Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

# RU-EMN – Best-in-class Platinum Group Metal-free Catalyst Integrated Tandem Junction PEC Water Splitting Devices


**PIs: Eric Garfunkel & G. Charles Dismukes***

**Presenter: G. Charles Dismukes**

**Rutgers, the State of University of New Jersey**


**6/13/2018**

1766-2016 RUTGERS 250

Project ID # pd160


This presentation does not contain any proprietary, confidential, or otherwise restricted information


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

# Project Overview

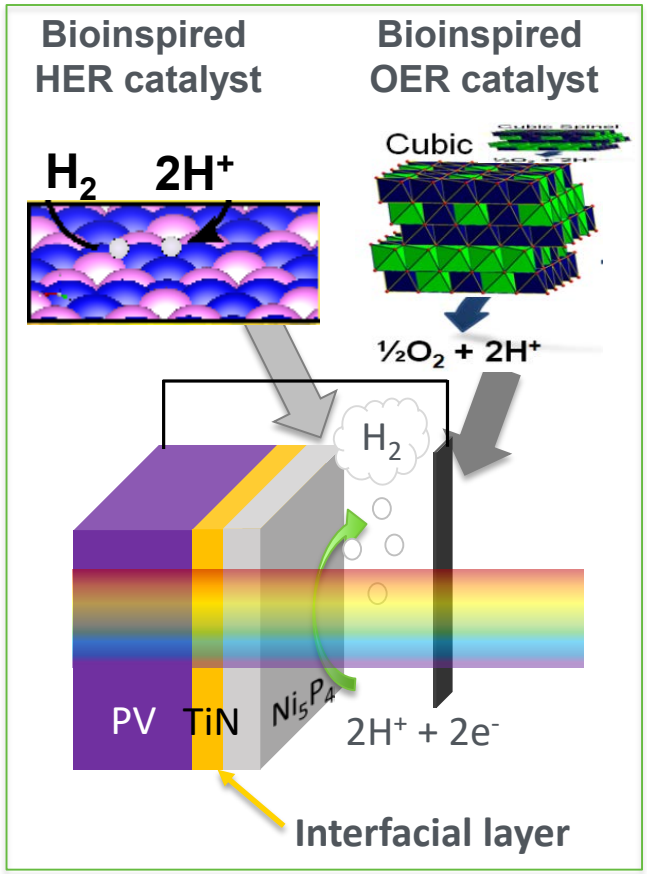
## Partners

**Rutgers PIs: E. Garfunkel & G. C. Dismukes,**
**coPI: M. Greenblatt**
**NREL: T. Deutsch, D. Friedman & A. Zakutayev**

| Award # | EE0008083 |
|---|---|
| Start Date<br>Yr 1 End Date<br>Project End Date | 09/01/17<br>08/31/18<br>TBD |
| Total DOE Share<br>Total Cost Share<br>Year 1 DOE Funding* | $750,000<br>$83,334<br>$250,000 |

## Vision

Identify the best technical approaches to fabricate both High Performance (HP) & High Value (HV) PGM-free PECs:
-Using HP PEC NREL-proprietary tandem III-V photovoltaic
-Using HV PEC NREL nitrides & Rutgers oxynitrides in tandem
-Using Rutgers-proprietary electro-catalysts for $O_2$ - and $H_2$ - evolution




## Impact

- Reveal performance limits of two limiting PV configurations (HP vs HV) using best PGM-free Cats.
- Identify & solve interfacing problems.

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

# Approach- Summary

## Project Motivation

**High-performance Photovoltaics:** State of the art material competing with NREL HP III-V tandems (STH 16.7%) is: Multi-junction Silicon (STH 3.9%).
**High-value (HV)** – emerging photoabsorbers (level 3 readiness): NREL-developed $ZnSnN_2$, coupled with $SrNbO_2N$ are potential efficient and low-cost with high potential impact on global energy economy. Early development hurdles.
**TiN vs $TiO_2$ -** Rutgers developed thin-film passivation and protection layer.
**$LiCoO_2$ OER catalyst –** Rutgers developed alkali cat. w. performance on par with PGM-catalysts.
**$Ni_5P_4$ HER catalyst -** Rutgers developed acid & alkali cat. w. performance on par with Pt.

## Barriers

**Replace PGMs catalysts with non-noble metal catalysts without compromising efficiency**
➔ Apply active thin-film of RU-eCats which are on par with PGMs catalysts.
**Reduce light losses in Cat/Absorber interface (5 nm $MoS_2/MoO_x$ ~ 25% current loss)**
➔ Uses optimum thickness of catalyst with protection/anti-reflective layers (6.8 nm $NiP_2$/4 nm TiN ~ no current loss).
**Photoelectrodes corrosion in alkaline electrolyte**
➔ Use proper protection layer with alkaline stable RU-eCats.
➔ Use compatible alkaline buffers.

## Key Impact – year 1

| Metric | State of the Art | Expected Advance |
|---|---|---|
| HP - STH | Non-PGM STH 10% | *Match or beat using non-PGM RU-eCats.* |
| HV - Parameter 1 *($BiVO_4$ benchmark)* | $J_{ph}\|_{E=1.23V\ RHE}$ = 1.5mA/cm$^2$, Stable >90% for 1h, material-cost | Improve two or more metrics. |

## Partnerships

HydroGEN partners:

**Daniel Friedman (NREL)**
III-V Semiconductor Epi-Structure Device Design and Fab
*MOCVD GaInP/GaAs growth & engineering capabilities*

**Todd Deutsch (NREL)**

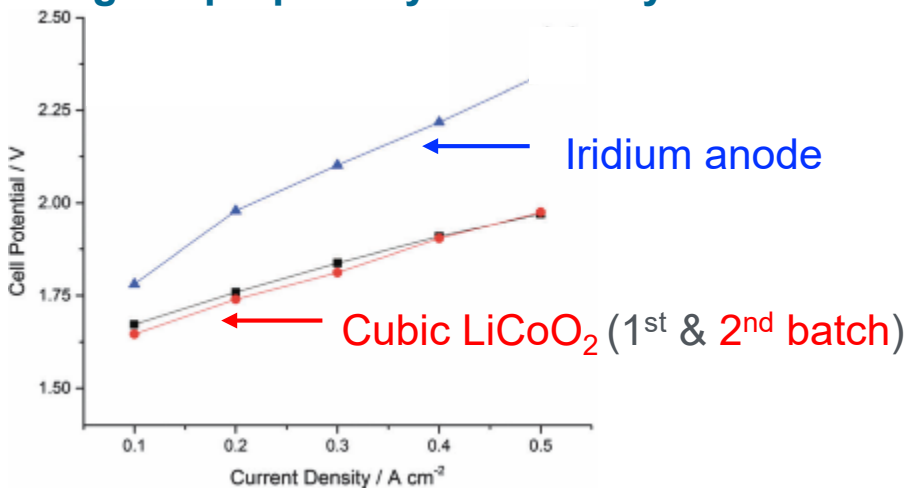
On Sun Characterization of Bulk and Interfaces
*Solar testing and benchmarking capabilities*

**Andriy Zakutayev (NREL)**
High-Throughput Thin-film Combinatorial Capabilities
*Multi-source and reactive sputtering capabilities*

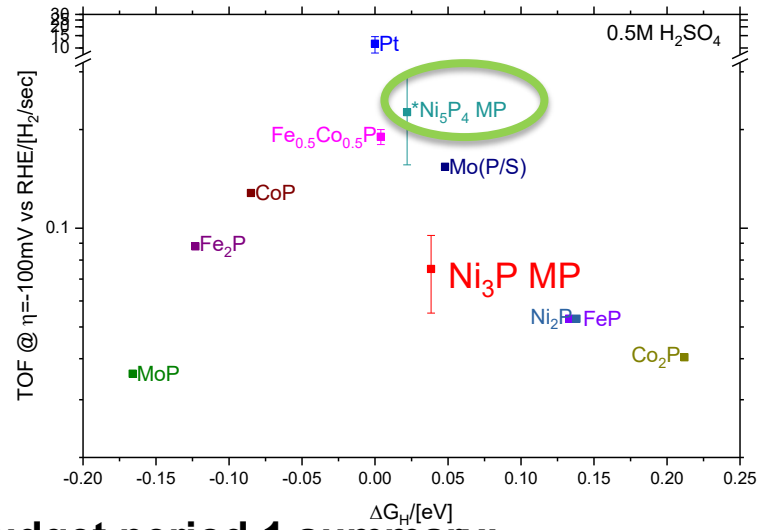
# Approach- Innovation year-1 Thrust

Design of catalyst/photoabsorber interfaces using PGM-free RU-eCats with state-of-the-art performance to NREL proprietary photoabsorbers.

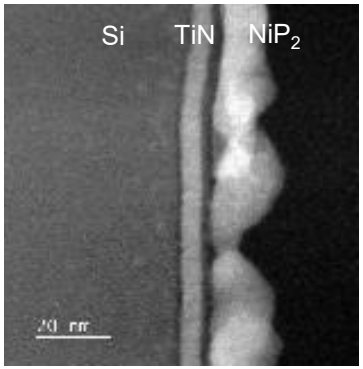
## Rutgers' proprietary OER catalyst

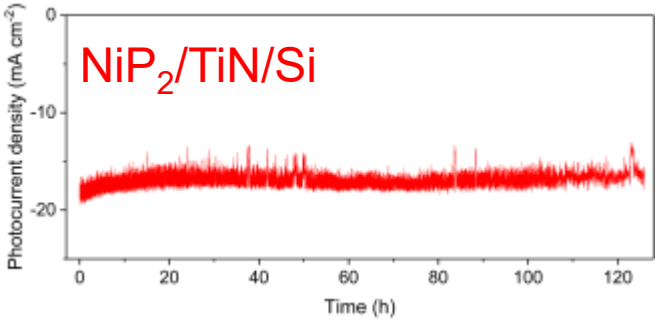



## Rutgers' proprietary HER catalyst




Designing RU-protection layer to stabilize photoabsorber interface and RU-eCat adhesion.



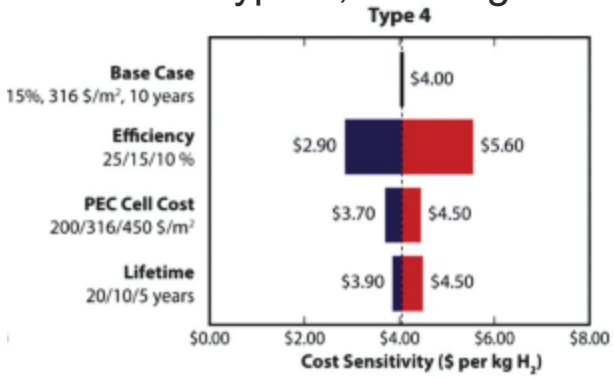

**Budget period 1 summary:**

Design, fabricate, characterize, and test first example of Rutgers protection (TiN) and eCat ($Ni_5P_4$, and $LiCoO_2$)layers on NREL HP (np-GaInP/$n^+$-GaAs) and NREL HV ($ZnSnN_2$).

# Relevance & Impact

| Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration[a] | | | | | |
|---|---|---|---|---|---|
| Characteristics | Units | 2011 Status | 2015 Target | 2020 Target | Ultimate Target |
| Solar to Hydrogen (STH) Energy Conversion Ratio [e, f] | % | 4 to 12% | 15 | 20 | 25 |

TEA of Type 4, tracking concentrator array PEC




Pinaud *et al. Energy Environ. Sci.* **6**, 1983 (2013)

•This project supports the development of non-PGM and scalable electrocatalysts for PEC water splitting. It will lower H2 costs by increasing STH efficiency, decreasing production costs using lower cost materials, and increase lifetime. These are critical to achieving the DOE target of hydrogen for <$2/kg.

**HydroGEN consortium**

Rutgers utilizes photoabsorbers and characterization facilities from three NREL nodes: 1) MOCVD GainP/GaAs growth & engineering capabilities (Friedman)[ 2) Solar testing and benchmarking capabilities (Deutsch); 3) Multi-source and reactive sputtering capabilities (Zakutayev).

This team develops innovative approaches to making interfaces with combined protection/anti-reflective layers. Bi- and tri-weekly meetings coordinating efforts have been undertaken.

Rutgers offers unique Nion STEM with ultra-high resolution EELS vibrational spectroscopy, Rutherford (and medium ion) backscattering spectroscopy and high resolution He-ion microscopy capabilities through collaboration.

# Approach- Milestones

| Milestones | Anticipated Qtr | Milestone Description (Go/No-Go Decision Criteria) | Milestone Verification Process (What, How, Who, Where) | Status |
|---|---|---|---|---|
| **#1** | Q1 | Determine which substrate has the best performance/cost while optimizing the loading of the $LiCoO_2$ catalyst | E vs OER < 500mV, stable for 24h, loadings ≥ RDE pellets, Electrochemical test in flooded cells, Rutgers | **complete** |
| **#2** | Q2 | Device test under illumination showing: $V_{OC}$ > 1.85 V, $J_{SC}$ > 10 mA/cm$^2$, and $\eta_{eff}$ > 25% | Photoeletrochemical benchmarking, NREL | **complete** |
| **Go/No-Go Crtieria for Thrust 1** | Q4 | Evaluation of high performance PEC device with renewable catalysts | STH> 10%, stability > 24h, and/or $J_{ph}$ (at 0 V vs. RHE) > 10mA/cm$^2$, Photoelectrochemical benchmarking, Rutgers and NREL | **50%** |
| **#3** | Q3 | Fabricate and report optimized $ZnSnN_2$ device | Optimize reflector - max reflectivity, Balancing the highest possible carrier mobility with closeness to 1.1eV bandgap, Rutgers | **25%** |
| **Go/No-go Criteria for Thrust 2** | Q4 | $LiCoO_2/ZnSnN_2$ photoanode fabricated and benchmarked against $BiVO_4$ | Must outcompete on (at least 2): $J_{ph}$ (1.5mA/cm$^2$ at 1.23 V vs. RHE), stability >90% after 1h, and material cost, Rutgers, NREL | **2%, started** |

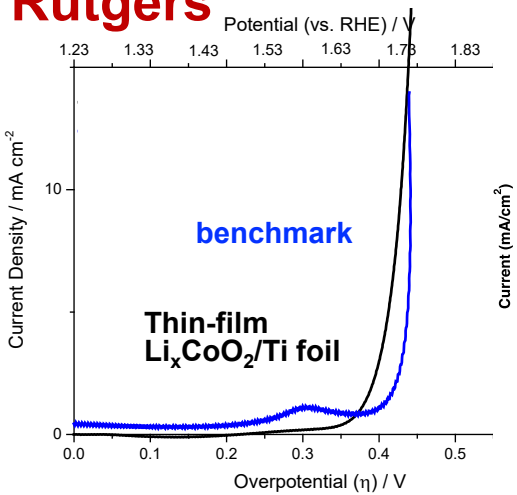
All milestones are completed or on-track for on-time completion

# Accomplishments – Overview

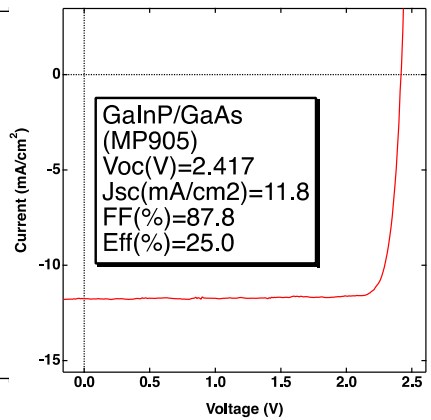
Q1 (end of 2017) | Q2 | now | Q3 | Q4 Go/No-Go decision

On-track

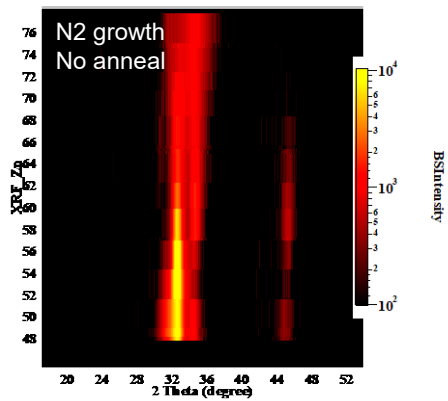
**Milestone #1** ✓ (HP anode) — **Rutgers**




**Milestone #2** ✓ (HP photoabsorber) — **NREL**




**Milestone #3** (HV synthesis photoabsorber) — **NREL**




**HP device:**

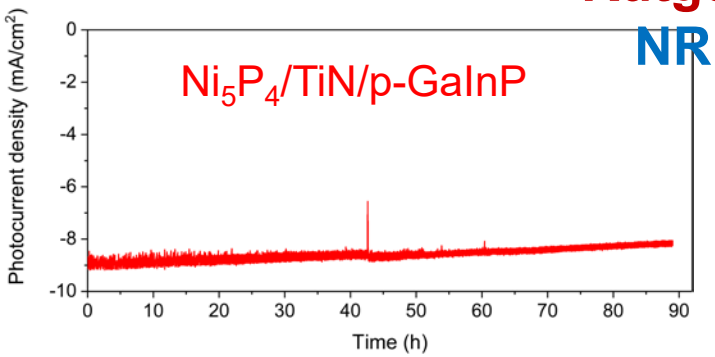
**STH >10% using PGM-free with III-V tandem device**

**HV photoanode:**

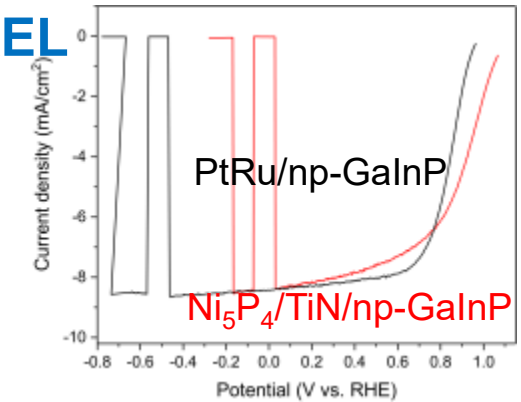
**$J_{ph}$ (1.5 mA/cm$^2$ at 1.23 V vs. RHE), stability**

**Promising data from Task #2 (HP catalyst/protection layer)** ✓

*Durability test* — **Rutgers**




*$Ni_5P_4$ is on par with PtRu* — **NREL**



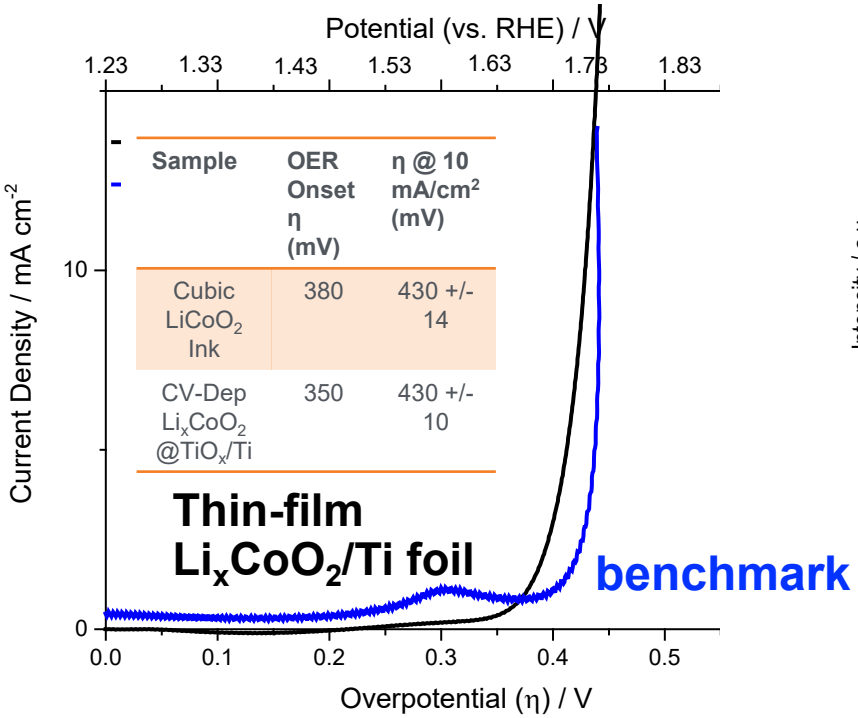

**NREL: III-V semiconductor node & semiconductor characterization nodes**

**NREL: High throughput experimental thin-film node**

# Accomplishments: Electrochemical (dark) anode

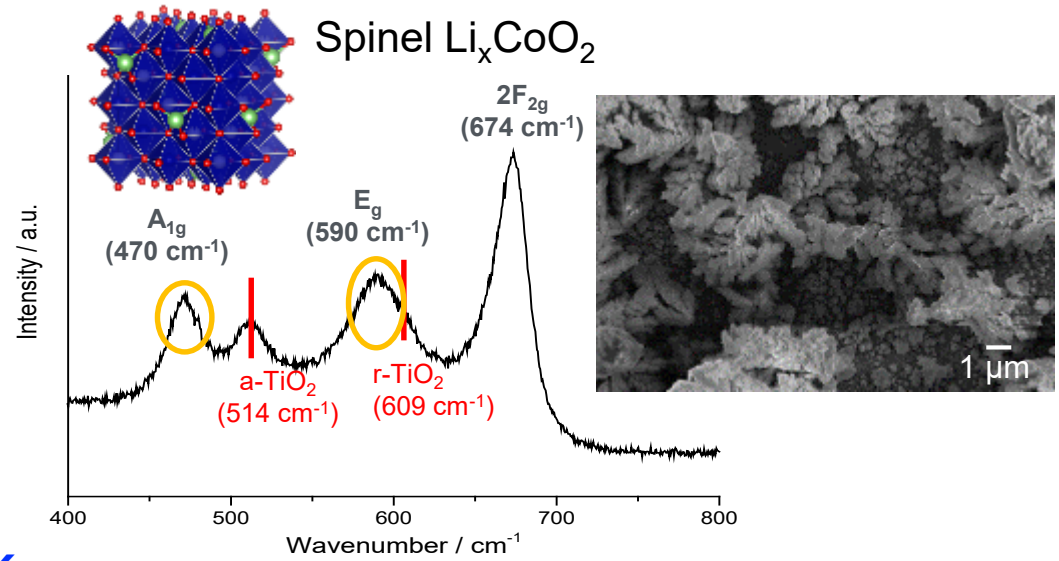
- Milestone 1 (**achieved Q1**) realize a stable non-PGM alkali $LiCoO_2$ electroanode (on par with published cubic-$LiCoO_2$ benchmark) with at least long-term stability (>1 day) required in milestone #1.

Overpotential achieved Milestone #1




| Sample | OER Onset η (mV) | η @ 10 mA/cm$^2$ (mV) |
|---|---|---|
| Cubic $LiCoO_2$ Ink | 380 | 430 +/- 14 |
| CV-Dep $Li_xCoO_2$ @$TiO_x$/Ti | 350 | 430 +/- 10 |

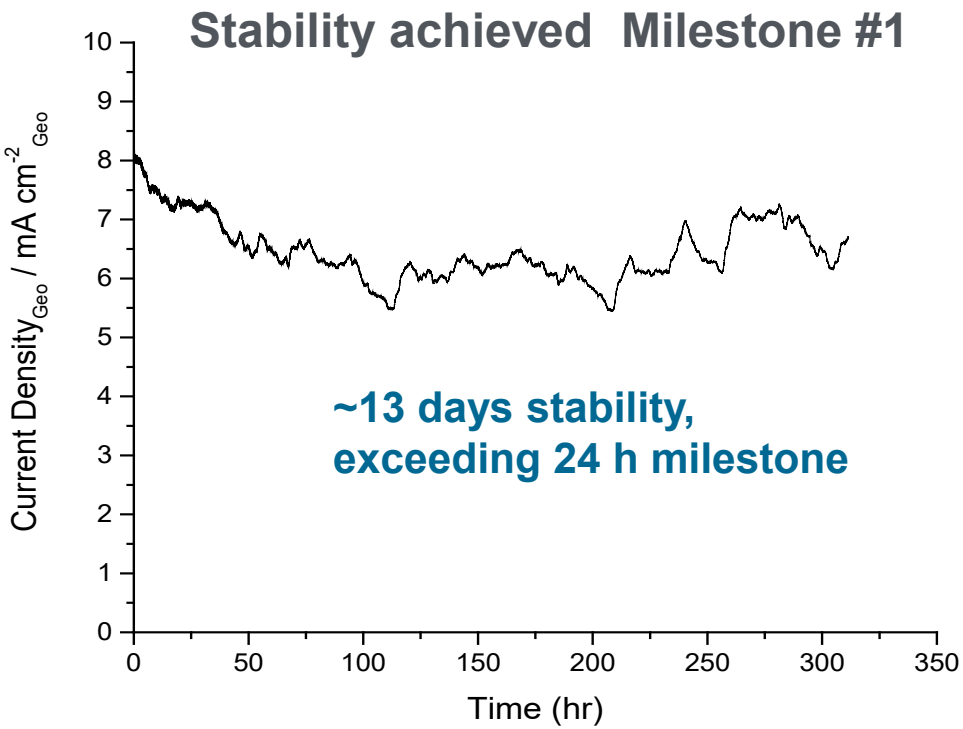
Characterizations (Raman/SEM)

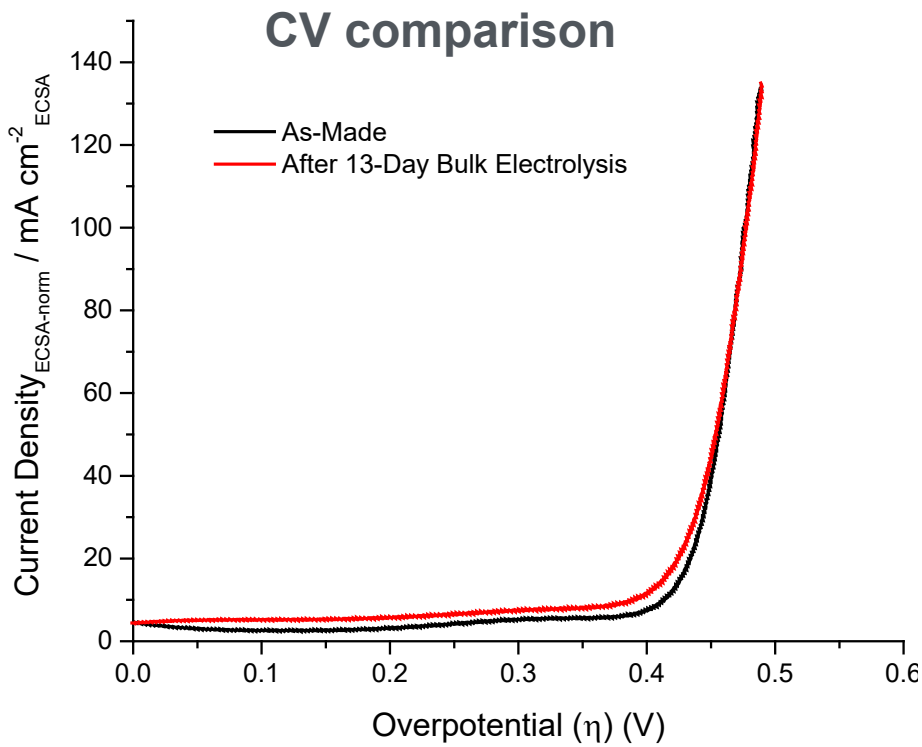



- Technical target: Overpotential, η ≤ 430 mV at 10 mA/cm2geo in pH 14 electrolyte

- Raman spectroscopy signals indicates localized spinel structure. XPS confirm only $Co^{3+}$ precluding unstable $Co_3O_4$ formation (Data not shown).

# Accomplishments: Electrochemical (dark) anode

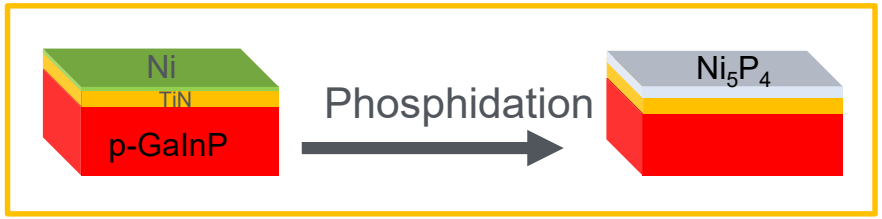


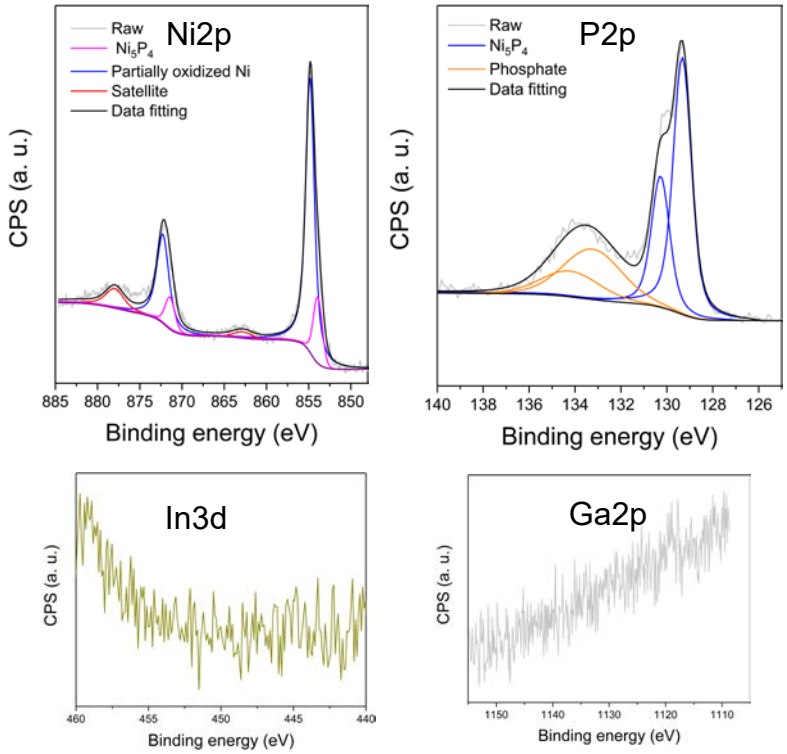

- Chronoamperometric analysis for OER confirms >12 days of stability.
- Surface area normalized CVs shows same intrinsic activity. Minor decreased activity (during durability test) is due to loss of surface area attributed to particle detachment.
- **Achieved Task 3 "Optimize $LiCoO_2$ electrode loading" and milestone 1.**

# Accomplishments:
## Successful integration of $Ni_5P_4$/TiN on p-type GaInP

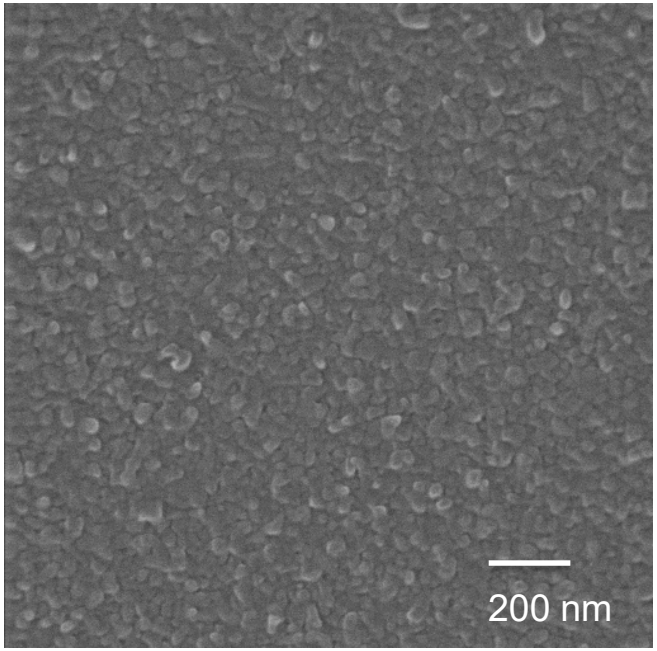
**Transferring optimized synthesis condition for proprietary NREL PV**
***- Synthesis development of catalyst/protection layers, Tech slide 1, 2***




**Top layer XPS**



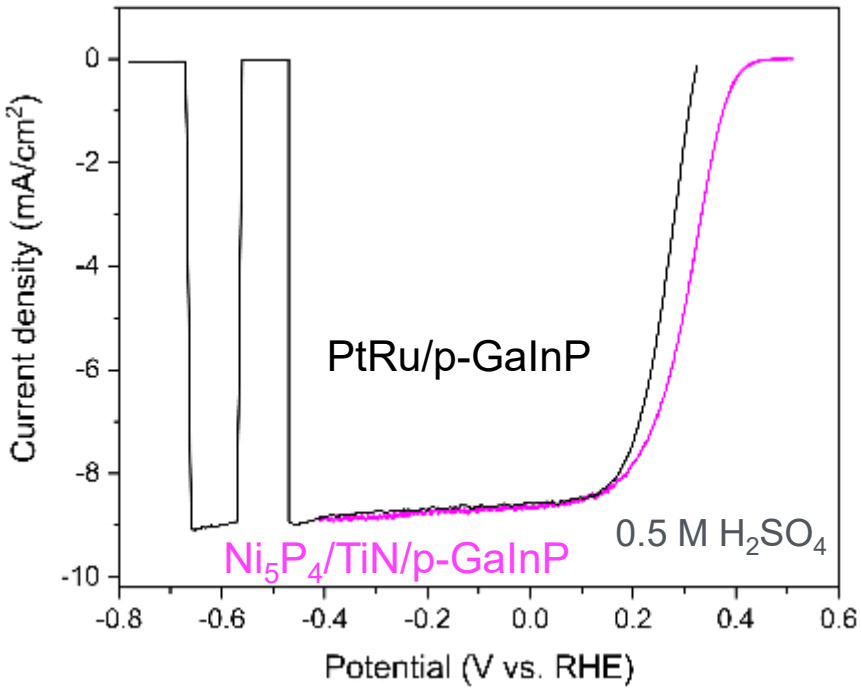

Helium Ion Microscope (HIM) image shows uniform catalyst coverage



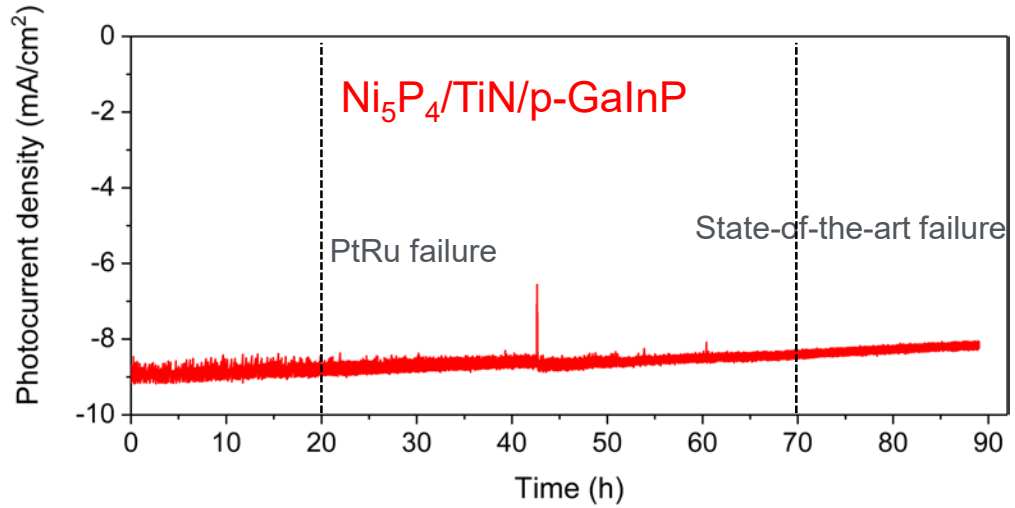

- Top layer XPS confirms successful formation of nickel phosphide catalyst without atomic diffusion of In and Ga

# Accomplishments:
## Successful integration of $Ni_5P_4$/TiN on p-type GaInP

### J-V Performance
### On par with PGM benchmark



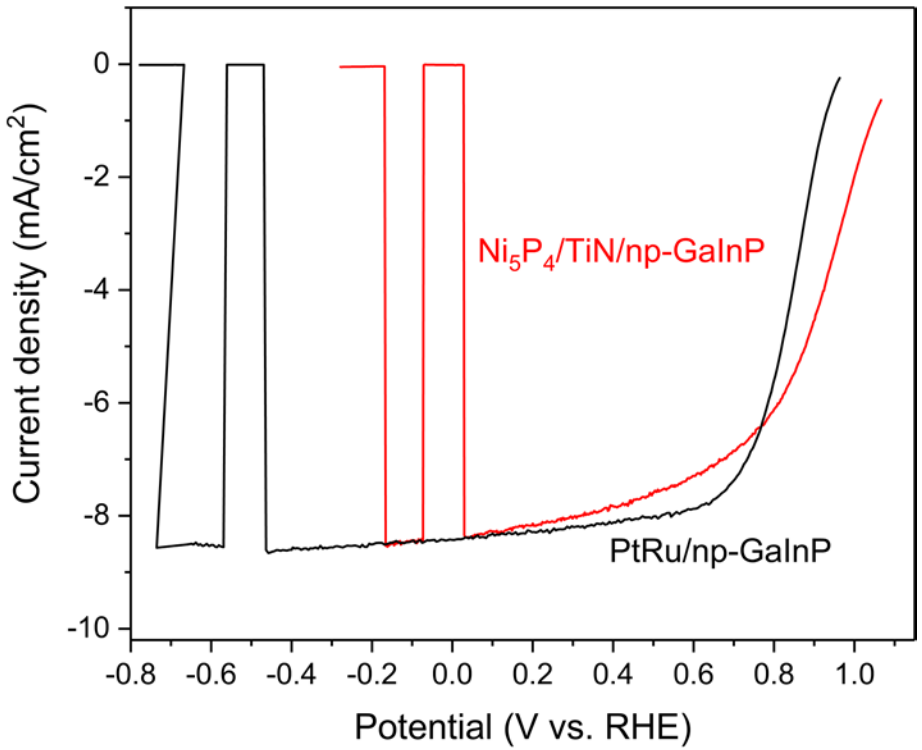

### Durability test



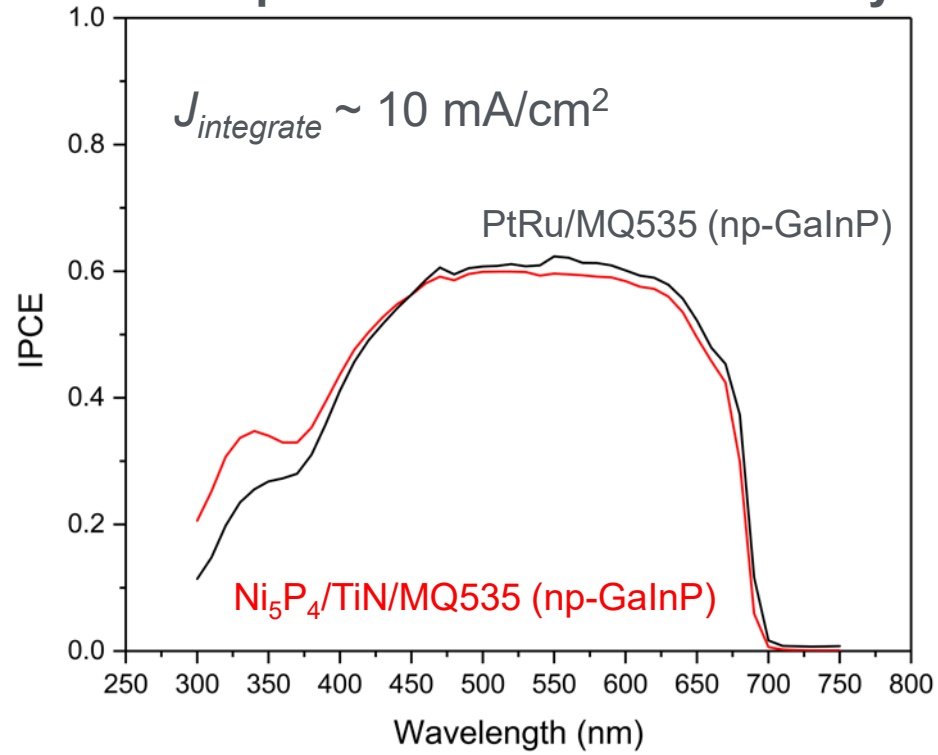

- $Ni_5P_4$/TiN layers on p-GaInP are on par with PtRu/p-GaInP. ($V_{onset}$ ,and $J_{sat}$)
- Durability test demonstrates 89 h stability of $Ni_5P_4$/TiN/p-GaInP device in acid
- **Achieved Task 2 "Optimize catalyst/photoabsorber (Nickel Phosphide/GaInP) interface"**

# Accomplishments:
# Benchmarking $Ni_5P_4$/TiN/np-GaInP at NREL_Deutsch

## J-V Performance 1st trial




## Incident photon-to-current efficiency

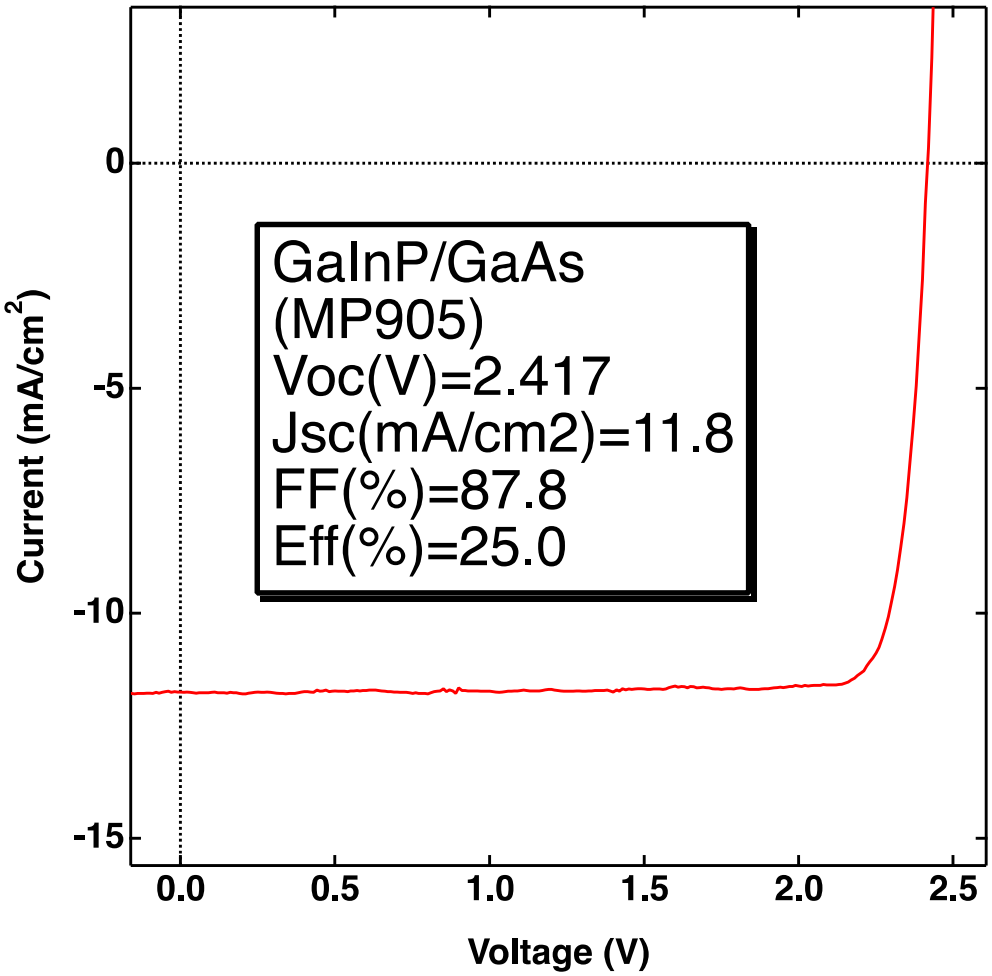



- PEC measurement were verified at the **NREL node**.
- Introducing buried junction np-GaInP increases $V_{onset}$ (from 0.4 V to 1.0 V vs. RHE).
- Test proves the performance of $Ni_5P_4$/TiN/np-GaInP is on par with benchmark PtRu/TiN/np-GaInP.

# Accomplishments:
## NREL fabrication of GaInP/GaAs high-efficiency PV

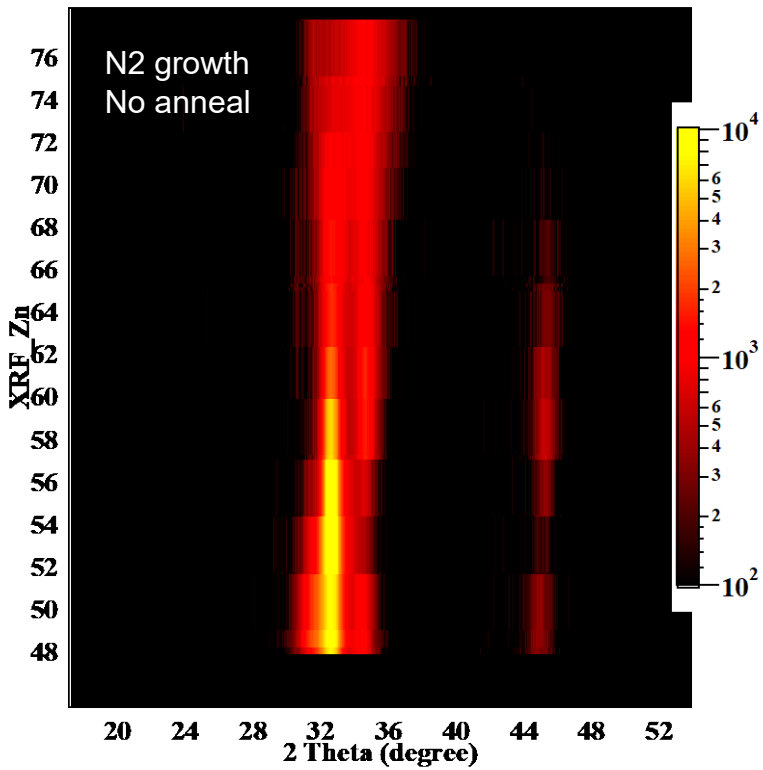
Milestone #2 (**achieved Q2**) fabricate a high-efficiency PV cell for photoabsorbers: $V_{OC}$ > 1.85 V, $J_{sc}$ > 10 mA/cm$^2$, and $\eta_{eff}$ > 25%

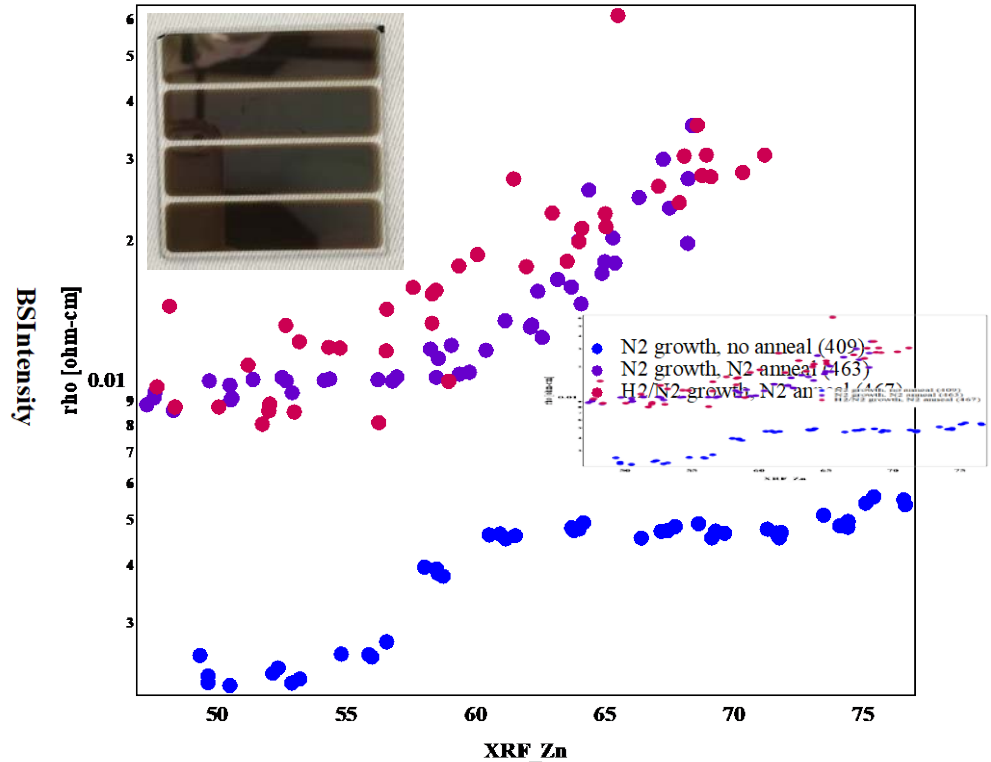
- NREL_Friedman node provided an upright tandem photoabsorber (GaInP/GaAs) that exceeds required properties. This photoabsorber will be coupled with RU-eCat and protection layer for unassisted water splitting.
- **Achieved Milestone #2**



# Accomplishments:
## NREL fabrication of thin-film $ZnSnN_2$

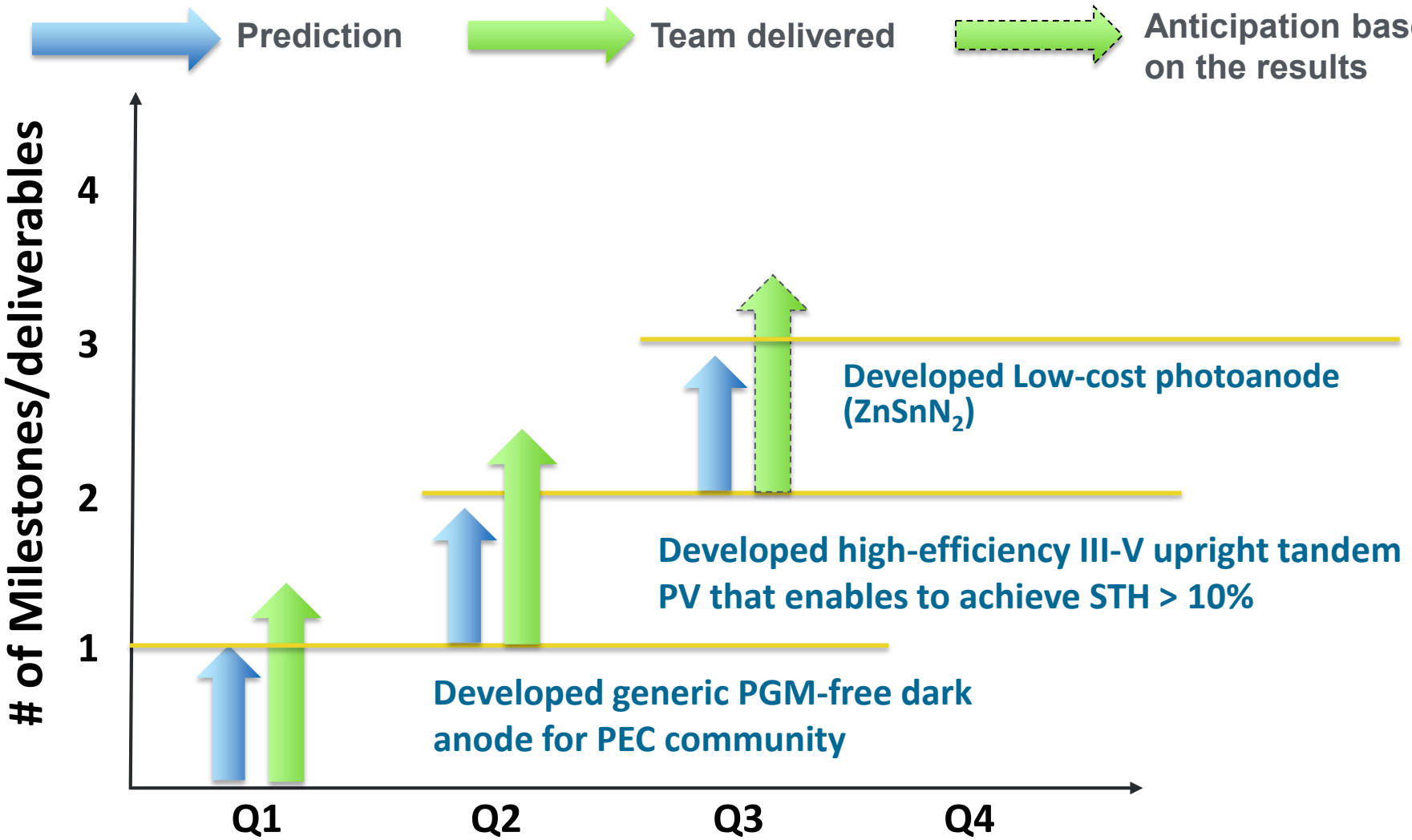
Milestone #3: Fabricate $ZnSnN_2$ thin film:




- NREL_Zakutayev node provided synthesis (confirmed by XRD, XRF) and investigated post-annealing conditions for $ZnSnN_2$ that can generate proper conductivity for photoanode applications.
- **Task9 On-track to achieve milestone #3,** "Fabricate $ZnSnN_2$ photoabsorber "

# Accomplishments - Outlook



# Collaboration: Multiple interactions with HydroGEN nodes

**NREL: III-V semiconductor & semiconductor characterization nodes**

**NREL: High throughput experimental thin-film node**

| Date | Meetings w/ | Presenter | Outcomes |
|---|---|---|---|
| 11/13/17 | **NREL**<br>**NREL** | N/A | HydroGEN kick-off meeting – project initiation |
| 1/26/18 | **NREL** | Rutgers | Understanding native oxides on GaInP for improving TiN adhesion<br>**(Task 2)** |
| 2/23/18 | **NREL** | Rutgers | Optimize fabrication conditions for $Ni_5P_4$ thin-film<br>Successful fabrication of $Ni_5P_4$/TiN on p-GaInP<br>**(Task 2)** |
| 3/16/18 | **NREL** | Rutgers | Characterization of $Ni_5P_4$/TiN/p-GaInP and npGaInP<br>Discussion for benchmarking test (IPCE)<br>**(Task 2,4, and Go-No/Go1)** |
| 3/22/18 | **NREL** | **NREL** | Optimization of fabrication condition for $ZnSnN_2$<br>**(Task 9, Milestone 3)** |
| 4/13/18 | **NREL** | Rutgers<br>**NREL** | Prove $Ni_5P_4$ is on par with PtRu on GaInP (Task 2, Go-No/Go1)<br>Fabrication of np-GaInP/np-GaAs tandem PV<br>**(Task 1, Milestone 2)** |

# Collaboration: Data sharing within HydroGEN

## Data sharing:

Verified data uploaded to HydroGEN site and Datahub. Quarterly reports with input from both RU and nodes shared in HydroGEN site and Datahub. This has allowed the continues sharing of progress, samples needed, problems encountered, verification of experimental test procedures. The continuous sharing of results have been critical to the fast paced progress on this project. Sharing to the water splitting R&D community will be realized through publication as well as opening access to the verified raw data in the datahub after the project period. Data shared in publications will be opened for sharing at the time of publication.

## HydroGEN community interaction:

| | Means of communication | Node/point of Contact(s) |
|---|---|---|
| **Pre-proposal submission** | In-person (ECS conference) | James Young NREL |
| | Telecon | Todd Deutsch NREL |
| **Post-award** | **Means of communication** | **Node/point of Contact(s)** |
| | Telecon | Todd Deutsch NREL |
| | Telecon | Michael Ulsch NREL |
| | In-person (Kick-off meeting) | Todd Deutsch NREL, Michael Ulsch NREL, Daniel Friedman NREL, Aditya Mohite LANL, PEC workgroup |
| | Biweekly Telecon for progress reports | Todd Deutsch NREL, Daniel Friedman NREL |
| | Telecon for progress report | Andriy Zakutayev NREL |
| | In-person (Seattle ECS meeting) | PEC working group |

# Proposed Future Work Y2 & Y3

## Thrust #1, High Performance PEC

**Scope:** Build complete PEC device based on NREL's incrementally advanced III/V-photoabsorbers & next generation RU-eCats.

- State-of-the-art PECs operate in acid electrolyte, where PGM-free anodes are not stable. Extending operation to alkali presents the first attempt to achieve this key-property for fully PGM-free operation.

**Y2:** Fabricate protection/catalyst layers for alkali operation. Improve performance under diurnal cycle (low current regime) where recombination & photocorrosion may increase. ***Outcome: stable operation for > 24h in alkali, stable performance under diurnal cycle.***

- Evaluating the long-term stability of the optimized device is crucial for an accurate H2A and LCA analysis. Cost-benefit analysis will quantify the impact of the achieved improvements over state-of-the-art PEC devices to achieve target of <$2/kg $H_2$.

**Y3:** Extended stability tests under solar concentration. Perform H2A and LCA modelling employing HydroGEN node. ***Outcome: Long-term stability, effect of electrolyte, effects of PGM-free catalysts on $H_2$ costs.***

## Thrust #2, High Value PEC

- State-of-the-art HV PECs show limited performance and stability. Thin-film fabrication of oxynitride and double inorganic perovskite salt (DIPS) based electrode represent level 3 (early stage development) photoabsorbers with low-cost potential.

**Y2-Y3: Development of level 3 photoabsorbers with HydroGEN nodes.** Build complete PEC device based on $ZnSnN_2$ photoabsorber/RU-eCat electrodes. Development of oxynitride and DIPS photoanodes collaboration with NREL High-Throughput Experimental Thin-film Combinatorial Capabilities (Zakutayev) and High-Throughput Processing node (Ulsh).

**Y2:** Develop buried junction-type oxynitride thin-film. Optimize protection/catalyst layers for oxy-nitride photocathode and DIPS photoanodes. ***Outcome: novel buried junction-oxynitride photoabsorber, stable operation in alkali, DIPS thin-film photoabsorber/photoelectrode.***

**Y3:** Stability tests under solar concentration, plus H2A and LCA modelling employing HydroGEN node.

- Direct comparison of cost-benefit analysis for HV and HP devices from same team for ultimately achieving DOE targets.

# Project Summary

*Q1 (end of 2017)* — *Q2* — *Q3* — *Q4 Go/No-Go decision*

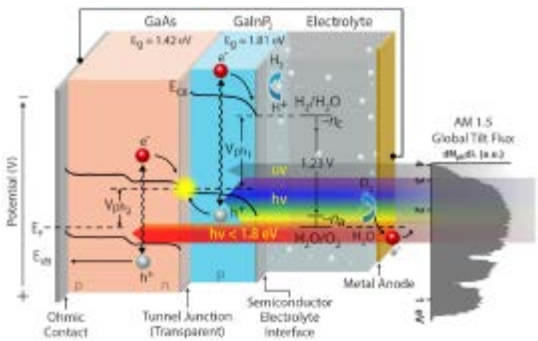
**Milestone #1** ✓ **(HP anode)**

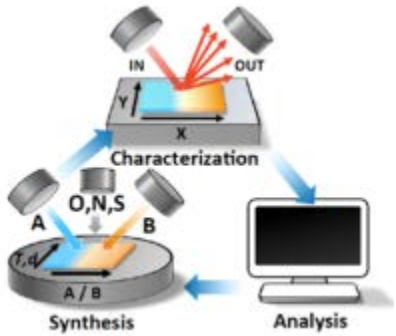
**Milestone #2** ✓ **(HP photoabsorber)**

**Milestone #3** **(HV synthesis photoabsorber)**

**On-track**

Achieved and exceeded all millstones; on-track to achieve Go/No-Go decision

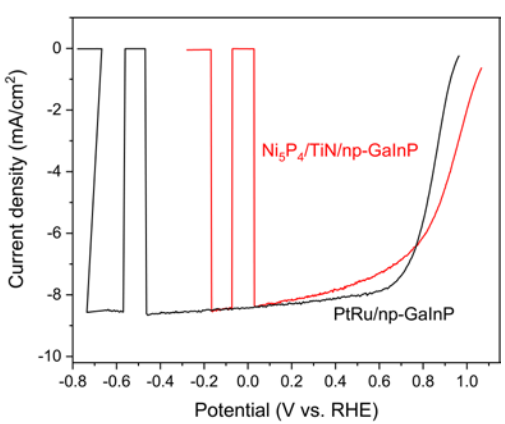


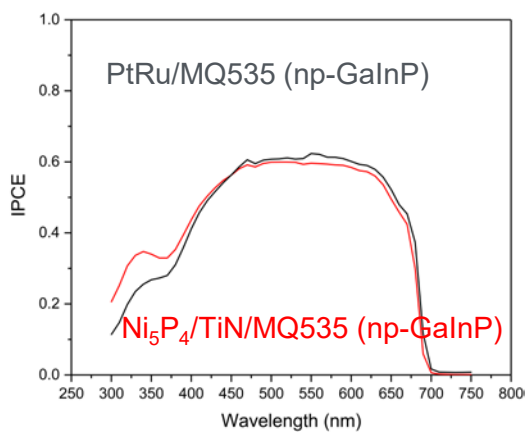




**NREL: III-V semiconductor & semiconductor characterization nodes**

**NREL: High throughput experimental thin-film node**

Effective utilization of HydroGEN nodes (6 meetings over 6 months)




Benchmarking test at NREL

# Thank you for your attention

1766-2016 RUTGERS 250

iAMDN Institute for Advanced Materials, Devices, and Nanotechnology

RUTGERS Energy Institute

Eric Garfunkel

Charles Dismukes

Martha Greenblatt

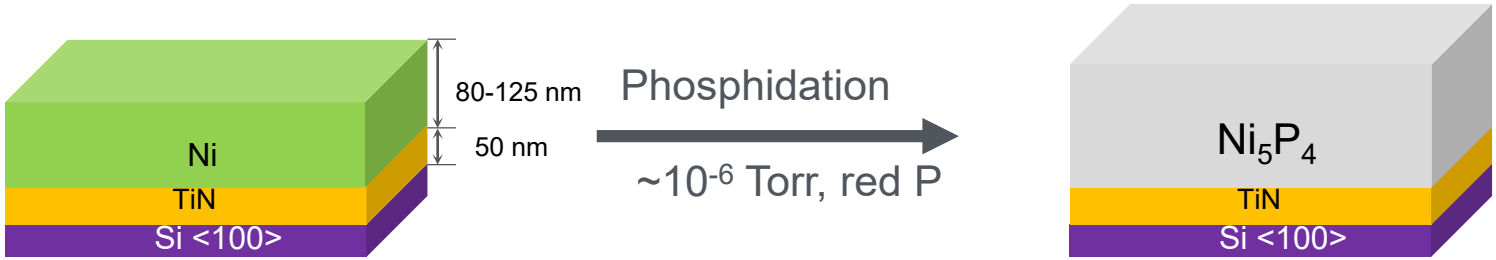
Anders Laursen

Shinjae Hwang

# Technical Back-Up Slides

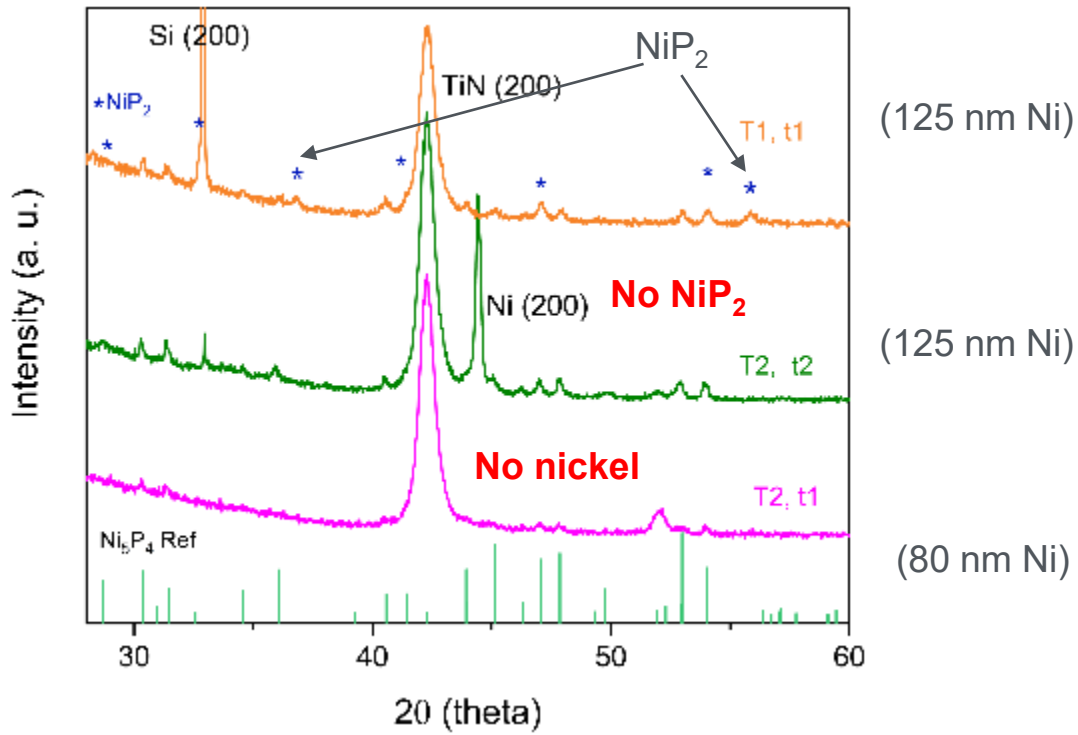
# Accomplishments:
## Low-temperature $Ni_5P_4$ thin-film synthesis

### Using Si-PV model for catalyst synthesis optimization

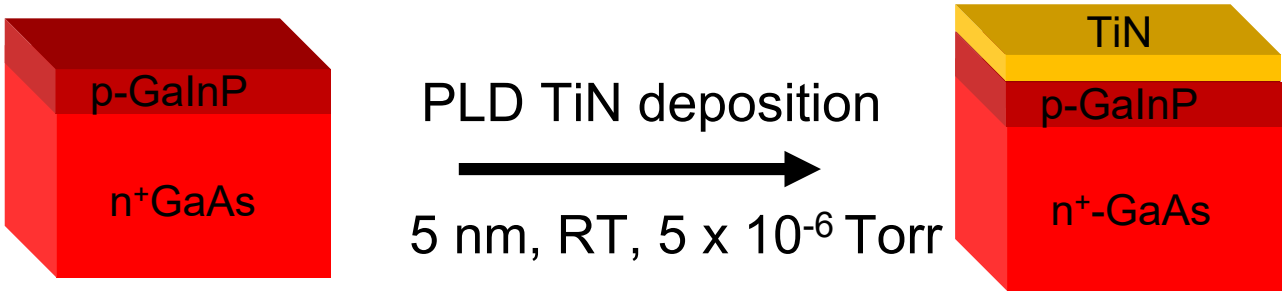


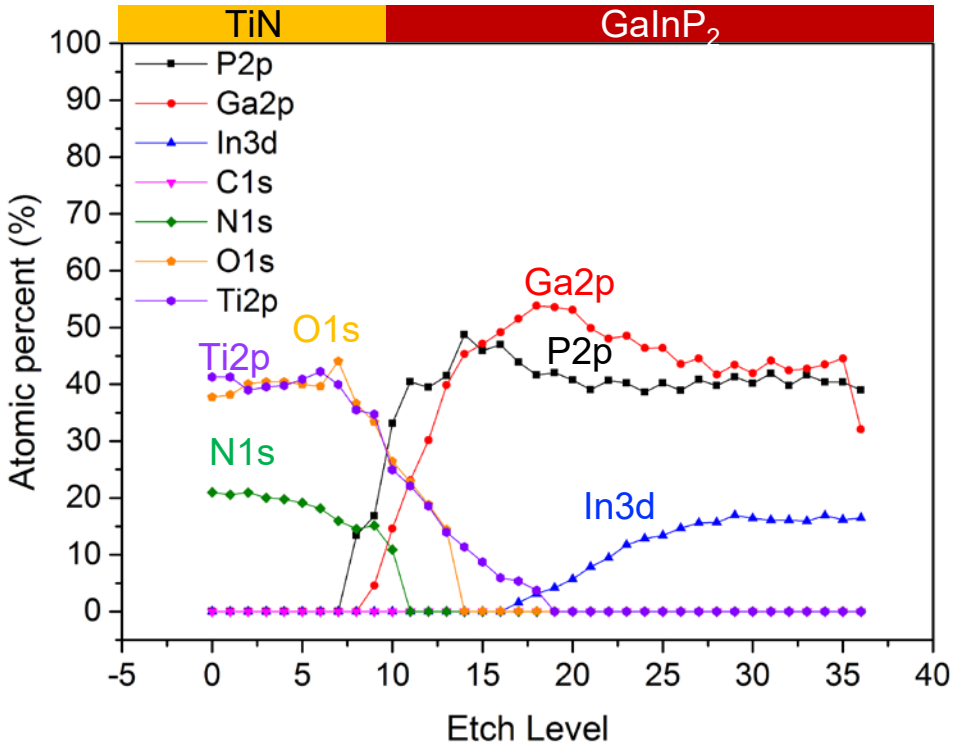

A thick layer is on purpose for getting X-ray diffraction

**Phase-pure crystalline $Ni_5P_4$ can be obtained with choice of temperature and time.**



# Accomplishments:
## Low-temperature fabrication TiN thin-film




**XPS depth profile shows no significant atomic diffusion was detected**