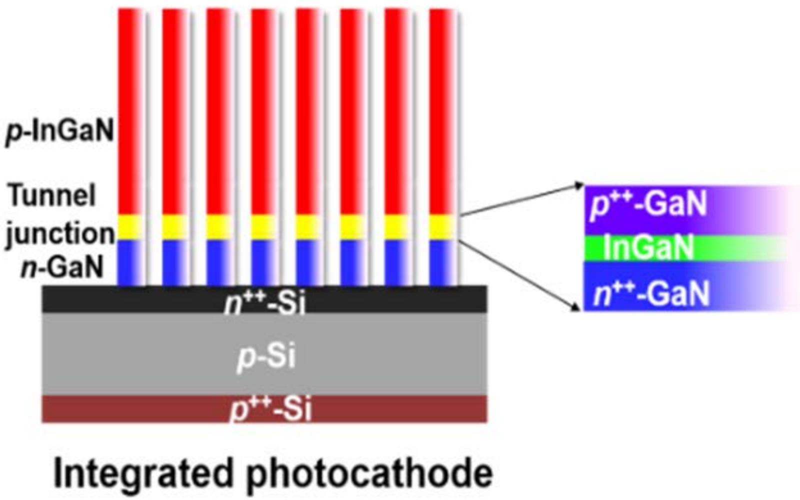
Appl. Phys. Lett. 96, 021908 2010.

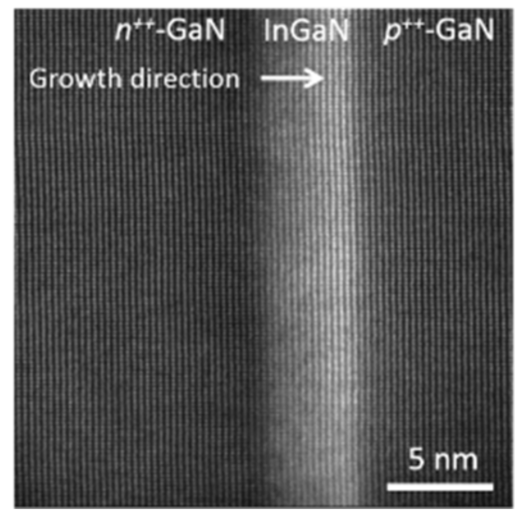
Approach- Innovation

- **The use of wide bandgap GaN nanowire tunnel junction to fabricate top photoelectrodes on Si.**
  - **Low resistivity, and reduced photovoltage loss.**
  - **Reduced defect formation due to the efficient surface stress relaxation.**



High performance LEDs and lasers have been demonstrated using such tunnel junctions by us recently.



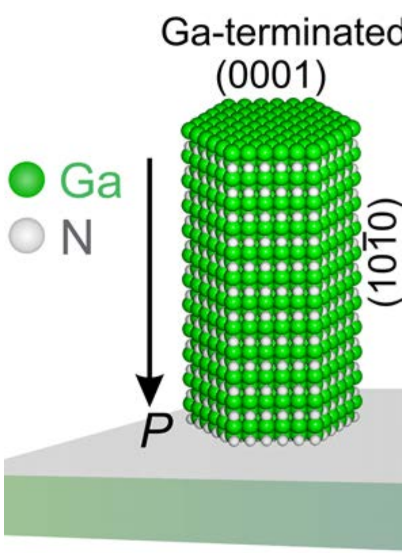


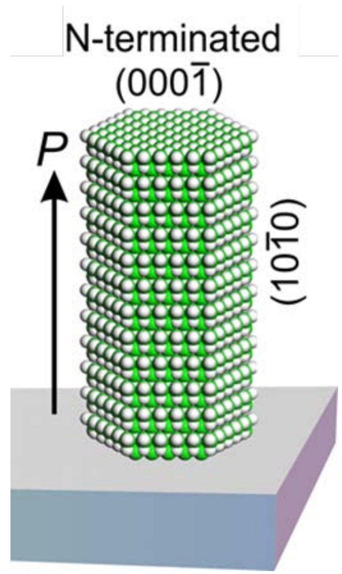
Resistivity of the p^{++}GaN/n^{++}GaN tunnel junction is significantly reduced by incorporating a thin InGaN quantum well through polarization engineering.

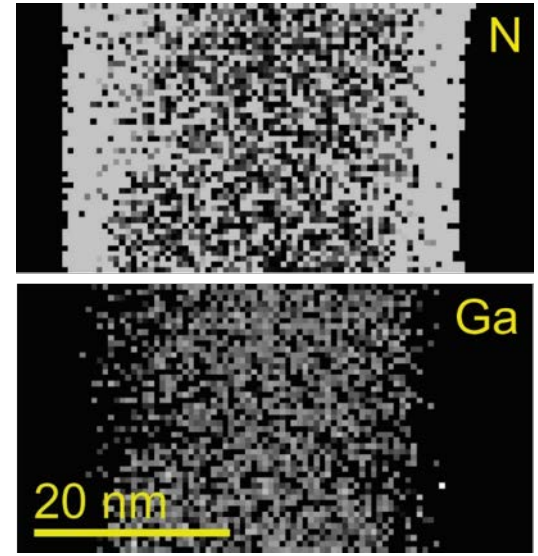
Adv. Ener. Mater., 7, 1600952, 2017. *Nano Lett.*,15, 2721, 2016.

Approach- Innovation

- **Surface protection by N-terminated GaN surfaces**







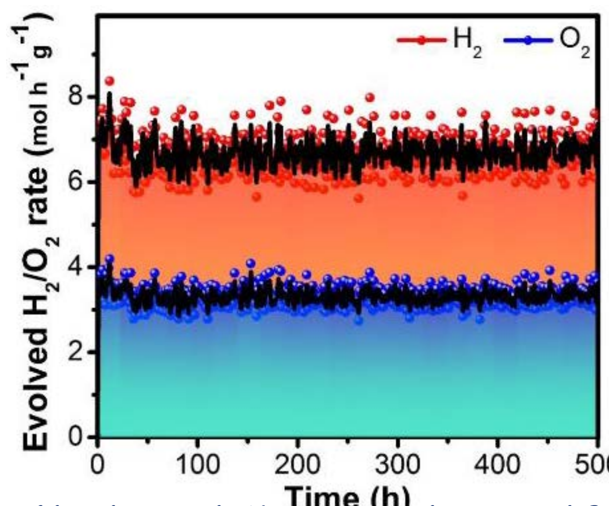
STEM studies reveal N-rich surfaces for MBE grown GaN nanowires.

Conventional GaN grown by CVD has Ga polarity.

- **Unstable in water splitting.**
- **Difficult to extract holes since polarization field points to the substrate.**

GaN nanostructures grown by MBE have N-termination.

- **Stable in water splitting**
- **Efficient hole extraction. since polarization field is aligned along the growth direction.**



No degradation was observed for 500 hours of photocatalytic water splitting reaction without surface protection.

Adv. Mater. 28 (38), 8388-8397, 2016.

Approach- Innovation

Budget Period 1 Scope of Work

- Demonstrate Ta_3N_5, BCTSSe, and InGaN top photoelectrodes on GaN nanowire tunnel junction, including both photoanodes and photocathodes that can exhibit a photocurrent density >10 mA/cm^2 and open circuit potential (OCP) >0.7 V.
- Demonstrate a double-junction photoelectrode on Si with OCP further enhanced by >0.5 V.

Importance toward validation of your technology innovation

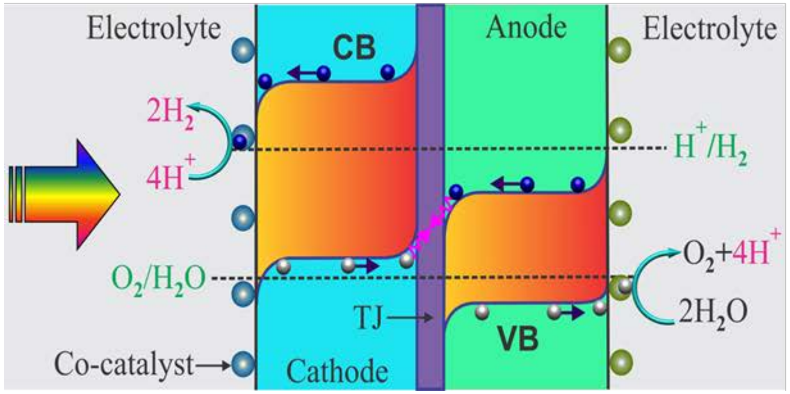
- The improved performance of the top photoelectrodes is essentially required to realize high efficiency, unassisted solar water splitting.
- A functional wide bandgap tunnel junction that can be fabricated on Si platform is a critical, yet missing component of a Si-based tandem solar water splitting device.

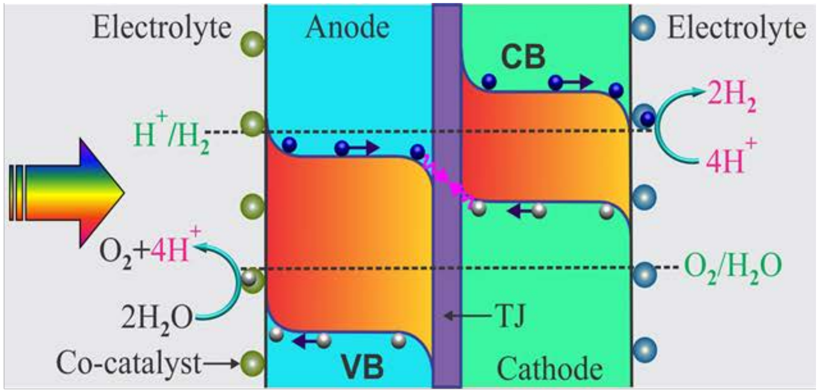
The Role of HydroGEN Consortium resources

- Ab-initio modeling, and computational materials diagnostics.
- In situ surface and PEC characterization, and performance validation.
- Co-catalyst deposition, testing and stability analysis.

Relevance & Impact

- The STH conversion efficiency and cost targets for purified, 300 psi compressed H_2 gas are 20% STH and $5.70 per kg H_2 by 2020. The tandem PEC device concept of stacking wide-bandgap and narrow-bandgap semiconductors is a proven method that can achieve the targeted STH efficiency. To date, all efficient tandem PEC devices are based on the state-of-the-art III-V semiconductor tandem photoelectrodes. However, the expensive GaAs substrates and photocorrosion severely limited its ability to achieve the cost goal.
- We aim to tackle the challenges of achieving efficient, cost-effective PEC water splitting devices by developing tandem photoelectrodes, which consist of a bottom Si light absorber and a 1.7-2 eV top light absorber (Ta_3N_5, BCTSSe, or InGaN). *High performance top photoelectrode will be fabricated on large area Si wafer using nanowire tunnel junction, and will be passivated by an ultrathin N-rich GaN to protect against photocorrosion and oxidation.*
- The outcome of this project is to develop monolithically integrated Si-based tandem photoelectrodes, with the objective to achieve high efficiency (up to 20%) and long-term stability (>1,000 hours) solar-to-H_2 conversion through PEC water splitting. The success of this project will help meet the DOE technical target for H_2 production from PEC water splitting.





Relevance & Impact

This project leverages the existing unique expertise and capabilities of HydroGEN Energy Materials Network (EMN). We have been working closely with the following to advance the proposed project:

1) Surface Analysis Cluster Tool, Glenn Teeter, NREL. Dr. Teeter and his team members have performed surface characterization and XPS measurements of GaN on Si wafer and have revealed the unique band alignment between GaN nanostructures and Si, which forms the basis for the design of GaN/Si PEC devices.
2) Ab Initio Modeling of Electrochemical Interfaces, Tadashi Ogitsu, LLNL. This collaboration provides important insights of electrochemical interface and PEC device optimization through ab-initio modeling and computational materials diagnostics.
3) Computational Materials Diagnostics and Optimization of Photoelectrochemical Devices, Tadashi Ogitsu, LLNL. Dr. Ogitsu and his team members have performed first principles studies of N-terminated GaN surfaces and the effect on solar water splitting. These studies are further correlated with the stability analysis of the photoelectrodes.
4) Probing and Mitigating Chemical and Photochemical Corrosion of Electrochemical and Photoelectrochemical Assemblies, Francesca Toma, LBNL. With the unique in situ techniques, including photoelectrochemical AFM and STM, Dr. Toma is investigating the behaviors of our top electrode materials, and this information will prove invaluable to our optimization efforts.
5) Surface Modifications for Catalysis and Corrosion Mitigation, Todd Deutsch, NREL. Dr. Deutsch and his team members have been working on the co-catalyst deposition and surface protection to identify the best strategy to protect the surface against photocorrosion and oxidation.

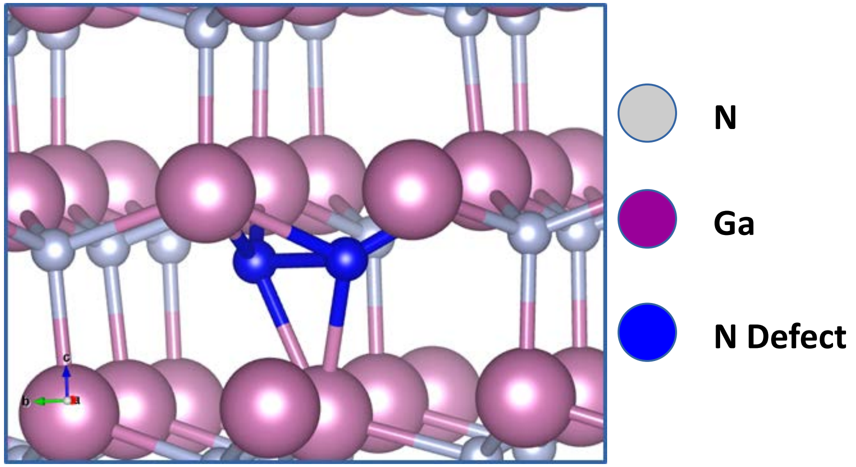
Accomplishments

Budget Period 1 Go/No Go Milestones:

- **Demonstration of the controlled synthesis and characterization of top photoelectrodes, including Ta_3N_5, BCTSSe, and InGaN directly on Si wafer.**
- **Demonstration of top photoelectrodes with energy bandgap ~1.7-2.0 eV on Si that can deliver photocurrent density >10 mA/cm^2 and open circuit potential (OCP) >0.7 V under standard one-Sun illumination.**
- **Proof-of-concept demonstration of a double-junction photoelectrode on Si, with OCP further enhanced by at least 0.5 V, compared to the stand alone top photoelectrode.**

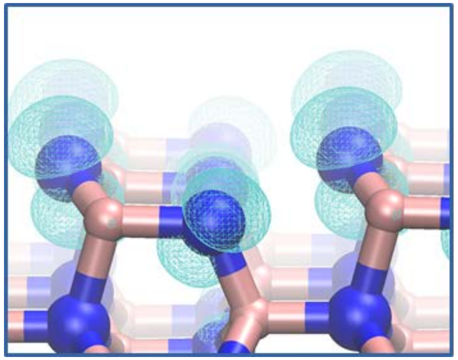
Meeting these milestones will validate the concept of using Si and GaN tunnel junction as a platform for the scalable production of solar hydrogen.

Accomplishments

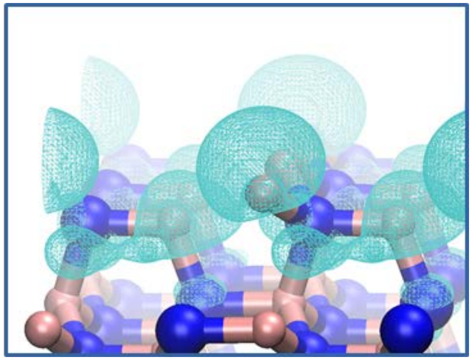


Materials Diagnostic (Ogitsu)

- Developed defects structure models to identify the origin of the OCP saturation
- Construction of defect phase diagrams is underway to identify detrimental defects, and to understand how working conditions (temperature, chemical potentials) affect the defect density, and hence identifying the optimal synthesis condition



N-rich surface: Dangling bond character of the VBM



Ga-rich surface: Bonding character of the VBM

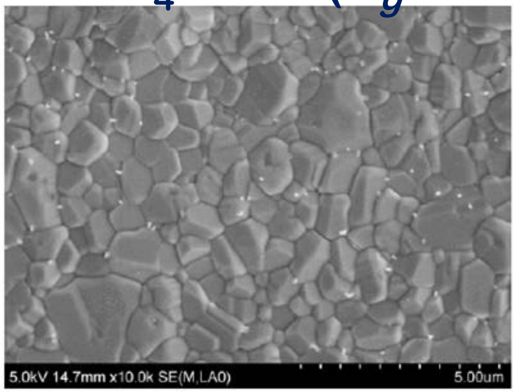
Interface Modeling (Ogitsu)

- Developed N/Ga-rich GaN surfaces to investigate the atomistic origin of chemical stability and performance
- Developed structure models of GaN/water interface to investigate chemical activities at the photoelectrochemical interface, and elucidate their influence on water-splitting reactions and materials stability

Theoretical models and interpretations will be validated by experimental characterization.

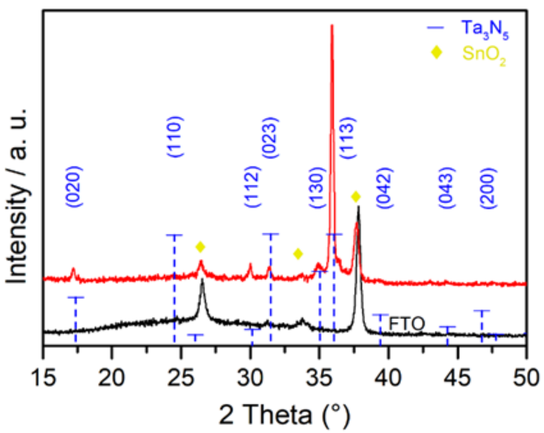
Accomplishments

- **Synthesized nearly phase pure Cu_2BaSnS_4 films (E_g ~1.7 eV).**



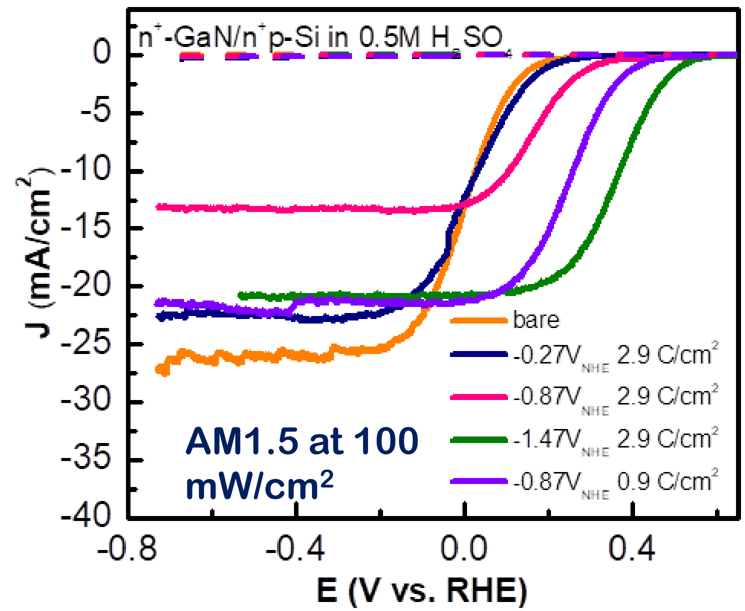
SEM image of CBTS film deposited on Mo-coated glass.

- **Synthesized crystalline Ta_3N_5 thin films (E_g ~2.0 eV).**



XRD of Ta_3N_5 (red) and bare FTO substrate (black).

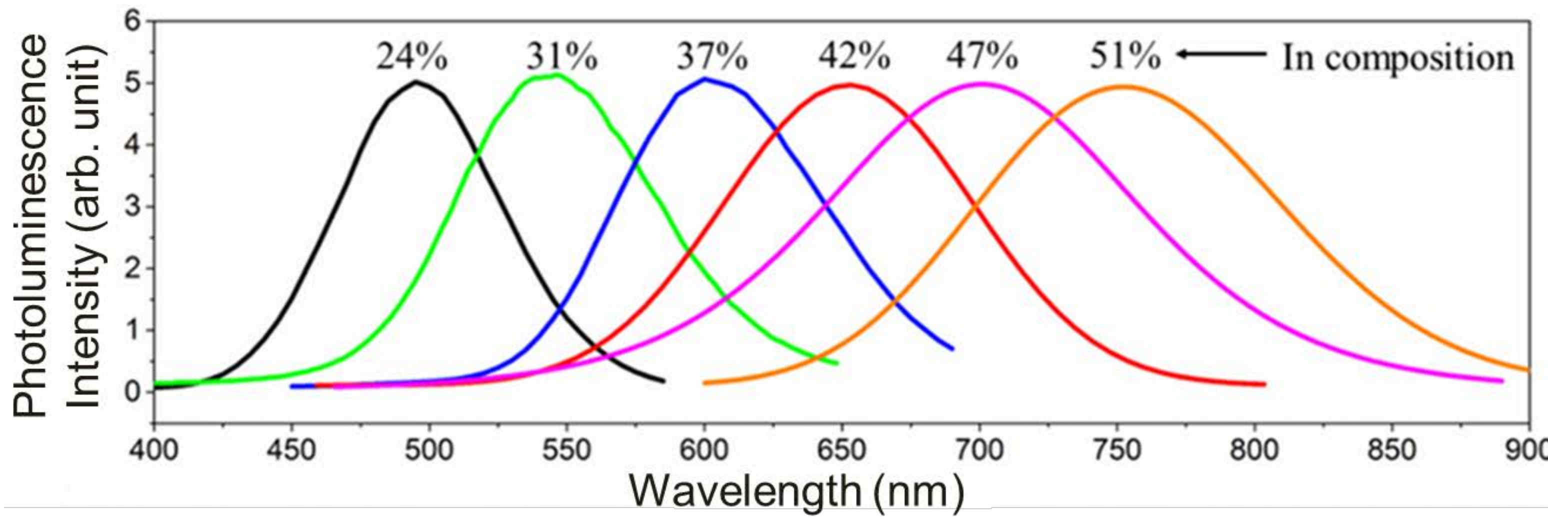
- **Developed a non-aqueous method for catalyst deposition to reduce complications caused by catalyst growth in aqueous systems.**

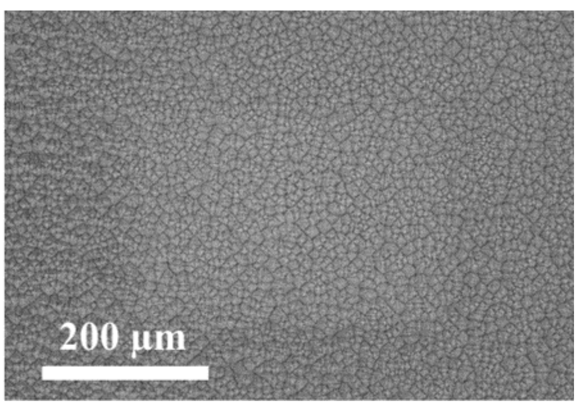


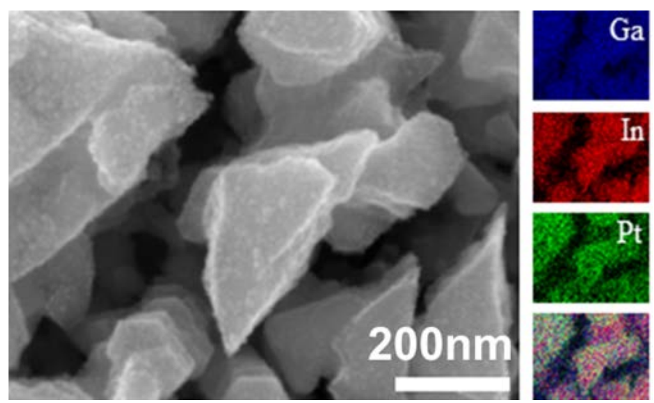
- **$PtCl_6^{2-}$ can be photoelectrochemically reduced in non-aqueous electrolyte (e.g. 0.1 M $EV(ClO_4)_2$ with 0.1 M $LiClO_4$ in MeCN (H_2O < 10 ppm)).**
- **HER performance of GaN/Si photocathode is improved by optimizing the non-aqueous PEC Pt deposition.**

Accomplishments

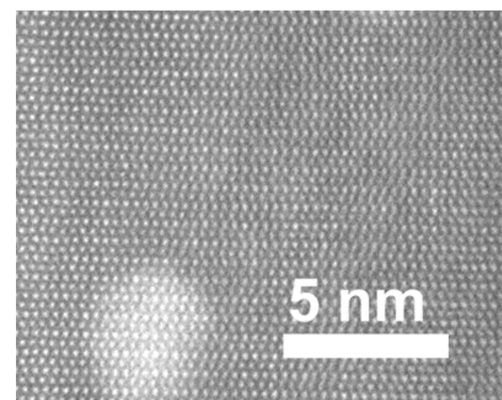
- **High quality InGaN nanostructures with indium composition up to 50% (bandgap ~1.7 eV) were achieved on Si wafer, which can serve as the top photoelectrode for a high efficiency tandem PEC water splitting device.**







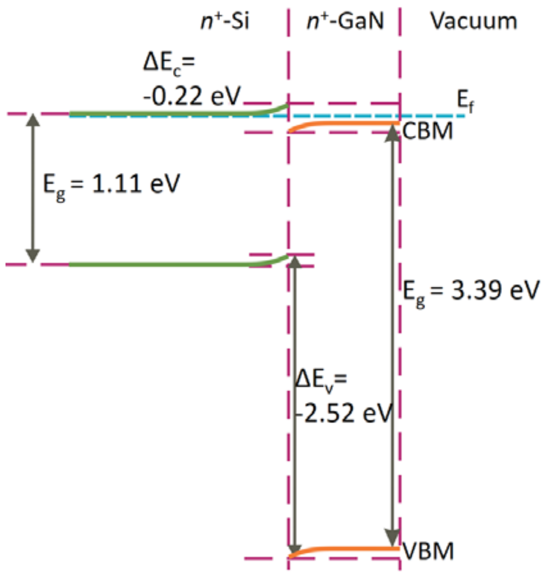
Top-view SEM image and EDX elemental mapping



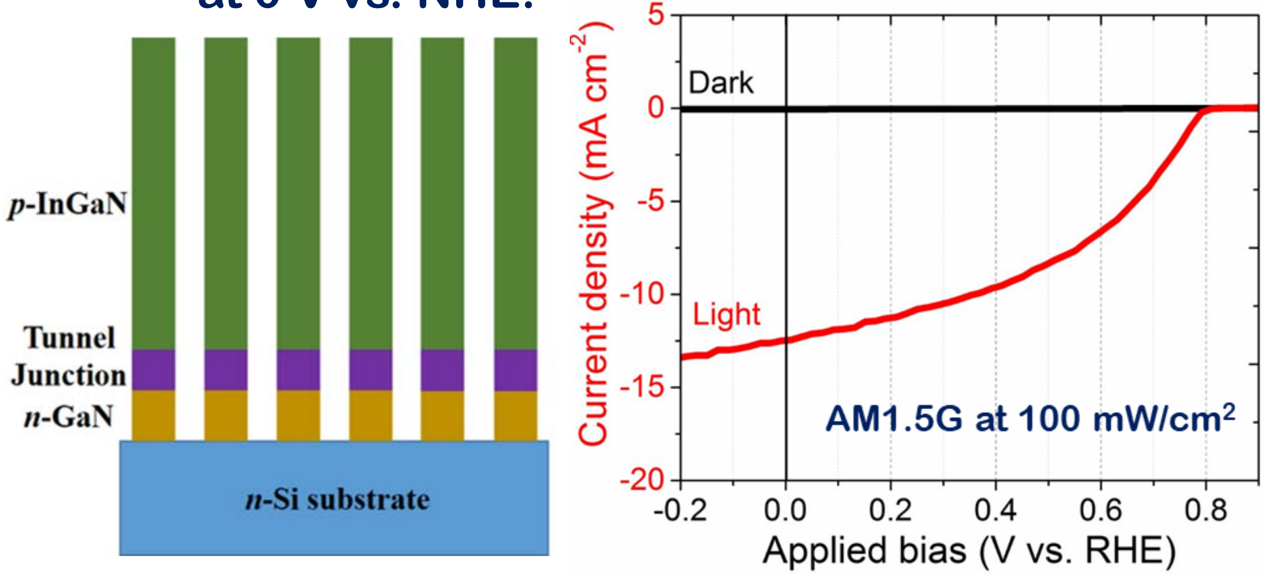
Superior quality InGaN with the presence of atomic ordering

Accomplishments

- **Discovery of negligible conduction band offset between GaN and Si. (Teeter)**



- **p-Type InGaN photocathodes were synthesized on n-type Si wafer through a GaN nanowire tunnel junction, with J_{ph} ~ 12 mA/cm^2 at 0 V vs. NHE.**



The negligible conduction band offset between GaN and Si allows for the efficient extraction of electrons from Si wafer, which forms the basis for the design of Si/GaN tandem PEC water splitting device.

Functional InGaN top photoelectrode is demonstrated on wide bandgap GaN nanowire tunnel junction on Si wafer.

Accomplishments

Outlook and Projected Outcomes

- Proof-of-concept demonstration of a double-junction photoelectrode on Si wafer, with OCP further enhanced by at least 0.5 V, compared to the stand alone top photoelectrode.

Confidence in meeting the Go/ No Go milestones: High

Major Impact

- This project will be instrumental to establish a Si-based platform for high efficiency PEC tandem water splitting devices and systems, which, to date, can only be achieved using prohibitively expensive GaAs-based materials.
- The stability of PEC water splitting devices will be fundamentally improved by utilizing N-terminated GaN protection layer.
- The semiconductor photoelectrodes are synthesized using industry ready materials, *e.g.*, Si and GaN based on standard semiconductor processing, and therefore the manufacture is controllable and scalable.

Collaboration: Effectiveness

G. Teeter, NREL

- **Surface Analysis Cluster Tool**

- Dr. Teeter has performed extensive X-ray photoelectron spectroscopy measurements of GaN nanostructures grown on Si wafer. His studies have revealed, for the first time, that the conduction band offset between Si and GaN is negligibly small, which validates the concept of integrating GaN tunnel junction nanowires with the Si bottom light absorber to realize a high efficiency tandem photoelectrode.
- Dr. Teeter has further performed measurements on the photovoltage of GaN/Si photoelectrode using X-ray photoelectron spectroscopy, which is critical to analyze the PEC performance.

T. Ogitsu, LLNL

- **Ab initio modeling of electrochemical interfaces node**
- **Materials diagnostics node**

- **Ab initio modeling node**
  - Developed surface structural models of N/Ga rich GaN (1010) and (1000) surfaces.
  - Electronic structure of the models were studied in order to elucidate the origin of chemical stability.
  - TMF user project has been submitted for supporting Dr. Toma's experiments.
- **Materials diagnostics node**
  - Developed defect structural models of GaN to identify types of defects responsible for the saturation of open circuit voltage.
  - This effort aims to understand and improve OCP saturation behavior.
- Our theoretical results will be validated by theoretical/experimental spectroscopic study in collaboration with characterization nodes.

Collaboration: Effectiveness

T. Deutsch, NREL

- **Surface modifications and protection**

- Samples exchange have been established with Univ. of Mich. And Boston College.
- Measurements are being performed on GaN, Ta_3N_5, and BCTSSe photoelectrode samples to provide critical feedback for the PEC device design and synthesis.
- Sample exchange and detailed measurements further helped cross-calibrate the testing systems of team members.
- Currently exploring various co-catalyst deposition methods (ALD, sputtering, and electrochemical deposition) to improve the PEC performance.

F. Toma, LBNL

- **Probing and mitigating chemical and photochemical corrosion of electrochemical and photoelectrochemical assemblies**

- Dr. Toma, in collaboration the team members completed and submitted a proposal entitled "*AP-XPS of GaN based materials for photoelectrochemical water splitting*" to the Advanced Light Source (ALS) at LBNL, which will enable a detailed in operando characterization of surface electronic structure of GaN-based photoelectrodes.
- Intensified sample exchange to probe and understand chemical and photochemical corrosion will take place in Q3. These studies will be correlated with calculations by Dr. Ogitsu, and provide direct evidence for the unique electronic structure of GaN and their impact on the stability of PEC water splitting.

Collaboration: Effectiveness

- **Specific activities and accomplishments incorporating project data in the HydroGEN data hub.**

Project data (>5 datasets until April 2018), including materials design, synthesis, characterization, and testing results are incorporated in the HydroGEN data hub and shared among all team members. The shared data include images, figures, and videos taken in the lab. These activities have proved to be highly effective and efficient in promoting collaboration and advancing the progress of this project.

- **Expected benefits to the HydroGEN Consortium and the broader water-splitting R&D community**

To date, stable and efficient PEC water splitting devices do not exist. This project is focused on the use of industry-ready materials, including Si and GaN to establish a Si-based platform for low cost, high efficiency PEC tandem water splitting devices and systems. Moreover, we have discovered that N-terminated GaN can effectively protect against photocorrosion and oxidation, thereby leading to highly stable solar water splitting that was difficult for conventional Si and III-V based photoelectrodes. Significantly, the semiconductor photoelectrodes are synthesized using standard semiconductor processing, and therefore the manufacture is controllable and scalable.

Proposed Future Work

Proposed Scope:

- Budget Period 2 (M12-M30): Si-based double-junction photoelectrodes with high efficiency targeting >15% STH.
- Budget Period 3 (M31-M36): Si-based double-junction photoelectrodes with long-term stability.

Estimated Budget (excluding cost share): $750,000

Intended Outcomes:

- Double-junction photoelectrodes with efficiency >15% and stable operation (>1,000 hrs) under standard solar light illumination.

Impacts:

- Establish a Si-based low cost and scalable platform for high efficiency and highly stable PEC water splitting devices and systems.

Any proposed future work is subject to change based on funding levels.

Project Summary

- This project is focused on the development of Si-based high efficiency PEC tandem water splitting devices, with major innovations including:
  - The use of nanowire tunnel junction to fabricate 1.7-2.0 eV top photoelectrodes, including Ta_3N_5, BCTSSe, and InGaN on Si wafer.
  - The discovery of N-terminated GaN to protect against photocorrosion.
- Major achievements to date:
  - Established effective collaborations with five EMN nodes.
  - Demonstrated 1.7 – 2 eV top photoelectrodes with improved performance.
  - Achieved functional nanowire tunnel junction on Si wafer.
  - Studied the mechanism for the stability of N-rich GaN photoelectrodes.
- The project is on the right track to meet Year 1 milestones.
- Success of this project will be instrumental to establish a low cost and scalable platform for high efficiency and highly stable PEC water splitting devices and systems by using industry ready materials, *e.g.,* Si and GaN.

Technical Back-Up Slides