Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Monolithically Integrated Thin-Film/Si Tandem Photoelectrodes

Zetian Mi

University of Michigan, Ann Arbor

Project ID # p163

NREL · Berkeley Lab · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

Project Overview

MONOLITHICALLY INTEGRATED THIN-FILM/SILICON TANDEM PHOTOELECTRODES FOR HIGH EFFICIENCY & STABLE PHOTOELECTROCHEMICAL WATER SPLITTING

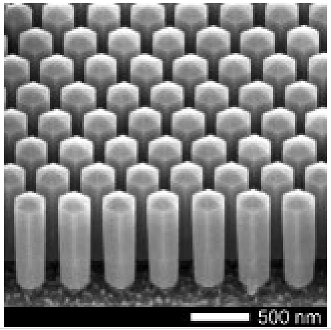
Zetian Mi, University of Michigan, Ann Arbor
Thomas Hamann, Michigan State University
Dunwei Wang, Boston College
Yanfa Yan, University of Toledo

Award #	EE0008086
Start/End Date	9/01/2017 – 08/31/2020
Year 1 Funding* Year 2 Funding*	$249,999 $373,530

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

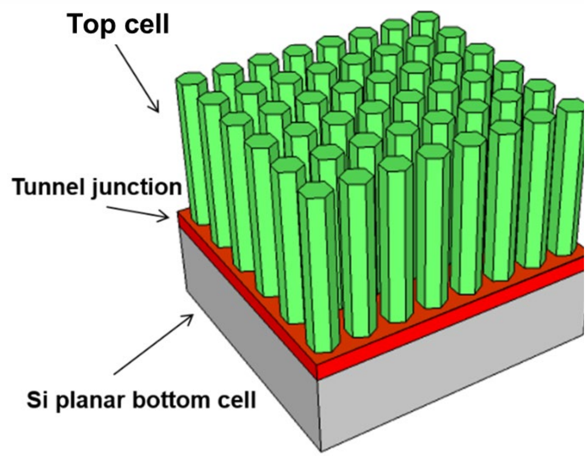
Project Vision

We propose to develop monolithically integrated thin-film/Si tandem photoelectrodes 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.



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 eV top light absorber (InGaN). We have previously developed:

- ***InGaN top photoelectrodes with E_g ~1.8-2.0 eV.***
- ***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	*~0.5 hr @ 16-19%*	*>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

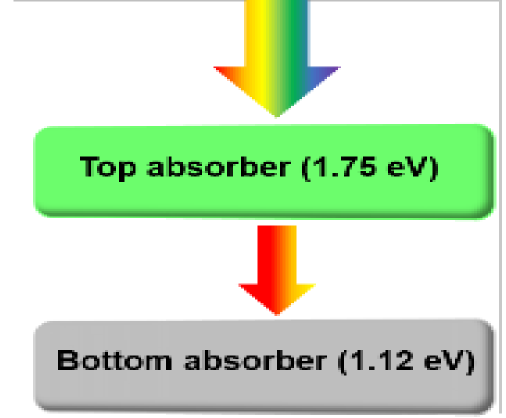
HydroGEN nodes

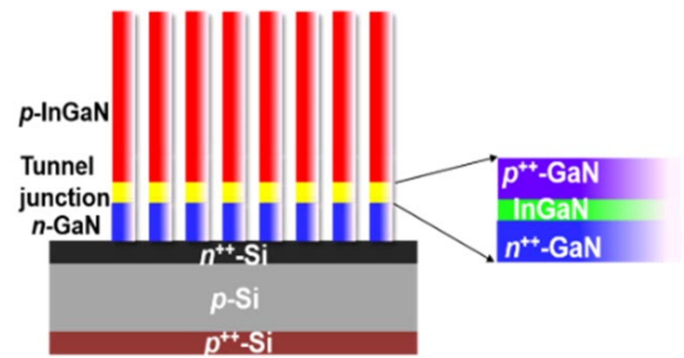
- **Glenn Teeter, NREL:** Surface analysis cluster tool, surface measurements
- **Francesca Toma, LBNL:** Photoelectrochemical AFM and STM
- **Tadashi Ogitsu, LLNL:** Ab initio modeling of electrochemical interfaces
- **Todd Deutsch, NREL:** Surface modifications and protection

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

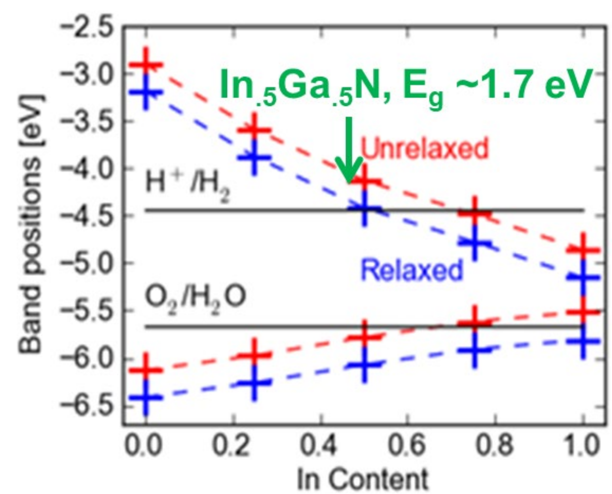
Approach- Innovation

- 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 $In_{0.5}Ga_{0.5}N$ photoelectrodes as the top light absorber.
  - Direct bandgap ~1.7 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.
- The use of GaN nanowire tunnel junction to fabricate top photoelectrodes on Si.
  - Low resistivity, and reduced voltage loss.
  - Reduced defect formation due to the efficient surface stress relaxation.





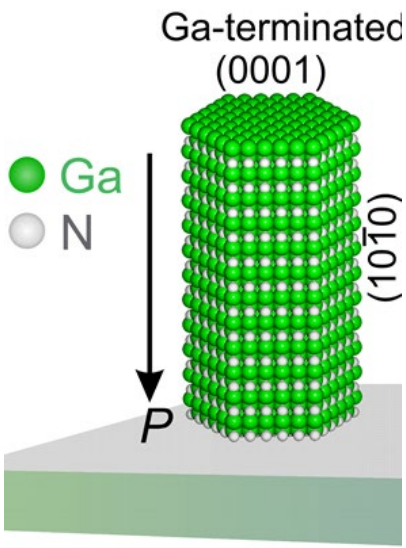
Integrated photocathode

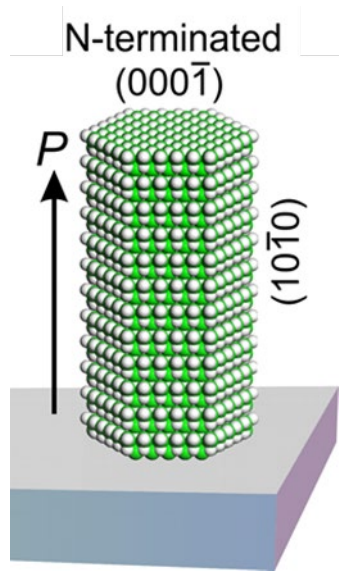


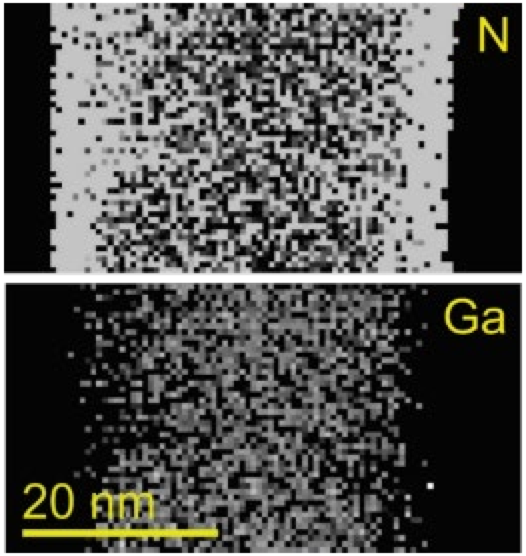
Appl. Phys. Lett. 96, 021908 2010.

Approach- Innovation

➢ Surface protection by N-terminated GaN surfaces





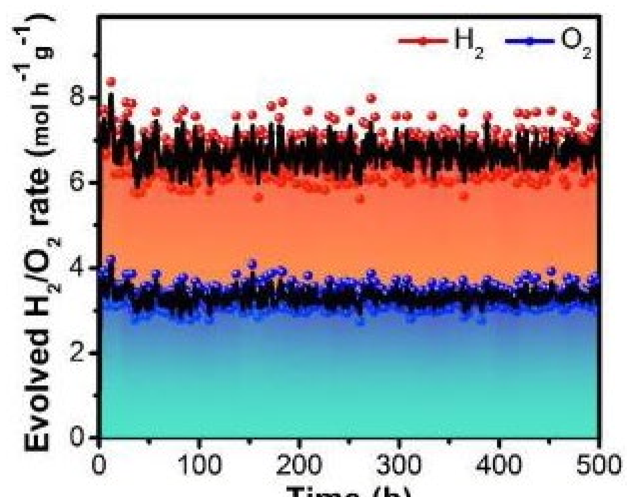


STEM studies reveal N-rich surfaces for MBE grown GaN nanowires.

Conventional GaN grown by CVD has Ga polarity.

GaN nanostructures grown by MBE have N-termination.

- **Unstable in water splitting.**
- **Stable in water splitting**



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

Adv. Mater. 28 (38), 8388-8397, 2016. *ACS Energy Lett.* 3, 2230, 2018

Approach - Innovation

Budget Period 3 Scope of Work and Go/No Go Milestones

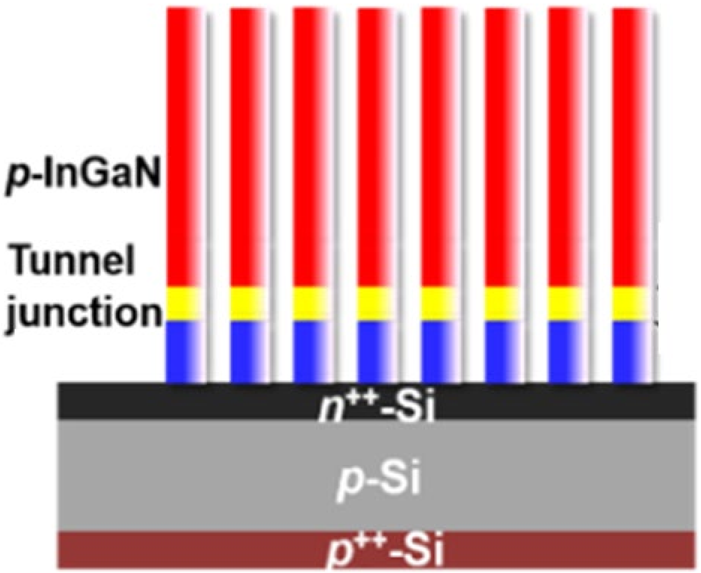
- Detailed studies on the PEC performance and stability test of double-junction photoelectrodes and the correlation with the design and synthesis parameters.
- Double-junction photoelectrodes with STH efficiency >15% and stable operation (>1,000 hrs)

Importance toward validation of technology innovation

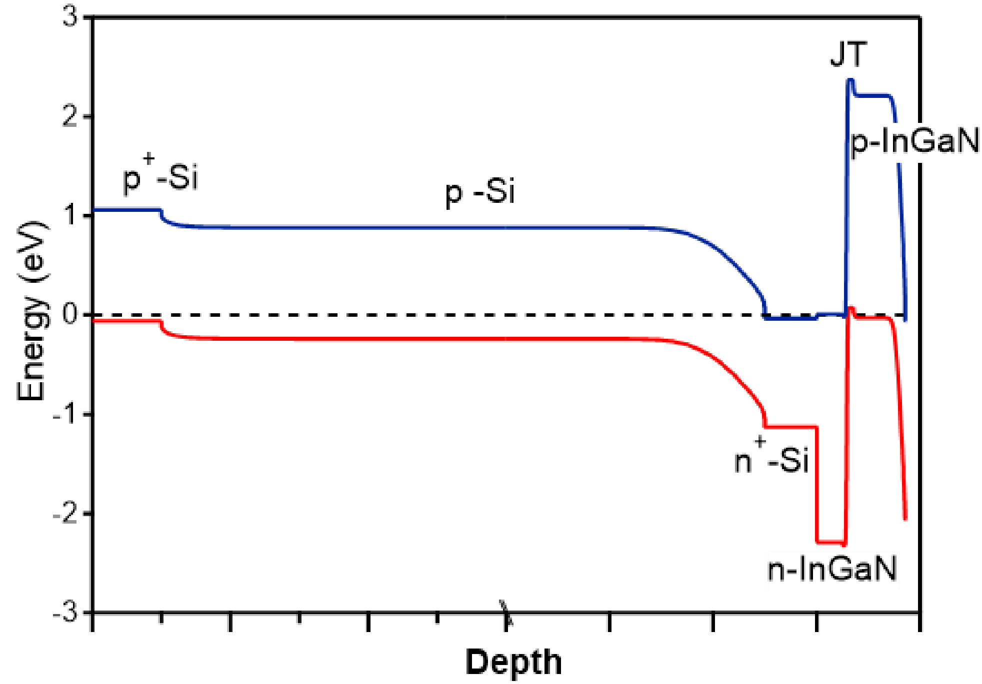
- The realization of unassisted solar water splitting >15% STH efficiency for a non III-V PEC device will pave the way for the low cost manufacturing of high efficiency PEC devices.
- The realization of stable operation >1,000 hrs in two-electrode, unassisted water splitting will help address the stability bottleneck.
- Collaborations with F. Toma, T. Ogitsu, and T. Deutsch provide a detailed theoretical and experimental understanding of the device design and performance.

Accomplishments: *Design of Si-based tandem photoelectrodes*

Y. Yan, Univ. of Toledo



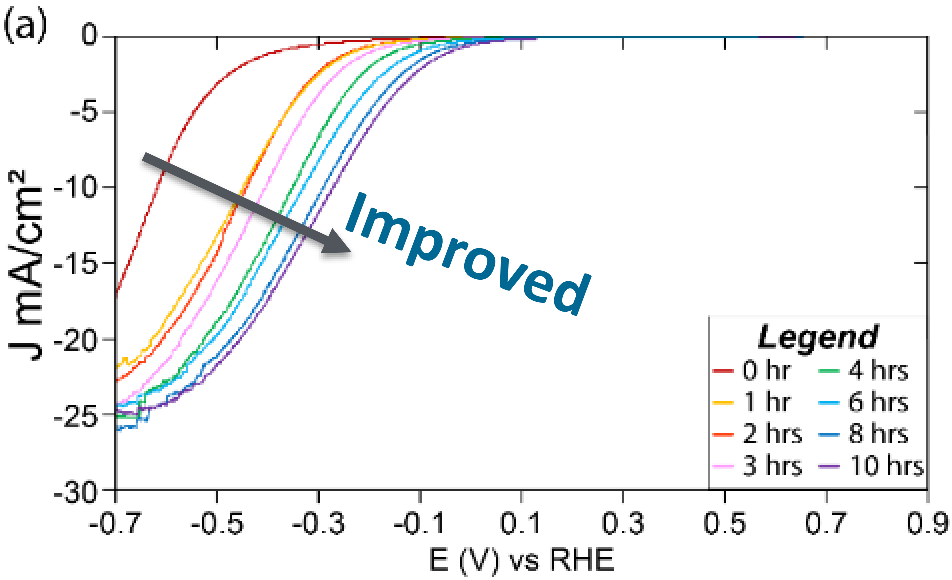
Integrated photocathode

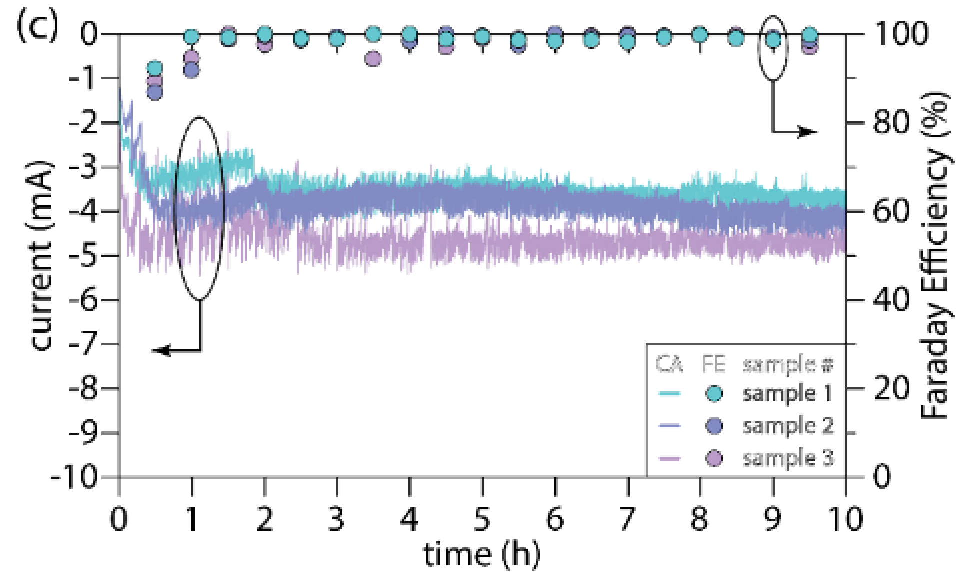


- Theoretical calculations showed InGaN/Si double-junction photoelectrodes can provide STH > 20%.
- Important parameters affecting STH efficiency include interfacial losses, contact barriers, bandgap, and defect densities (see back up slides for details).

Accomplishments: *Self-healing and stability studies of GaN/Si Photocathode*

F. Toma, LBNL

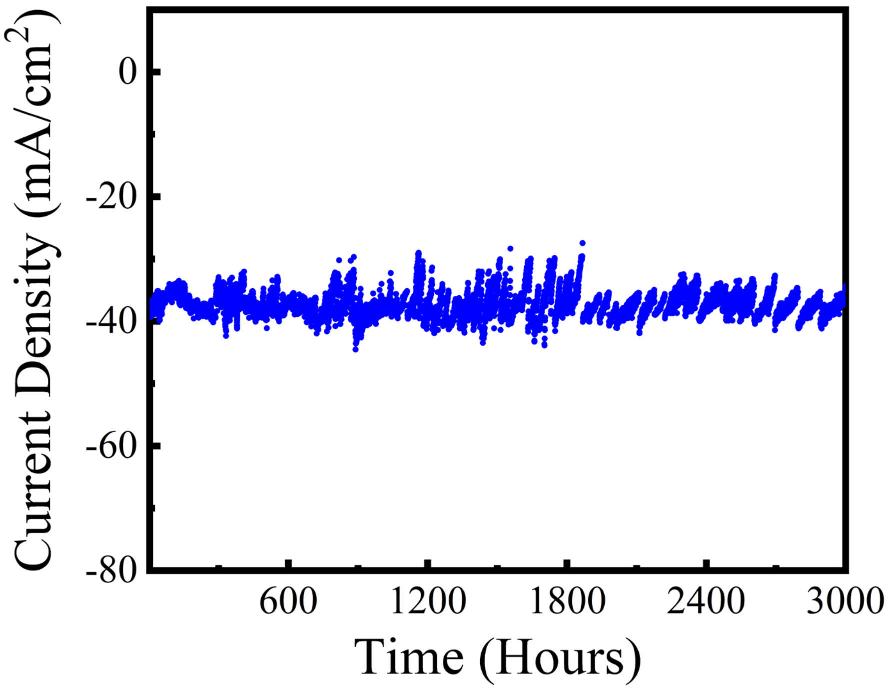


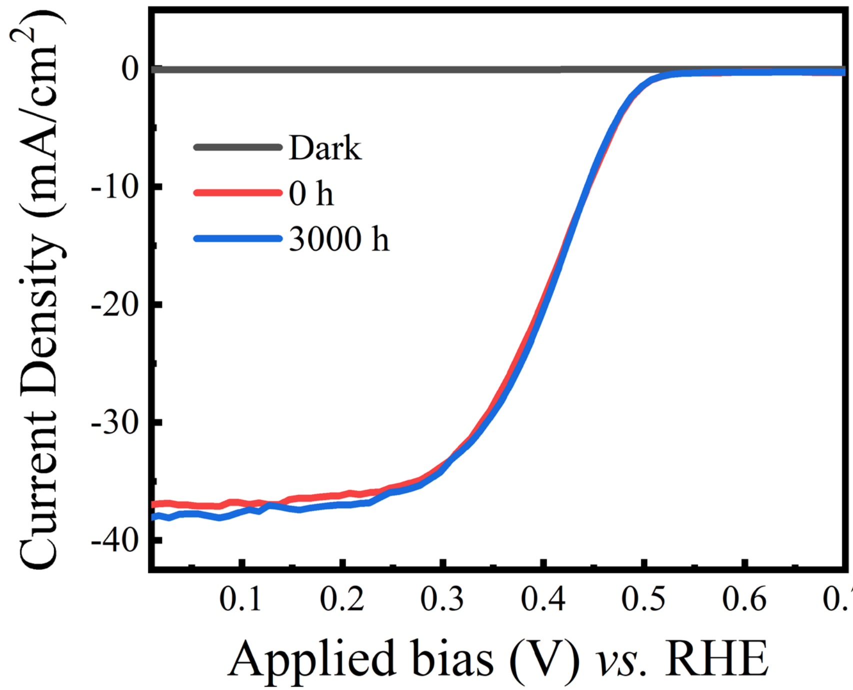


- **Improved J-V performance over time.**
- **Stable photocurrent over the testing period (~10 hrs).**
- **Faradaic efficiency reached to 100% in 1 hr and remained at ~100% during the testing. No electrocatalysts were applied in this measurement, demonstrating the extraordinary stability and photocatalytic activity of III-nitrides.**

Accomplishments: *Long-term stability of GaN/Si Photocathode ~ 3,000 h*

Z. Mi, U-Mich





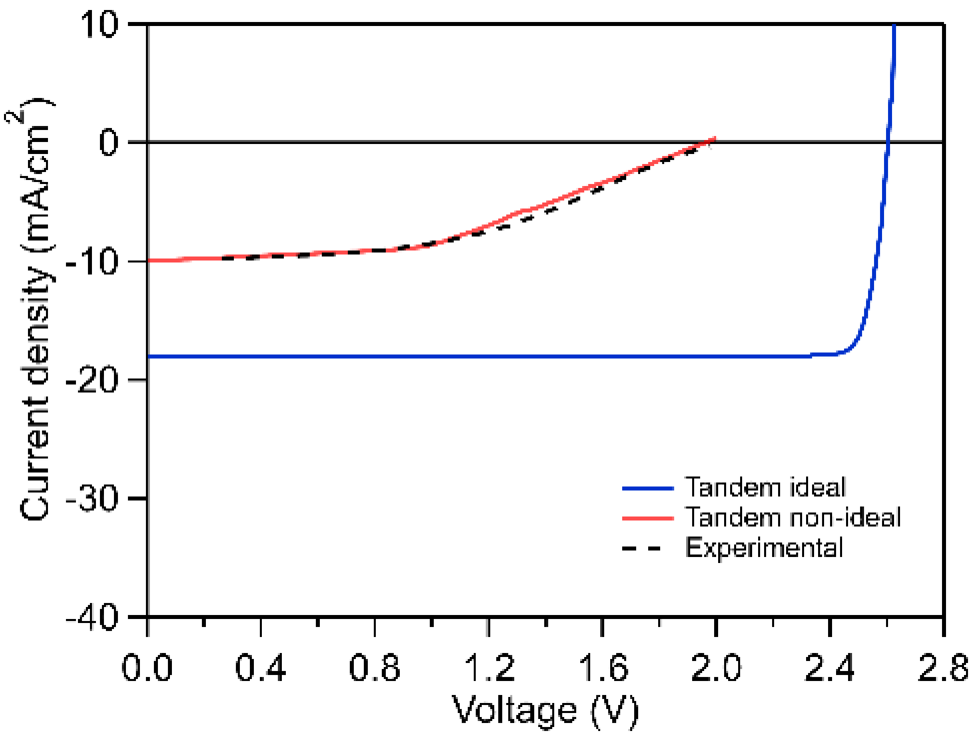
- **Pt co-catalyst regenerated GaN/Si photocathode, *with no extra protection*, showed stability ~ 3000 h with no degradation.**
- **No degradation in J-V characteristics after 3000 h experiments.**

Vanka, et al., *J. Mater. Chem. A* 2019,7, 27612-27619.

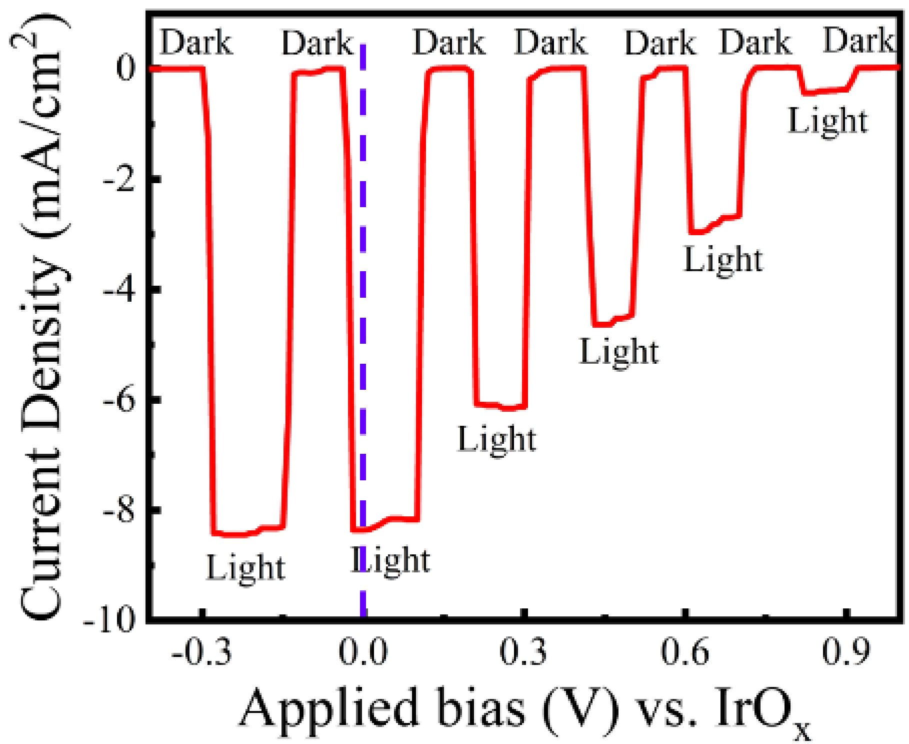
Accomplishments: *The first demonstration of Si-based double-junction photoelectrodes with STH efficiency >10%*

Z. Mi, Y. Yan, D. Wang, T. Hamann

Theoretical calculation



Two electrode measurement



- ➢ **Theoretically Si/InGaN tandem electrode can give STH > 20%.**
- ➢ **Demonstrated a STH efficiency ~ 10.5%.**

Accomplishments

Outlook and Projected Outcomes

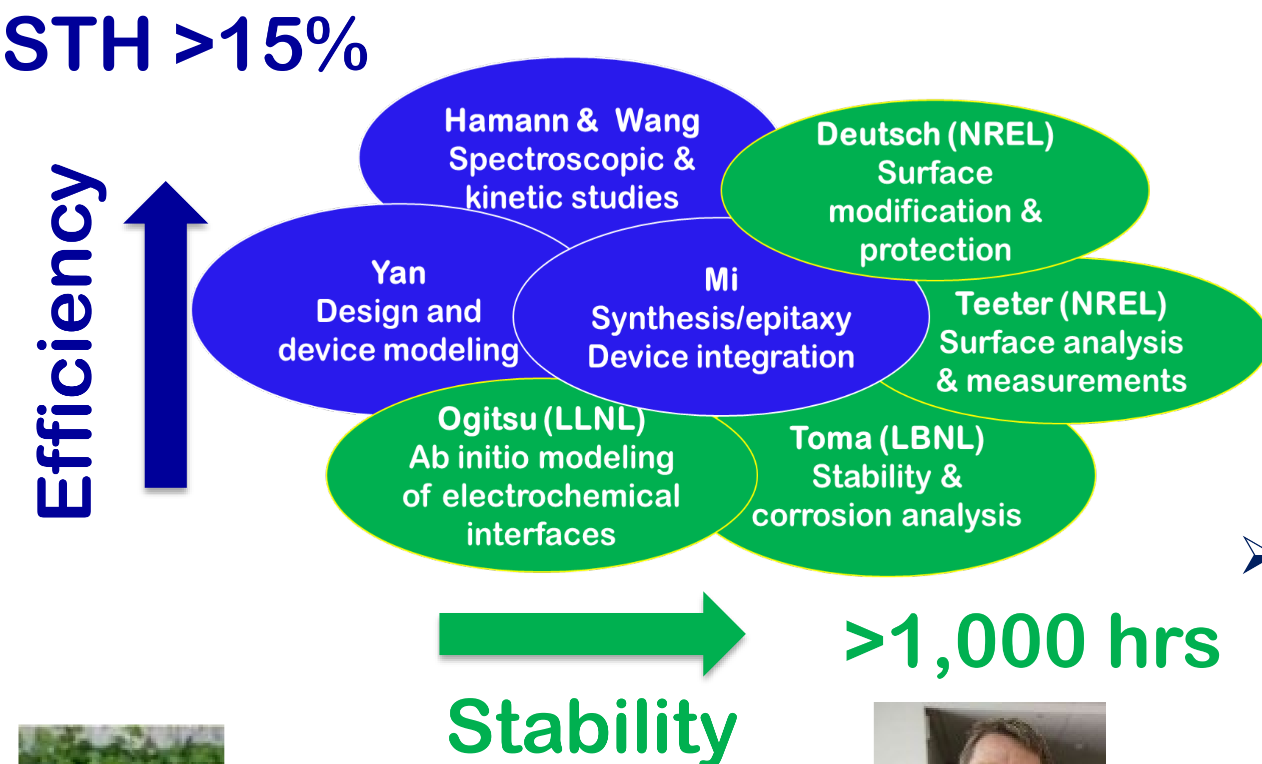
- Perform detailed spectroscopic and kinetic studies and further improve the STH efficiency.
- Perform a detailed investigation of the stability of InGaN and Si photoelectrodes, with the goal to achieve stable operation >1,000 hrs in two electrode measurement configuration.

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: *Role of the team members and nodes*



- **Francesca Toma, LBNL:**
  Photoelectrochemical AFM and STM

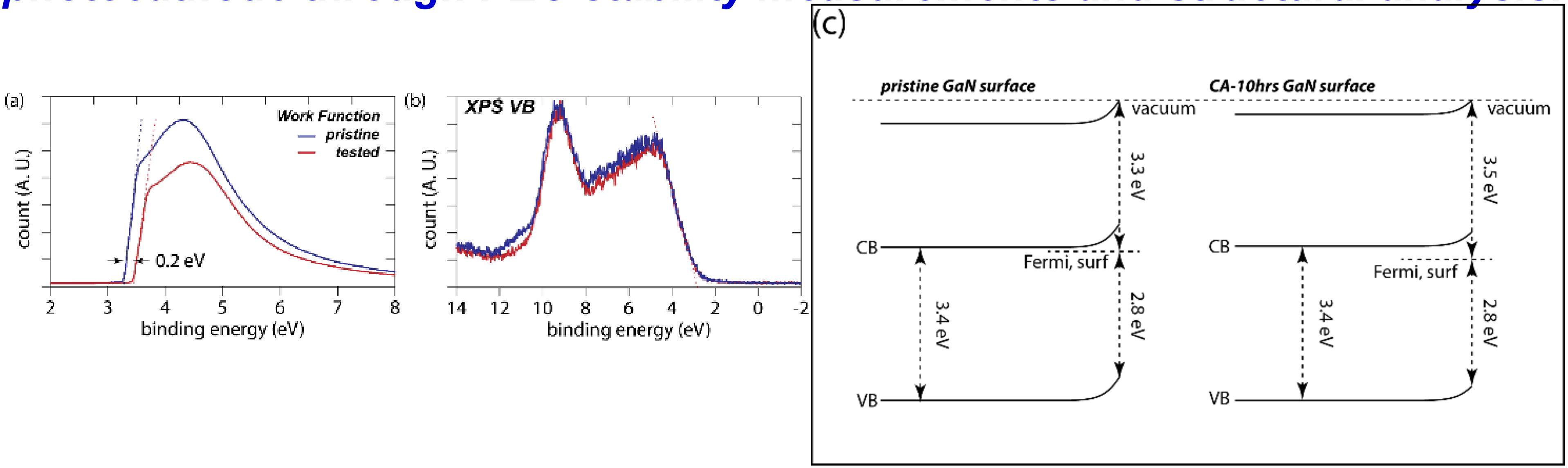
- **Tadashi Ogitsu, LLNL:**
  Ab initio modeling of electrochemical interfaces

- **Todd Deutsch, NREL:**
  Surface modifications and protection

Collaboration Effectiveness

F. Toma, Z. Mi

Toma, Ogitsu, and Mi investigated the self healing process of GaN/Si photocathode through PEC stability measurements and structural analysis.

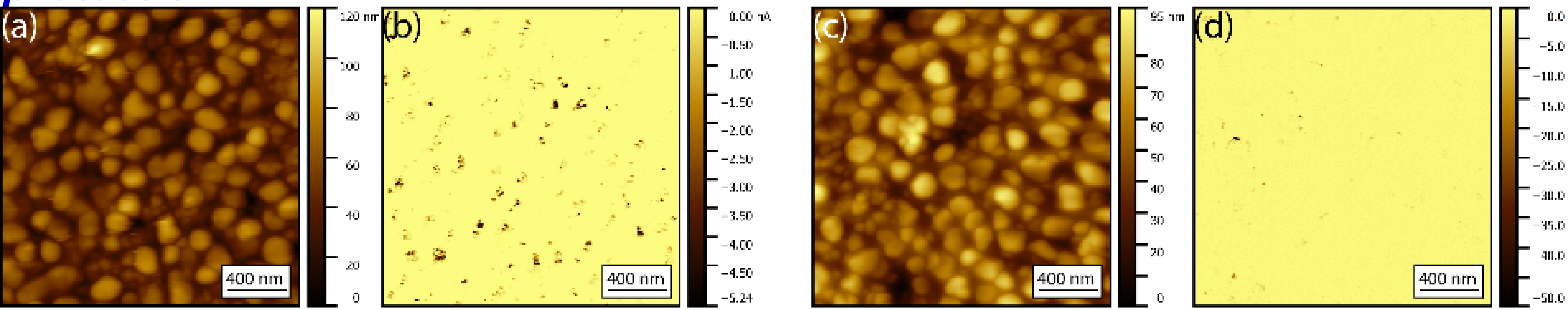


- **To understand the origin of the improved charge carrier transport, the work function and the valence band edge of the modified surface was obtained by secondary electron cutoff and XPS.**
- **(a) and (b) show the work functions and valence band edges of pristine and tested GaN surfaces. We found that the work function of the tested surface increased about 200 meV while the valence band remained the same.**
- **With this increase in the work function, the band bending of the surface was alleviated, leading to a lower energy barrier and thus more efficient charge carrier extraction (see (c)).**

Accomplishments

F. Toma, Z. Mi

Toma and Mi demonstrated the self healing process of GaN/Si photocathode along with in-situ structural analysis, and PEC performance and demonstrated excellent stability of GaN/Si without extra surface protection.

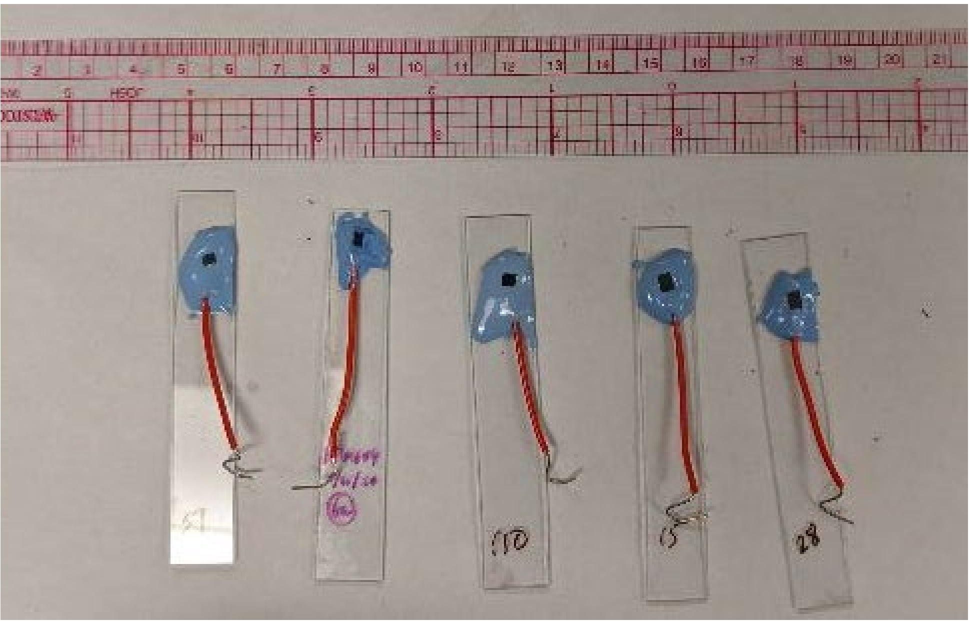


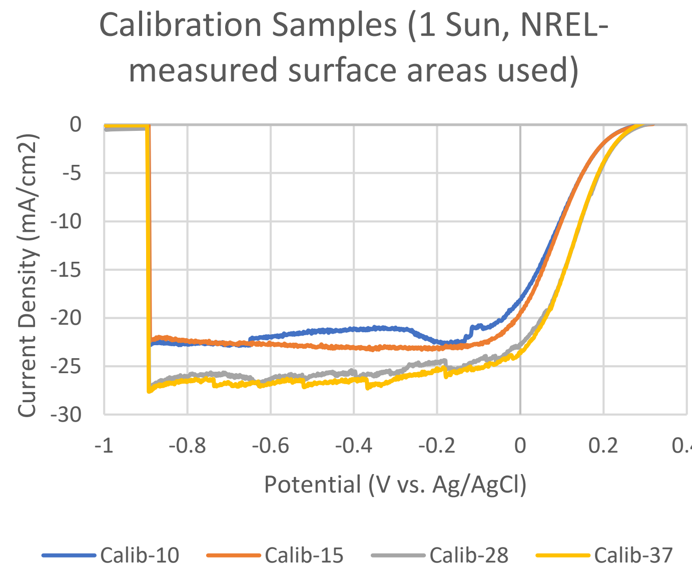
- **Under front illumination, the pristine sample required an additional bias of -0.4 V to trigger a measurable photocurrent of ~50 pA. On the contrary, the CA-10 hrs tested sample can generate two orders of magnitude higher photocurrent without applying any bias. This clearly indicated that the newly formed species during the first few hours CA testing greatly improved the PEC performance of GaN / Si photocathode, consistent with the results obtained from PEC measurements.**
- **The dark current for both samples were negligible in both cases, indicating that the measured signals under illumination mainly arose from the photoelectrons.**
- **Furthermore, no obvious change of surface morphology was observed, which, to some extent, explains that the decrease of surface resistance and improved charge carrier transport evidenced by EIS can be attributed to the reduced surface charge recombination.**

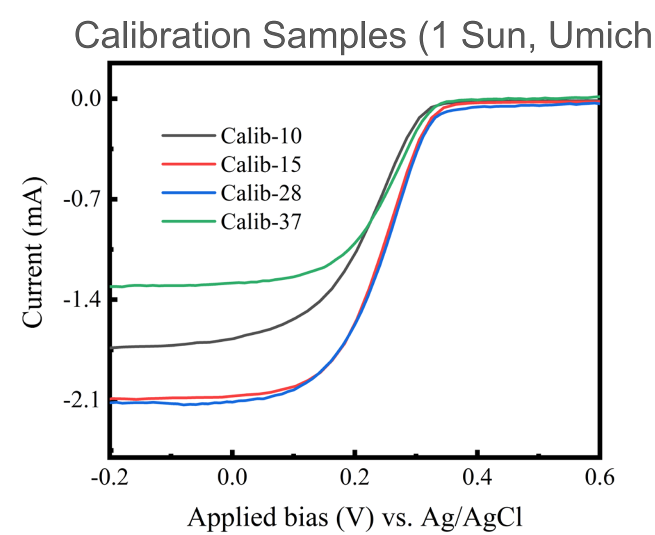
Collaboration Effectiveness

T. Deutsch, Z. Mi

Mi and Deutsch tested GaN/Si samples for cross calibration and co-catalyst deposition on GaN/Si photocathode.







- **Major challenges in cross calibration are surface area measurement protocols, lamp intensity and sample stability.**

Collaboration Effectiveness

T. Deutsch, Z. Mi

Mi and Deutsch tested GaN/Si samples for cross calibration and co-catalyst deposition on GaN/Si photocathode.

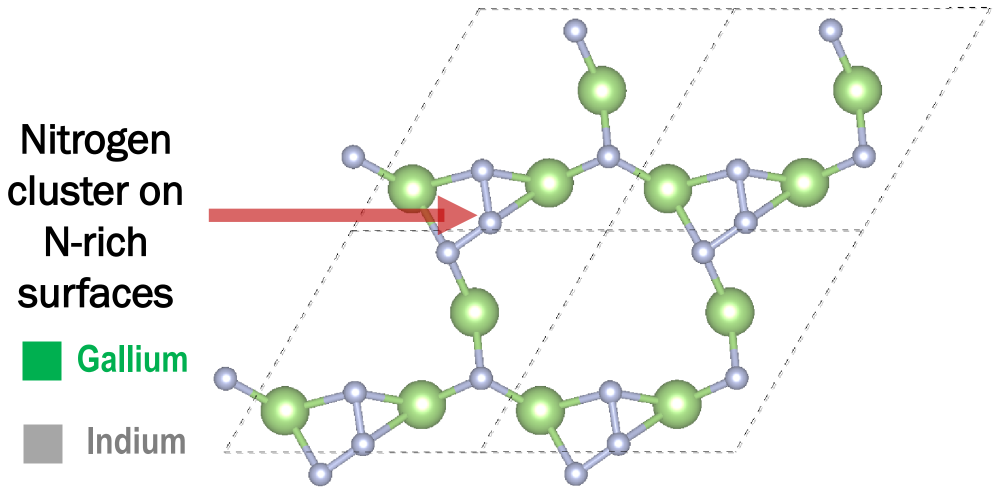
Sample name	NREL			Umich		Variations in surface area measurements between NREL and UMich
	Measured J at 0 V vs. RHE (mA/cm^2)	Area (cm^2)	Measured I at 0 V vs. RHE (mA)	Area (cm^2)	Measured I at 0 V vs. RHE (mA)	
Calib 10	23	0.077	1.71	0.06	1.73	28%
Calib 15	22.2	0.098	2.1756	0.08	2.1	23%
Calib 28	24.1	0.091	2.1931	0.07	2.118	30%
Calib 37	23.9	0.057	1.3623	0.05	1.308	14%

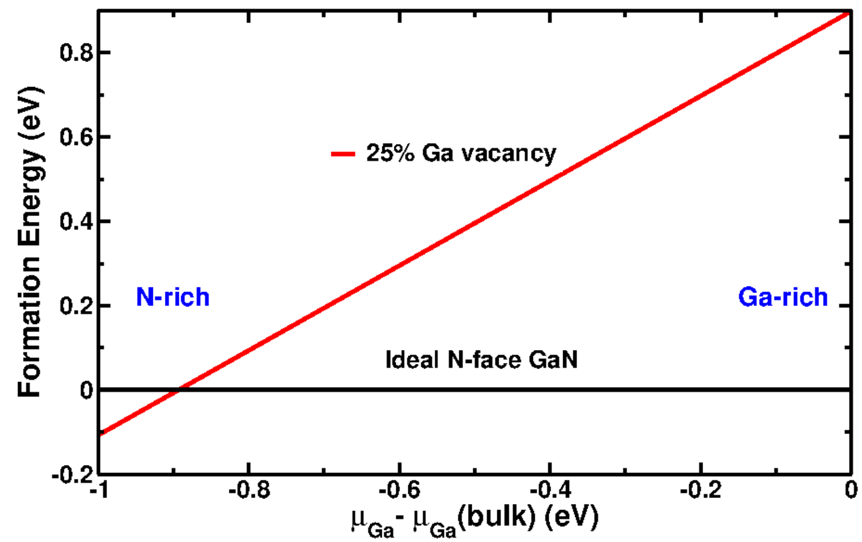
- **Photocurrent: Nearly identical current (mA) (at 0 V vs. RHE) was observed in both NREL and UMich measurements, confirming the sample stability and reproducibility.**
- **Surface Area: Surface area variations are 10-30%. NREL will give details of how to get apertures, with precise area, for PEC samples. UMich in collaboration with NREL will refine the surface area measurement protocols.**
- **NREL IPCE measurements: Intensity dependent studies are required for different wavelengths.**

Collaboration Effectiveness

T. Ogitsu, LLNL

Ogitsu conducted first-principles calculations and studied the origin for the stability of N-rich $(000\bar{1})$ GaN.





- **Our simulations point to the formation of nitrogen clusters on the surface with 25% Ga vacancy (N-rich).**
- **Formation energy calculation also shows that this surface (red line) is more stable than the pristine one (black line) at the N-rich condition.**

Collaboration: Effectiveness

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

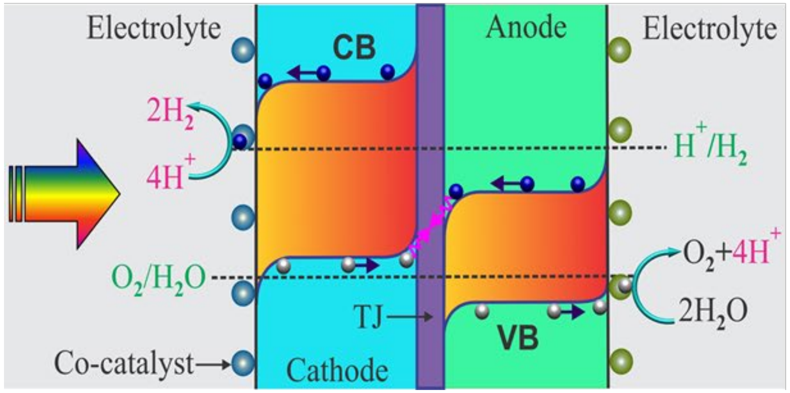
  Project data, including materials design, synthesis, characterization, and testing results are incorporated in the HydroGEN data hub and shared among team members. The shared data include images, figures, and videos taken in the lab. These activities have proved to be effective and efficient in promoting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

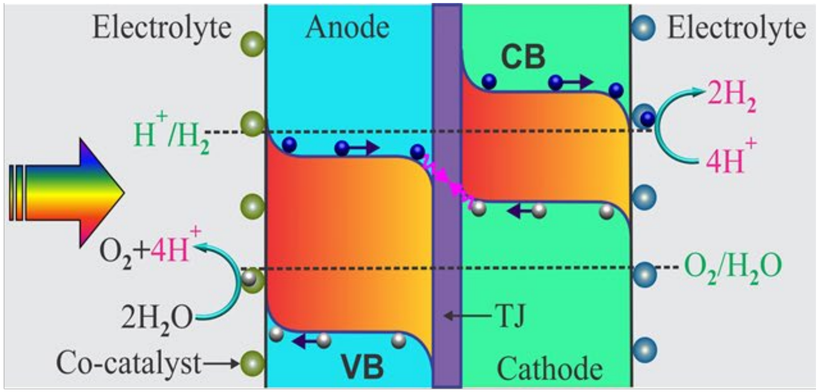
- **Expected benefits to the HydroGEN Consortium and the broader water-splitting R&D community**

  To date, stable and efficient PEC water splitting devices do not exist. This project is focused on the use of industry-ready materials, e.g., Si and GaN to manufacture low cost, high efficiency PEC tandem water splitting devices and systems. We have achieved the most efficient Si-based double-junction photoelectrode. Moreover, we have discovered that N-terminated GaN can effectively protect against photocorrosion and oxidation, 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.

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 (InGaN). *High performance top photoelectrode is fabricated on large area Si wafer using nanowire tunnel junction and is 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) 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, Toma revealed that GaN/Si photoelectrodes, without any extra surface protection, showed no sign of any performance degradation during continuous PEC water splitting, which is in stark contrast for the rapid degradation of conventional high efficiency photoelectrodes.

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. Preliminary studies revealed the underlying mechanism for the extraordinary stability of N-rich GaN-based photoelectrodes.

3) 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.

Proposed Future Work

Proposed Scope:

- Budget Period 3 (M25-M36): (1) Detailed studies on the PEC performance and stability test of double-junction photoelectrodes and the correlation with the design and synthesis parameters. (2) Double-junction photoelectrodes with STH efficiency >15% and stable operation (>1,000 hrs)

Estimated Budget (excluding cost share): $375,000

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 defect-free nanowire tunnel junction to fabricate 1.7-2.0 eV top photoelectrode directly on low cost, large area Si wafer.
  - The discovery of N-terminated GaN to protect against photocorrosion.
- Major achievements to date:
  - Established productive collaborations with three EMN nodes.
  - Demonstrated, for the first time, Si-based double junction photoelectrode with STH > 10%.
  - Discovered N-rich GaN and has demonstrated efficient and stable PEC water splitting without using any extra surface protection for ~3,000 h.
- 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.

Publications & Presentations

Journal publications since last AMR:

1. S. Vanka, K. Sun, G. Zeng, T. A. Pham, F. M. Toma, T. Ogitsu, and Z. Mi, “Long-term stability studies of a semiconductor photoelectrode in three-electrode configuration” J. Mater. Chem. A 2019, 7, 27612-27619.
2. Y. Wang, Y. Wu, J. Schwartz, S.H. Sung, R.Hovden, and Z. Mi, "A Single-Junction Cathodic Approach for Stable Unassisted Solar Water Splitting" Joule 2019, 3, 2444–2456.
3. H. Hajibabaei, D. J. Little, A. Pandey, D. Wang, Z. Mi and T. W. Hamann, “Direct Deposition of Crystalline Ta3N5 Thin-Films on FTO for PEC Water Splitting”, ACS Appl. Mater. Interfaces 2019, 11, 17, 15457-15466.
4. Y. Wang, J. Schwartz, J. Gim, R. Hovden, and Z. Mi, "Stable Unassisted Solar Water Splitting on Semiconductor Photocathodes Protected by Multifunctional GaN Nanostructures", ACS Energy Lett. 2019, 4, 7, 1541-1548.

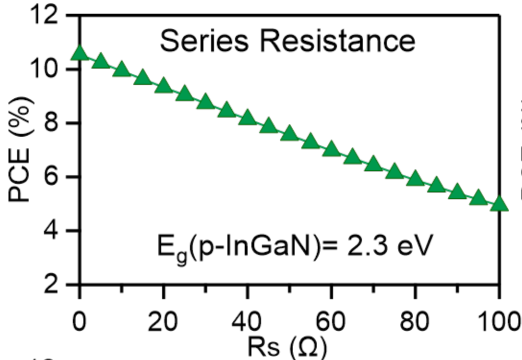
Conference presentations since last AMR:

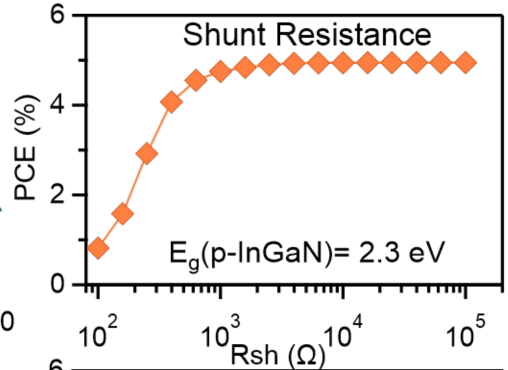
1. (Invited talk) Z. Mi and S. Vanka, “Monolithically Integrated Gallium Nitride and Silicon Photoelectrode for Efficient and Stable Artificial Photosynthesis”, 236th ECS Meeting Atlanta, Georgia, Oct. 13-17, 2019.
2. (Plenary talk) Z. Mi, “Emerging applications of III-nitride nanocrystals,” International Conference on Nitride Semiconductors, Bellevue, Washington, July 7-12, 2019.
3. (Keynote speaker) Z. Mi, “Gallium nitride: A platform towards practical artificial photosynthesis,” 102nd Canadian Chemistry Conference and Exhibition, Quebec City, Canada, June 3-7, 2019.
4. G. Zeng, S. Vanka, G. Liu, J. K. Cooper, Z. Mi and F. M. Toma, “GaN Protection Layer on Si Photocathode for Photoelectrochemical Water Splitting”, 236th ECS Meeting Atlanta, Georgia, Oct. 13-17, 2019.
5. S. Vanka, B. Zhou, N. Pant, A. Roberts, K. Kulkarni and Z. Mi, “InGaN/Si Tandem Photocathode for High Efficiency Unassisted Solar Water Splitting,” International Conference for Nitride Semiconductors, Bellevue, Washington, July 7-12, 2019.
6. S. Vanka, B. Zhou, N. Pant, A. Roberts, K. Kulkarni and Z. Mi, “InGaN/Si Tandem Photocathode for High Efficiency Unassisted Solar Water Splitting”, 61st Electronic Materials Conference, University of Michigan, Ann Arbor, Michigan, June 26-28, 2019.

Technical Backup Slides

Design of Si-based tandem photoelectrodes

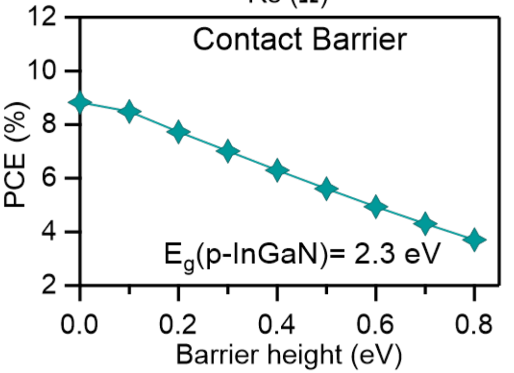
Y. Yan, Univ. Toledo

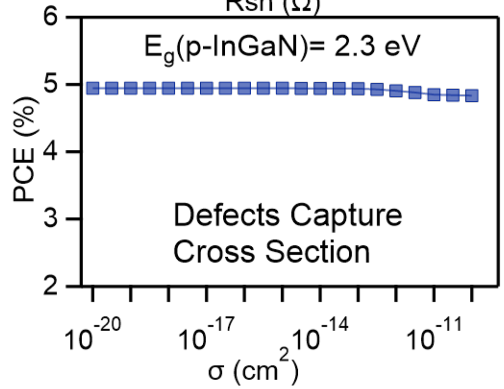


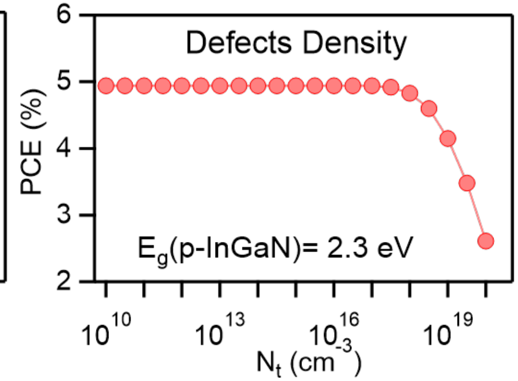


Simulated parameters of top cell

Junction	Rs (Ω/cm^2)	Rsh (Ω/cm^2)	$q\phi$ (eV)	σ_e (cm^{-2})	σ_h (cm^{-2})	E_t (eV)	N_t (cm^{-3})
ideal	0	∞	0.00	1e-18	1e-18	0.10	1e13
non-ideal	10^2	10^3	0.60	1e-15	1e-15	0.25	1e18





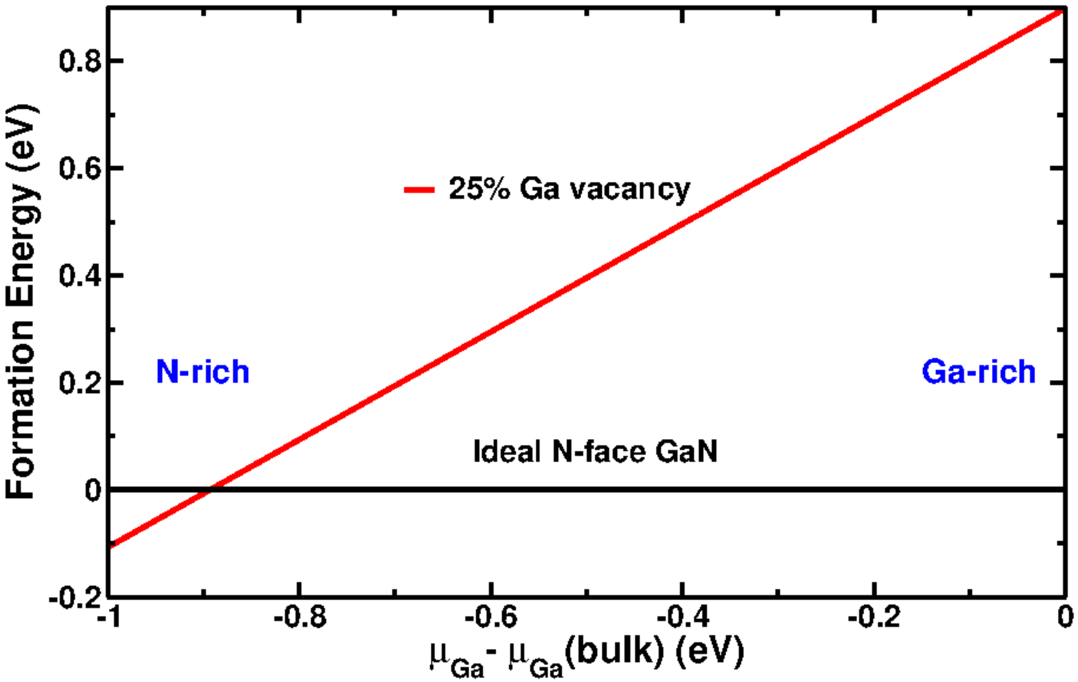


Rs and Rsh are series and shunt resistances
$q\phi$ contact barrier/s
N_t defect density
σ_e and σ_h electron and hole capture cross sections

- **Non-ideality factors, including Rs, Rsh, contact barrier/s, and defect density and their capture cross section, play a significant role in improving the STH efficiency.**

Surface Models of N-rich $(000\bar{1})$ GaN

T. Ogitsu, LLNL

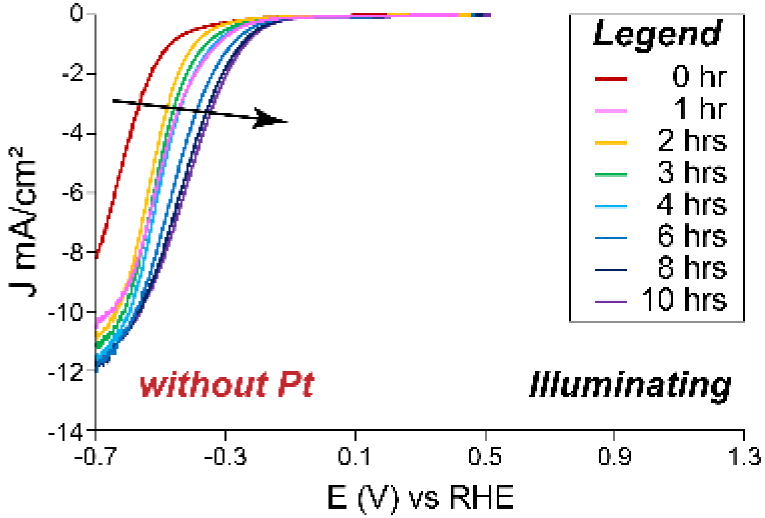


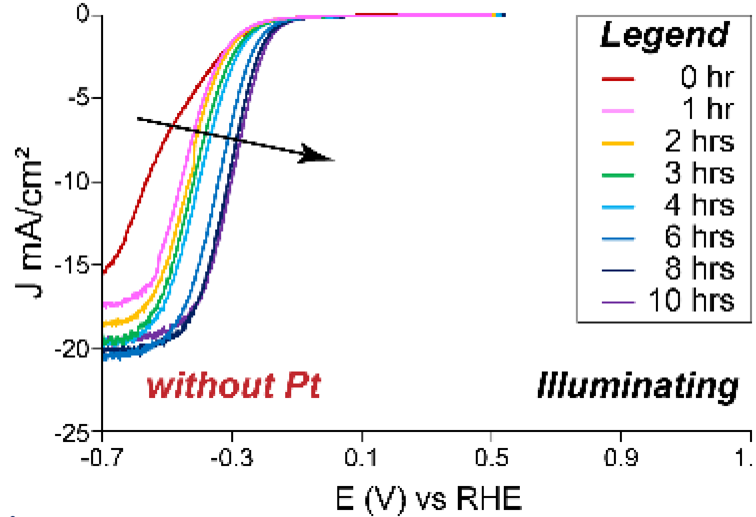
Surface with 25% Ga vacancy is more stable than the pristine one at the N-rich condition

- **Simulations reveal several possible non-stoichiometric surfaces that are stable than the pristine surface**
- **Integrating simulation results with LBNL's experiments is ongoing to understand the electronic properties of GaN surfaces under experimental conditions**

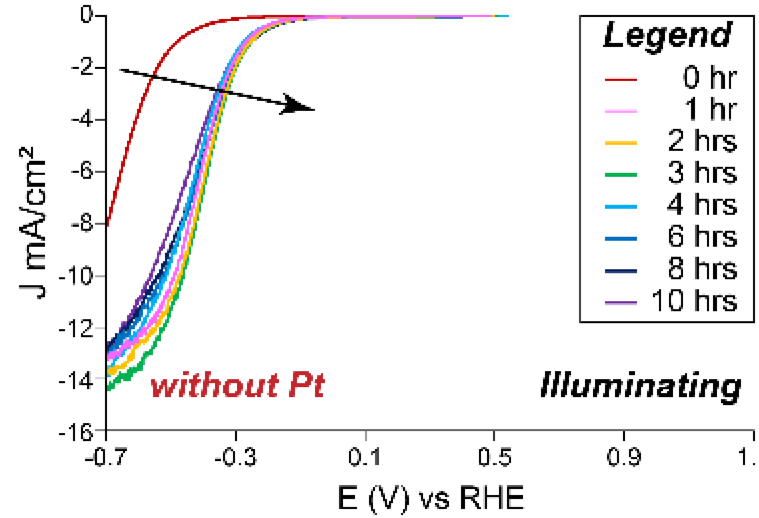
PEC Performance of GaN Protected Si Photocathodes

F. Toma, LBNL



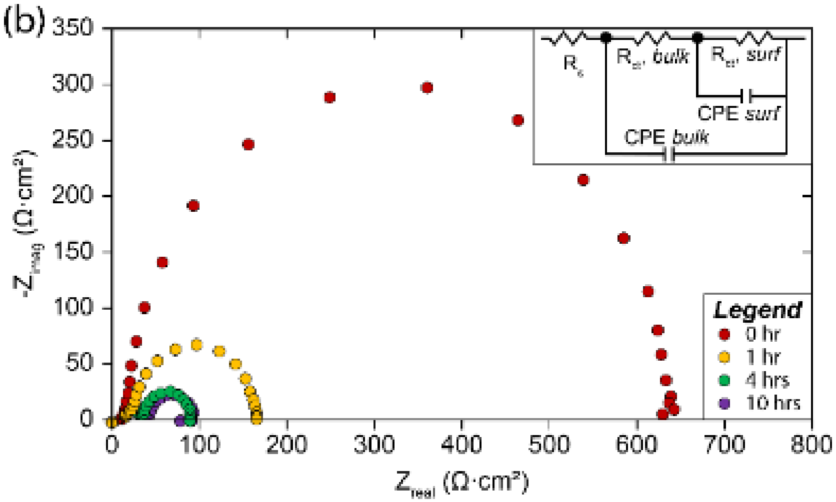


- GaN protected Si photocathodes with various thicknesses (5 to 150 nm) were studied and showed no degradation (initial performance improvement was observed).
- The performance is similar and has no dependence on the thickness of GaN, due the near-perfect conduction band alignment between GaN and Si. This is in direct contrast to conventional TiO_2 protection layer, which is compromises charge carrier transport.

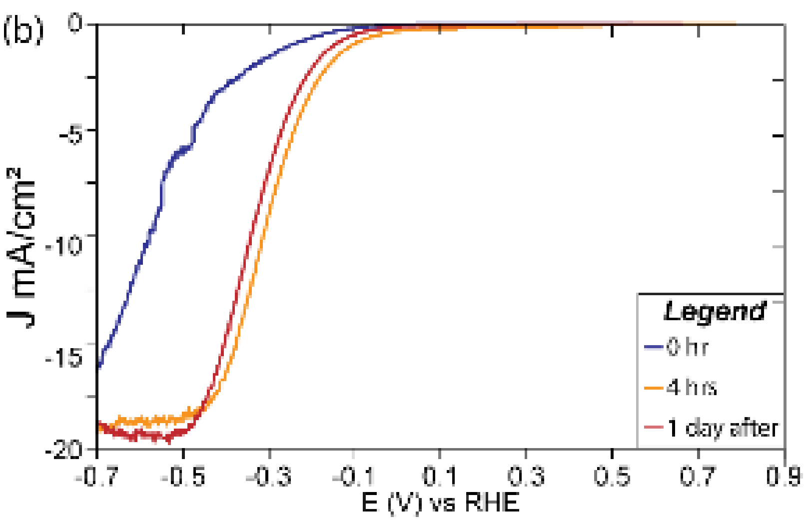


PEC Performance of GaN Protected Si Photocathodes

F. Toma, LBNL



	R_s	R_{ct}, bulk	R_{ct}, surface	CPE surface	CPE bulk
pristine	10.24	16.67	611.5	1.53×10^{-6}	1.33×10^{-6}
CA-1hr	11.97	17.56	136.7	1.94×10^{-6}	1.73×10^{-6}
CA-4hrs	17.42	15.32	109.2	2.41×10^{-6}	6.90×10^{-7}
CA-10hrs	17.39	18.21	104.7	3.05×10^{-6}	7.33×10^{-7}



- **EIS evidenced a decrease of surface resistance, indicated a surface change during the PEC process**
- **Working electrode was stored in drawer after the test (for 4 h) and dried, revisited after a day, and the PEC performance was almost the same, demonstrated this self-improving was a permanent change rather than organic species contamination**