Tunable Photoanode-Photocathode-Catalyst Interface Systems for Efficient Solar Water Splitting

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Project ID# PD121

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Overview

Timeline

- Project Start Date: Sept 1, 2014
- Project End Date: Aug 31, 2017
- Percent complete: 89%

Barriers addressed

- AE. Materials Efficiency – Bulk and Interface
- AF. Materials Durability – Bulk and Interface
- AI. Auxiliary Materials
- AJ. Synthesis and Manufacturing

Budget

- Total Project Budget: $749,996
  - Total Recipient Share: NSF disallows
  - Total Federal Share: $749,996
  - Total DOE Funds Spent: $667,496 as of 4/10/17

Unfunded Collaborators

Current:

- Andrew Rappe (Upenn)
  - Ni-P HER theory

EMN (pending):

- Andriy Zakutayev (NREL)
  - $ZnSnN_2$ photoabsorber
- Todd Deutsch (NREL)
  - High flux/diurnal analysis
- Daniel Friedman (NREL)
  - $GaInP_2$/GaAs photoabsorber

Relevance

Objectives:

Long-term: Effectively leverage the knowledge base of materials chemistry developed in the prior years to fabricate semiconductor/catalyst interfaces, both at the photoanode and photocathode, that utilize abundant elements and low cost fabrication methods. Combine these individual cells in tandem forming a monolithic device that attains or exceeds the DOE benchmark STH efficiency (~10%).

Specific to Current Year (2016-2017):

- Develop a novel passivation layer (TiN) that prevents corrosion of the low bandgap photoabsorber (Si).
- Fabricate a photocathode consisting of a low cost photoabsorber (Si), HER catalyst (nickel phosphide, here NiP_2), and a passivation layer (TiN). Test performance and stability under acidic and basic conditions.
- Investigate wider bandgap semiconductors as complementary tandem photoabsorbers in the photoanode, specifically perovskite oxynitride ($SrNb(O/N)_3$) tantalum nitride (Ta_3N_5), and halide double perovskite ($Cs_2AgBiBr_6$)

Relevance to DOE H_2 & FC Program

(DOE section 3.1.5 of FCTO Multi-Year Research, Development, and Demonstration Plan)

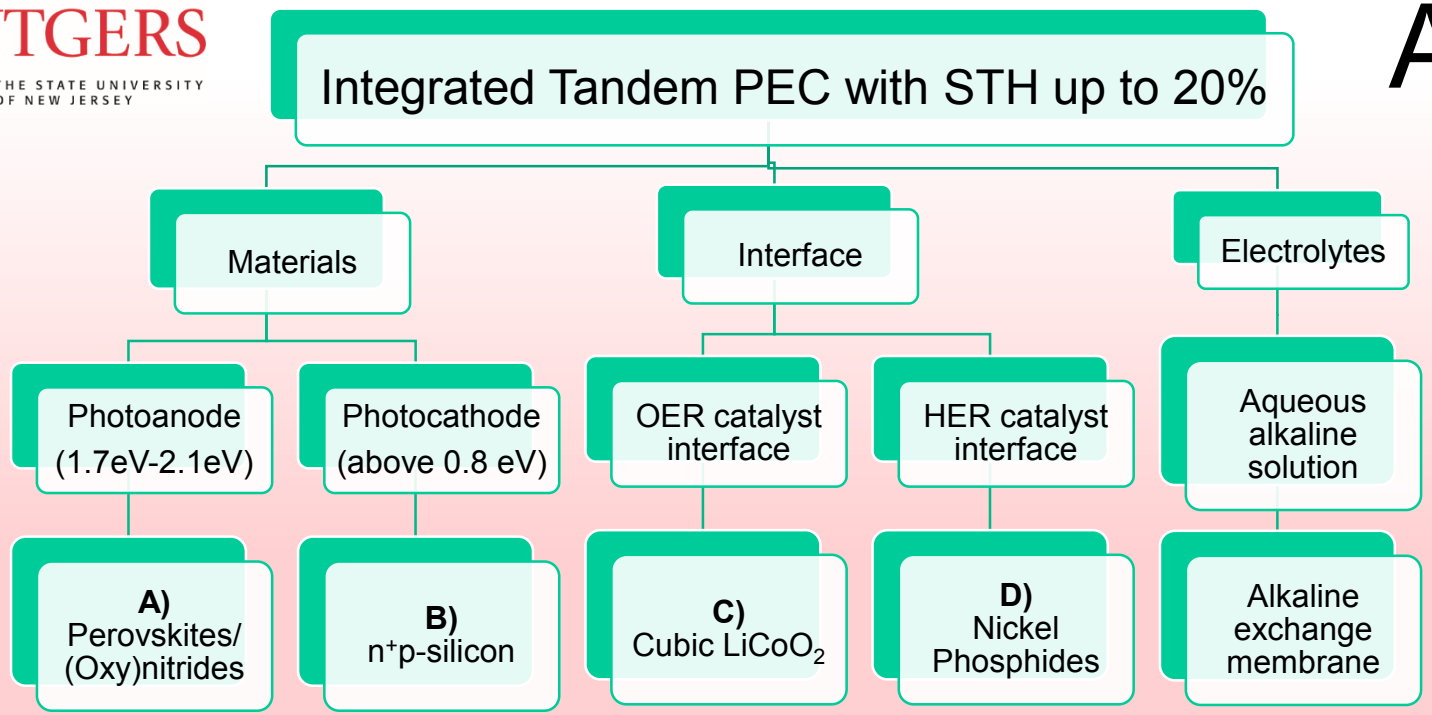
Materials Efficiency – Bulk and Interface (Barrier AE): Developing methods that utilize Si adds value the high efficiencies of commercial cells. When paired with a TiN, absorption and injection efficiency is high.

Materials Durability – Bulk and Interface *(Barrier AF)* – Fabricated photocathode shows long term stability (>24 hours) while retaining high performance (145mV overpotential vs Pt for HER at 10mA/cm^2)

Auxiliary Materials *(Barrier AI)* – With TiN passivation, silicon can now be employed as both a substrate and a low bandgap photoabsorber in the photocathodic half cell. This reduces interfaces and materials costs.

Synthesis and Manufacturing *(Barrier AJ)* – Wide bandgap photoabsorber thin films that are fabricated by spin coating has significantly lower capital costs compared to CVD or PVD techniques.

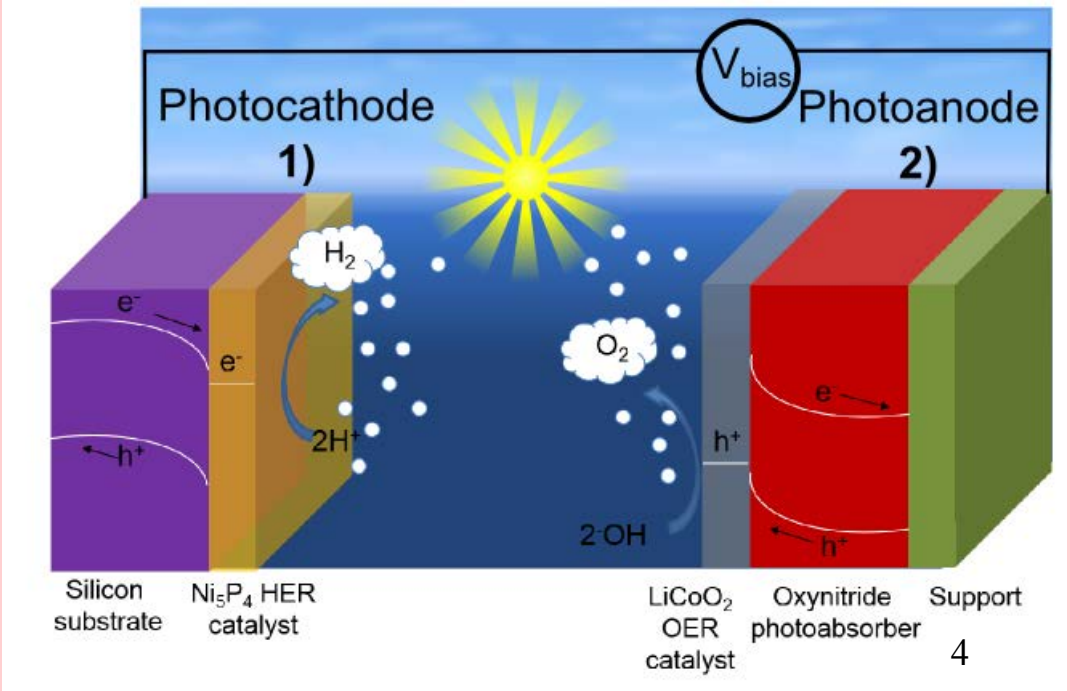
Approach



Project Focuses for FY2017:

A-D and combinations thereof

- Prepare and characterize thin films of **A**) $SrNbO_2N$, Ta_3N_5, and $Cs_2BiAgBr_6$
- Fabricate functioning half cells, **1** and **2** (right) from the combination of **A** + **C** and **B** + **D** using above developed methodology
- Benchmark half-cells for stability and performance



Approach – this year

Photocathode

- HER catalyst/passivation/photoabsorber = $NiP_2/TiN/n^+p\text{-}Si$

  - Determine most optimal nickel phosphide compound (Ni_xP_y) for integration with device
  - Identify a passivation layer that is transparent, highly conductive, has good band matching with Si, and prevents the formation of nickel silicides
  - Fabricate and characterize performance of device in both acidic and basic electrolytes

- Future effort (FY 2017)
  - Optimize system variables:
    - Film thickness (passivation layer and HER catalyst), different nickel phosphide polymorphs (Ni_5P_4, and Ni_3P), fabrication steps (temperature, time)
  - Begin long term testing >100h using choronoamperometry
  - Stabilize interface, investigate corrosion mechanism
    - Time-dependent AFM, ion scattering and cross-section TEM will monitor surface and interface changes

Approach – this year

Photoanode

- Double perovskites as a wide band gap photoabsorber material
  - Synthesized bulk powders of $Cs_2AgBiBr_6$. Verified the stability and optical properties of this class of compounds.
  - Developed a method to thin films with these materials

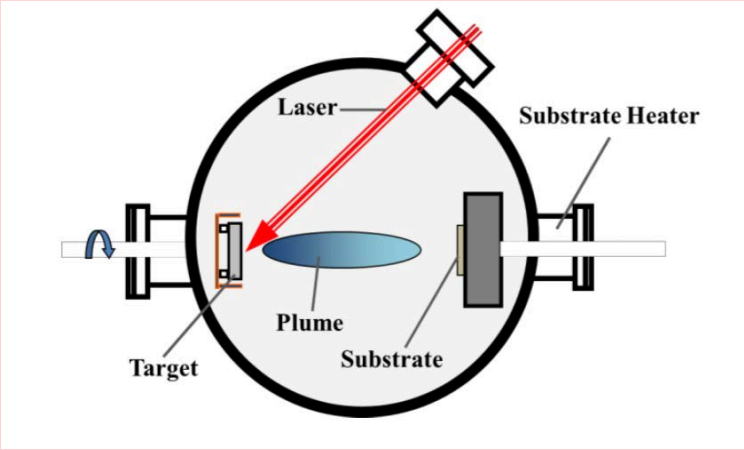
- Ta_3N_5 as a wide band gap photoabsorber material
  - Synthesized thin films of Ta_3N_5
  - Confirmed viability of a tandem photoabsorber: Ta_3N_5 on Si.
  - Tested Ta_3N_5 as a photoanode for OER
  - Developed a passivation layer that is transparent, conductive, and stable

- Future effort (FY 2017)
  - Determine the band structure of $Cs_2AgBiBr_6$ thin films experimentally
  - Develop a half device: $LiCoO_2$/passivation layer/photoabsorber #1 and #2
    - Achieve a clean interface between OER catalysts and photoabsorber and establish baseline performance
    - Introduce passivation layer (NiO et. al.) between OER catalyst and phoabsorber to increase stability of devices

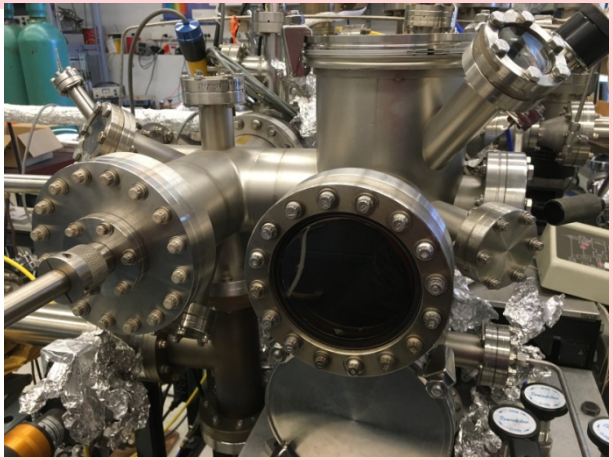
Accomplishments:
Photocathode device

Developed a thin film fabrication route to a complete device

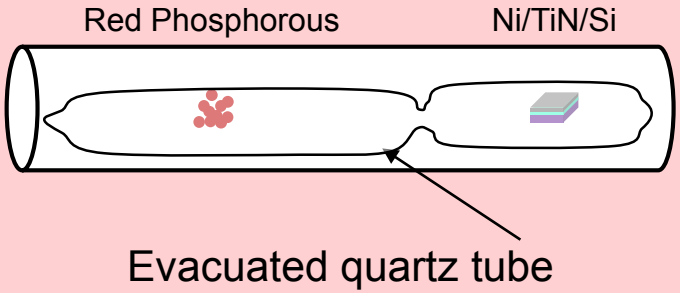
Pulsed laser deposition

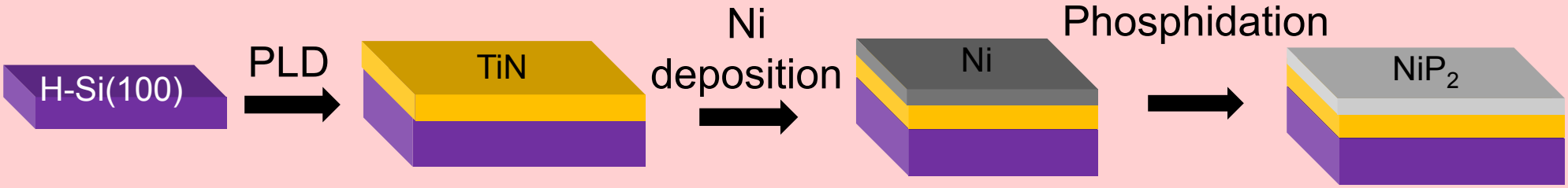


Thermal evaporation



Chemical vapor phosphidation

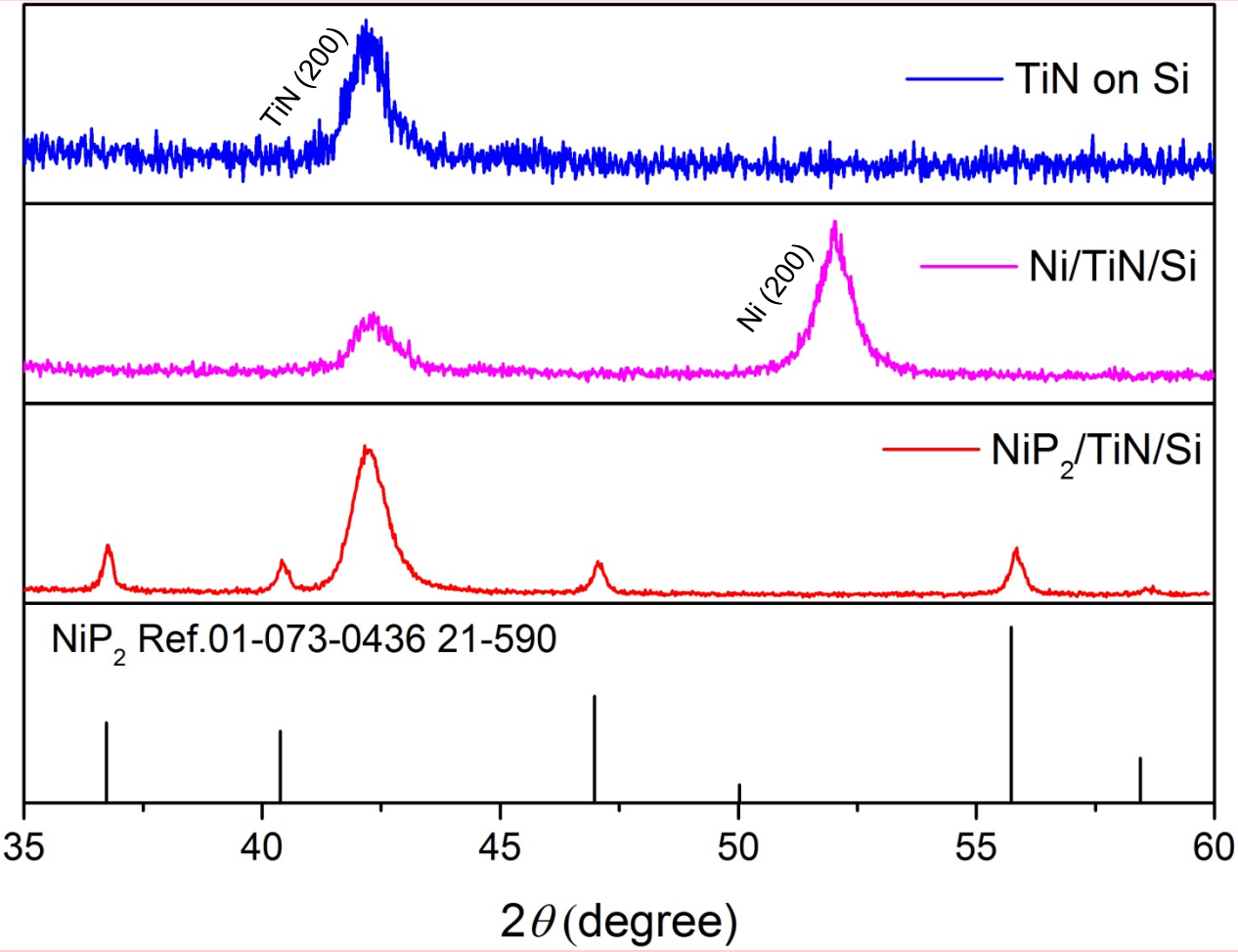




Accomplishments:
Photocathode device

Atomic Structures Characterized

XRD for each fabrication step



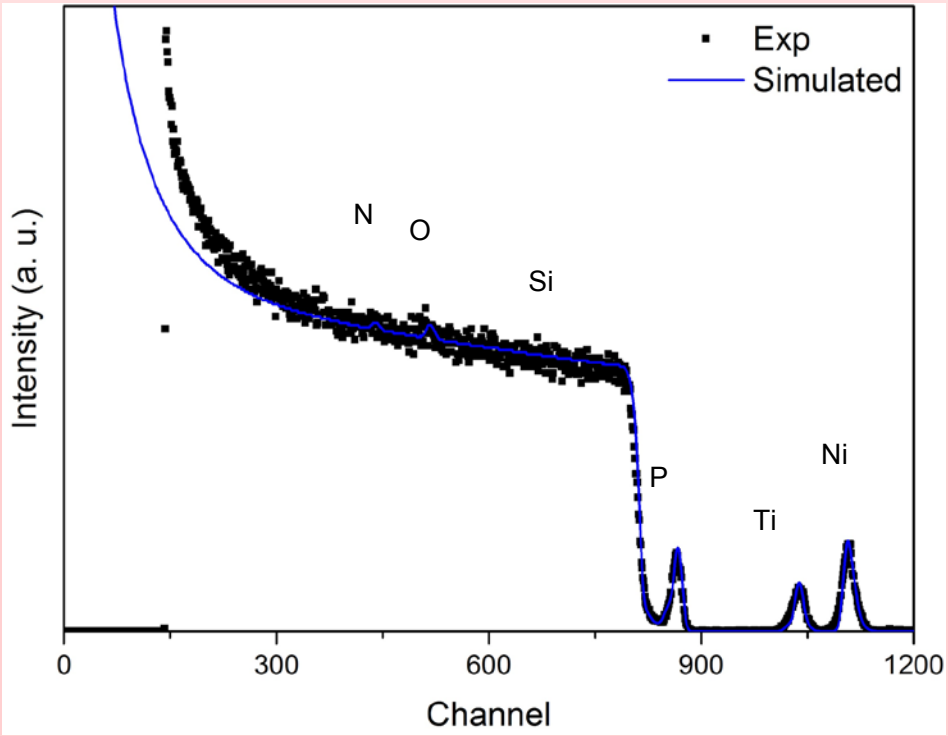
- To determine crystalline phase of each layer, thicker layers (~ 50 nm) of TiN and Ni were deposited.
- TiN shows an oriented (200) peak, which is the same orientation as the cubic Si substrate (100).
- Oriented, thermally evaporated Ni is observed.
- Polycrystalline NiP_2 was successfully prepared by conversion from Ni by chemical vapor phosphidation. Other Ni_xP_y compounds can be prepared similarly.

Accomplishments:

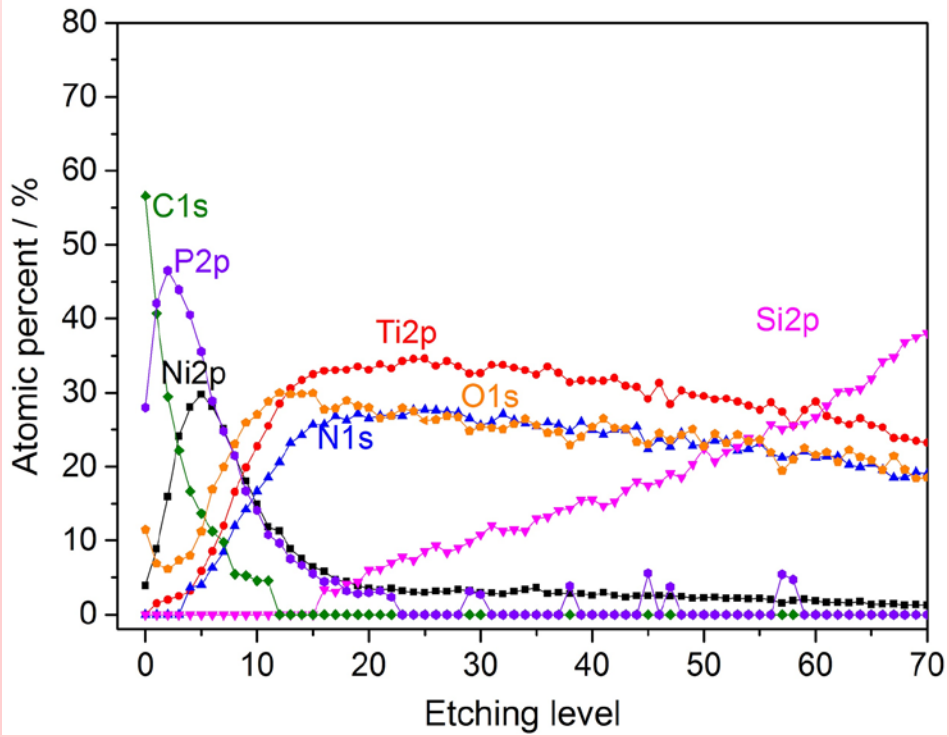
Photocathode device

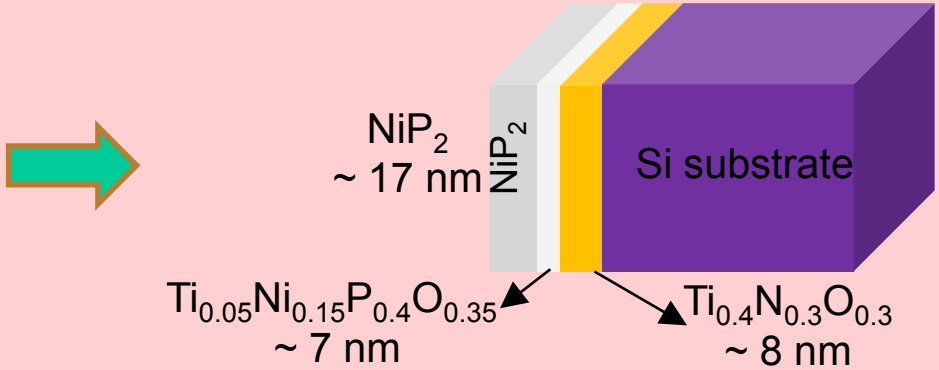
Thin Films Characterized

Rutherford backscattering spectrometry (RBS)



Depth resolved XPS

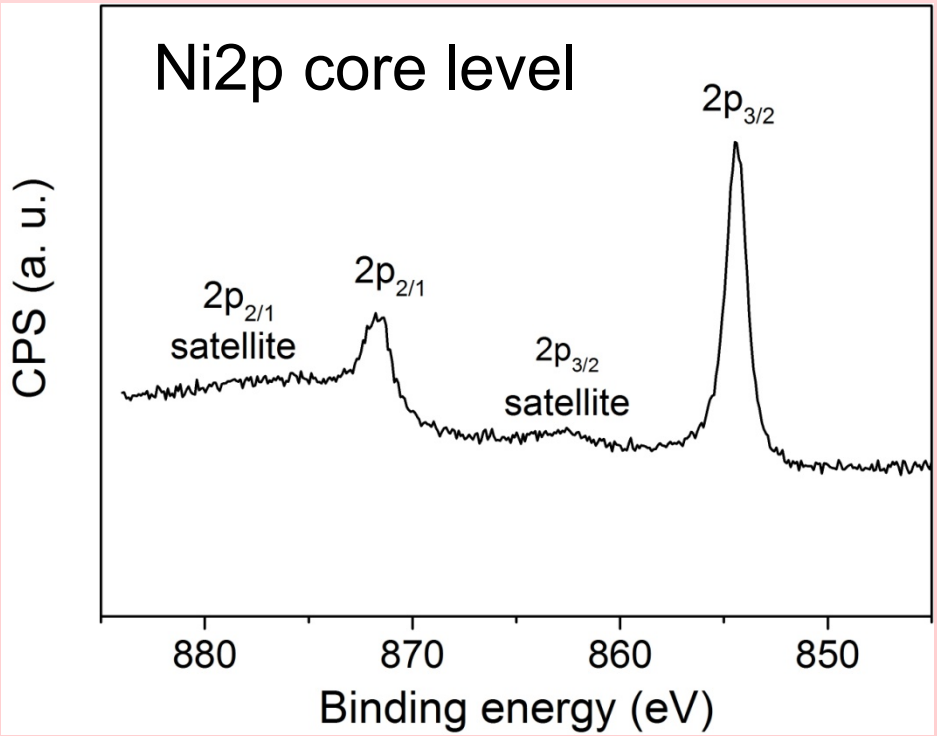


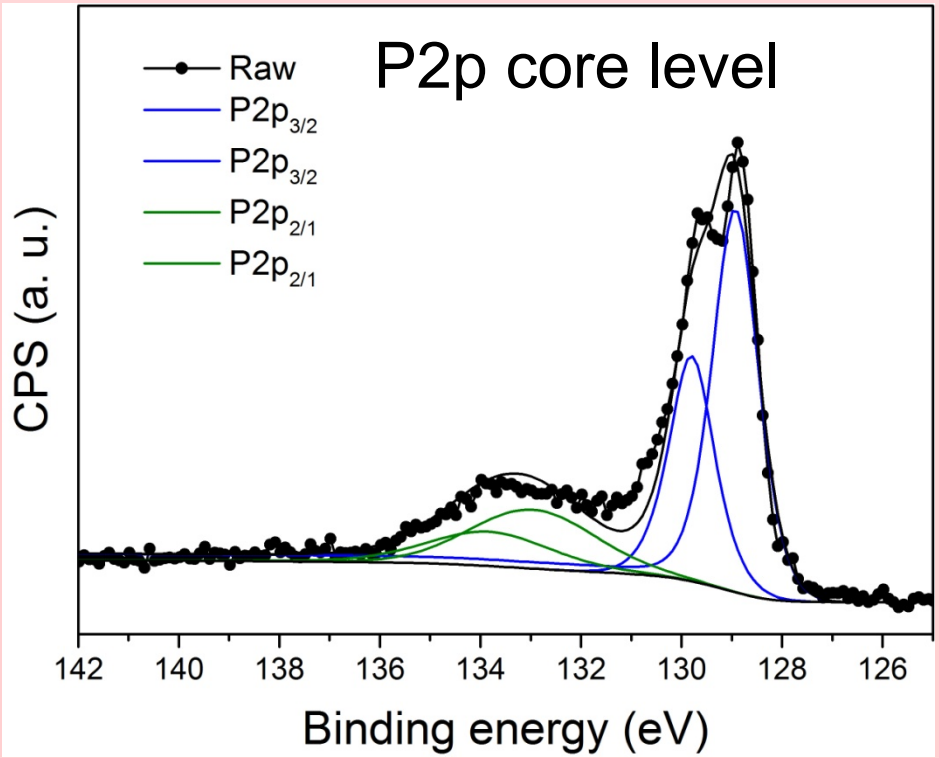


The cations are well resolved by RBS and depth resolved XPS identifies the anions. The two data sets can made into a composite representation of the fabricated film.

Accomplishments:
Photocathode device

X-ray Photoelectron Spectroscopy





- Ni 2p core level spectrum shows metallic Ni feature without surface oxidized Ni.

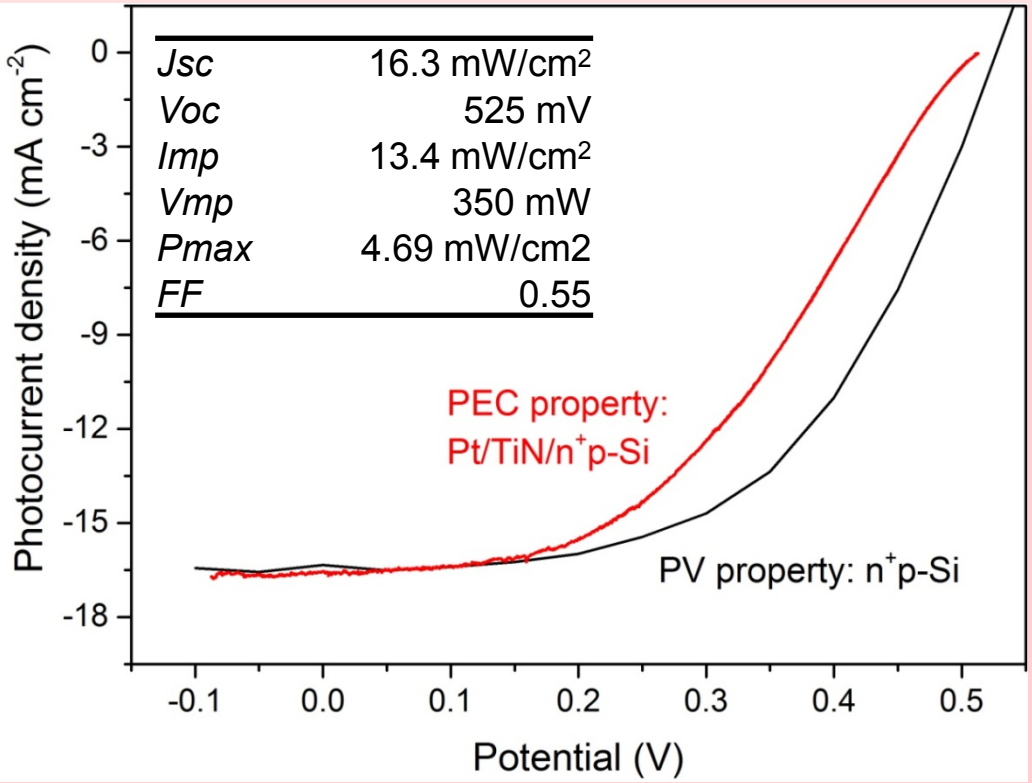
- P 2p core level spectrum shows that main phosphorous has metallic character.

Accomplishments:

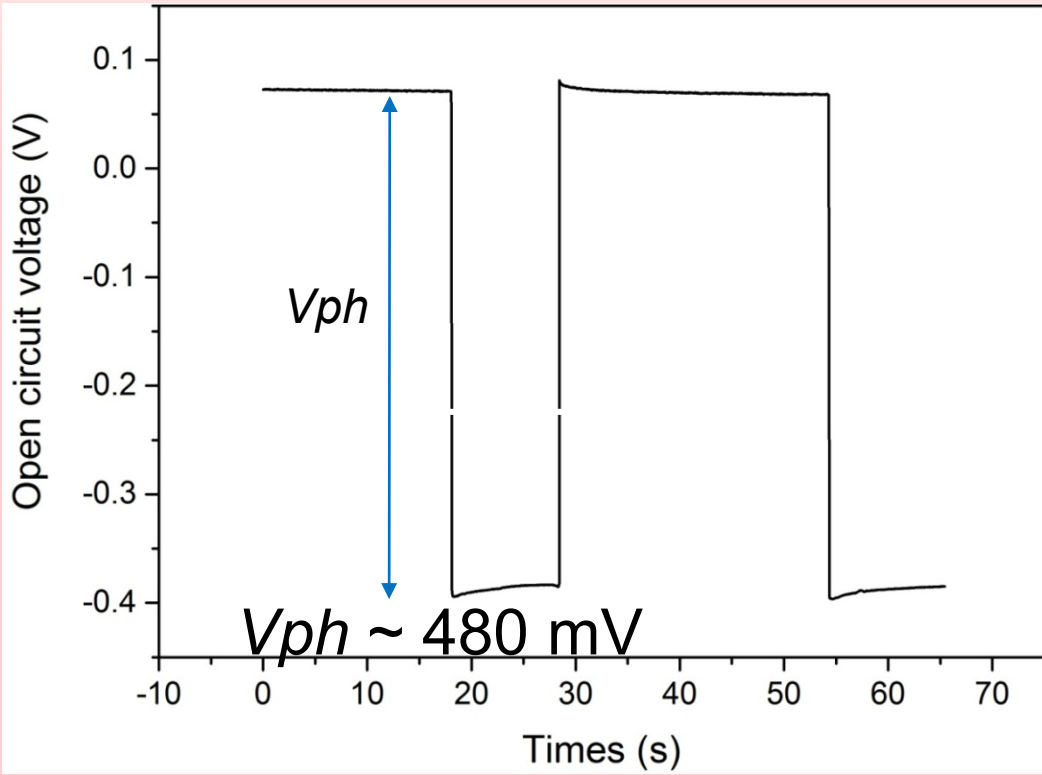
Photocathode device

Photo-properties of NiP_2/TiN/n^+p-Si

PV



PEC



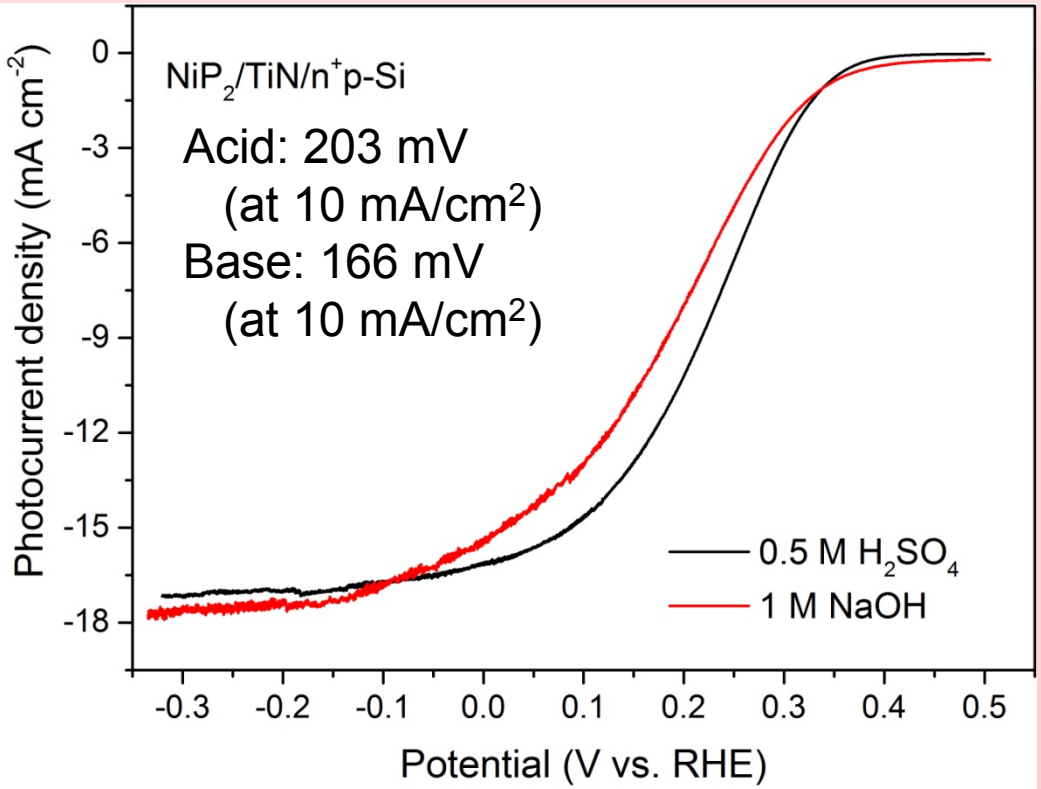
- The *Jsc* of the PEC measurement from Pt/TiN/n^+p-Si (reference) sample shows similar *Jsc* to a solar simulated PV (n^+p-Si). This indicates the TiN passivation layer has negligible light absorption.

- The *Vph* of the PEC, measured by the difference between light and dark OCP demonstrates that the NiP_2 and TiN layer did not significantly change the *Voc* of Si photoabsorber.

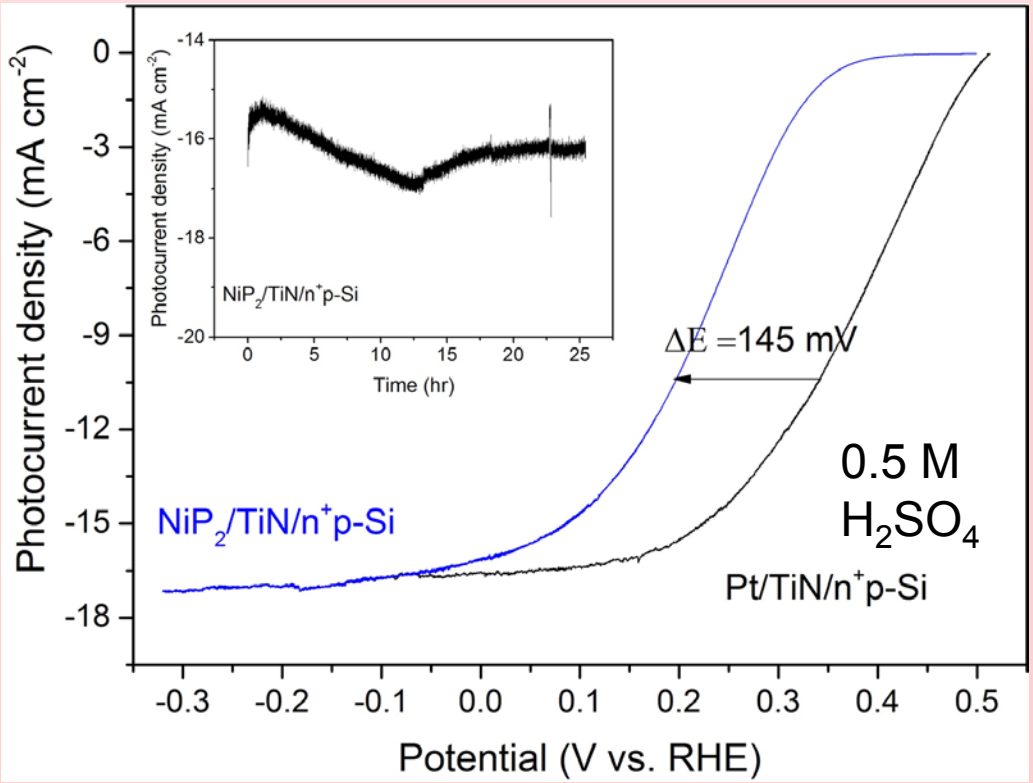
Accomplishments:
Photocathode device

Photoelectrochemistry

Activity



Stability

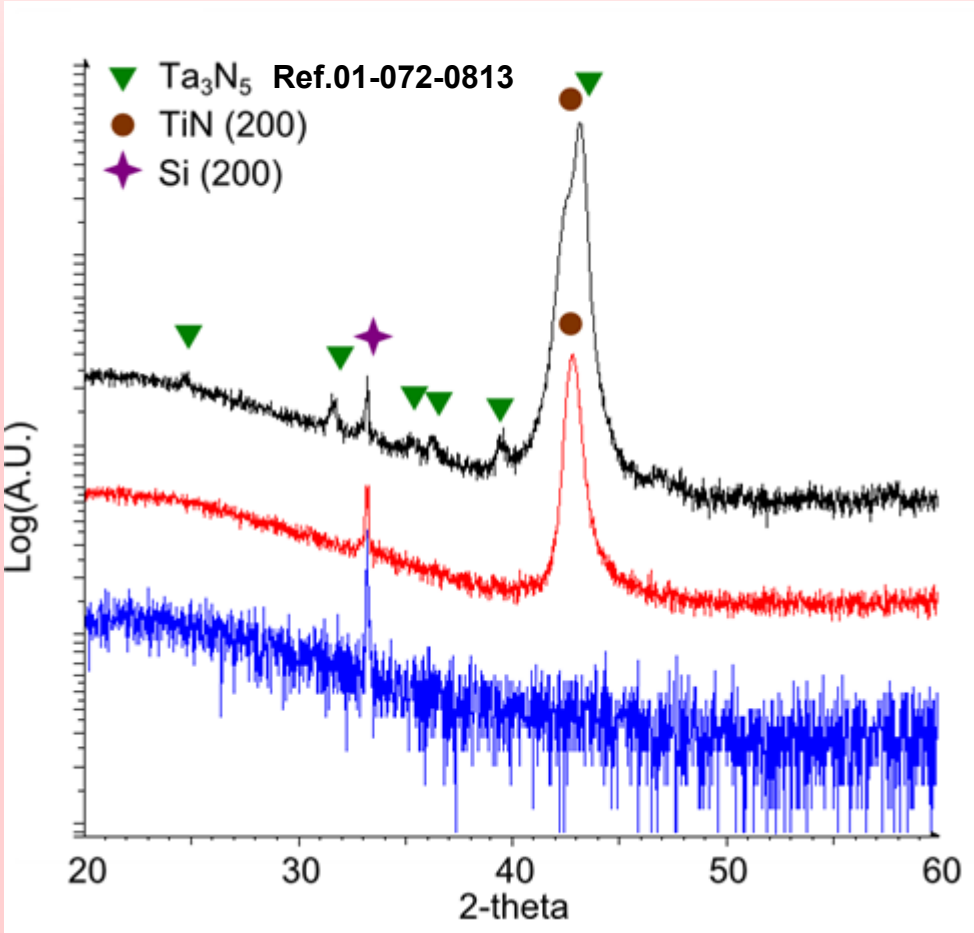


- NiP_2/TiN/n^+p-Si shows high activity in both acidic and basic media. *Jsc* of both averaged cyclic voltammorgrams suggest that light absorption interference is negligible from the NiP_2 and TiN layer (compared to *Jsc* of n^+p-Si). In acidic media, NiP_2 requires only a 145 mV overpotential against a Pt^0 catalyst, and it shows photostability for more than 25 hours without failure.

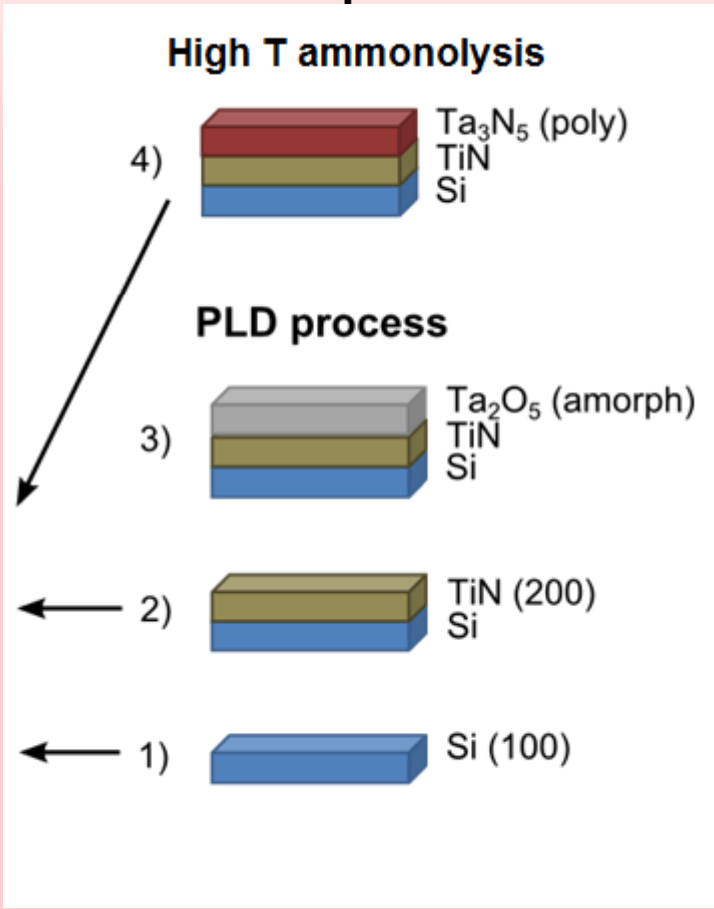
Accomplishments:
Photoanode device

Ta_3N_5 photoabsorber

XRD



Fabrication Steps

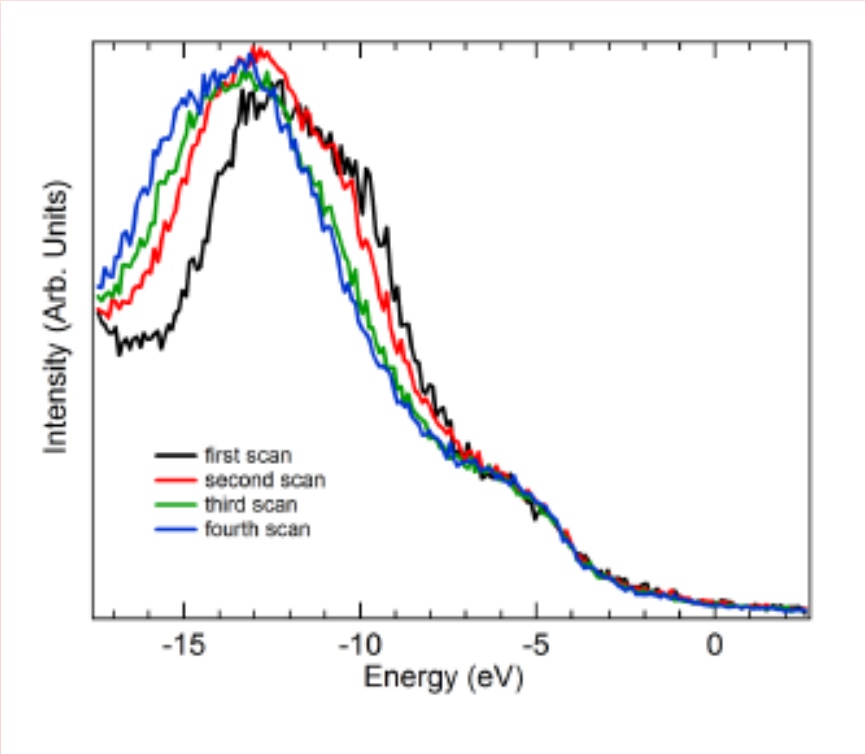


- TiN is (200) oriented while Ta_2O_5 is deposited amorphous. During ammonolysis, the Ta_2O_5 is converted to a polycrystalline Ta_3N_5.

Accomplishments:
Photoanode device

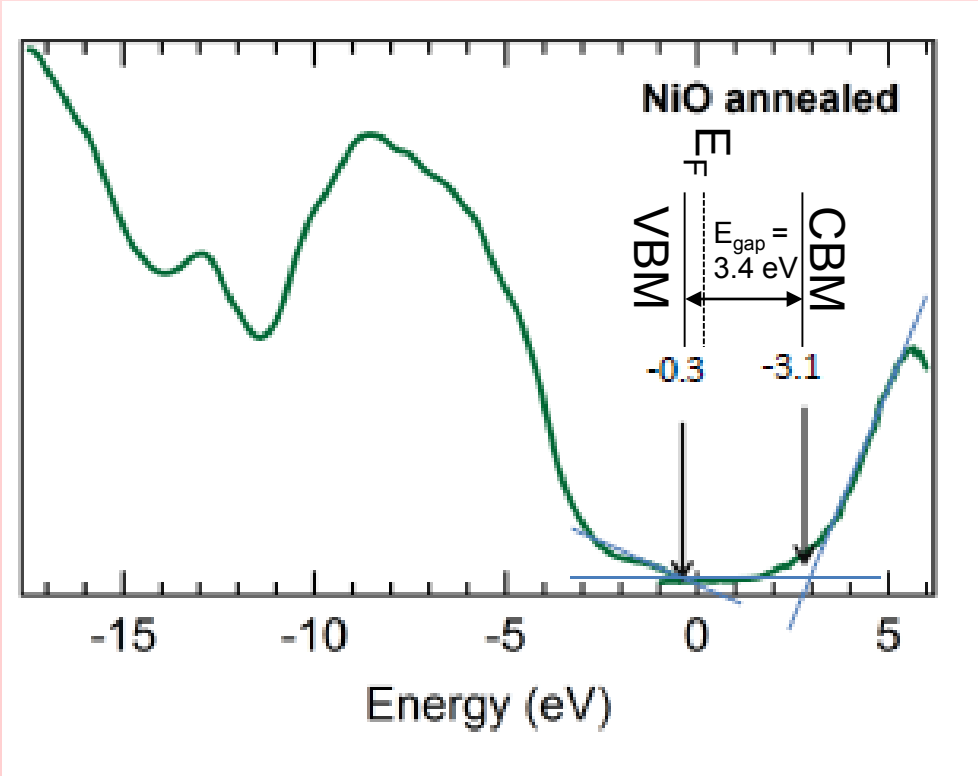
Photanode NiO passivation layer developed

UPS



- Freshly sputtered NiO films charge due to insulating behavior. A post-sputter anneal (data not shown) allows higher hole conductivity. Conductivity changes from insulating to metallic (ρ < 50 Ω·cm)

Inverse/Photoemission Spectroscopy

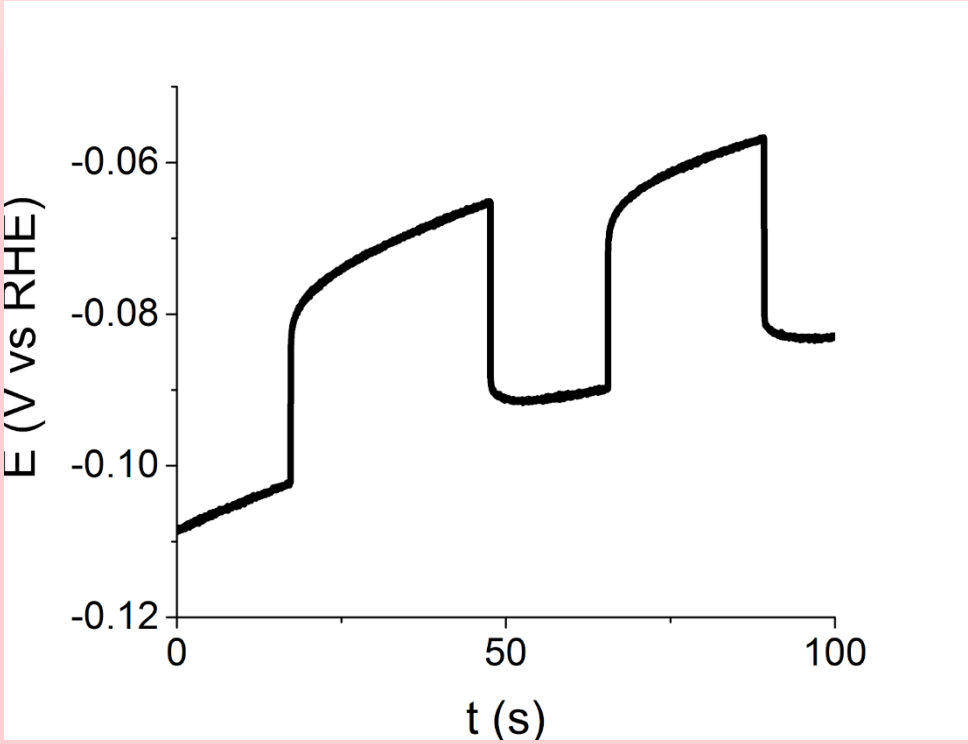


- The experimentally determined band gap of the annealed NiO is wide (E_{gap} = 3.4eV), which further promotes its candidacy as a passivation layer in the photoanode.

Accomplishments:
Photoanode device

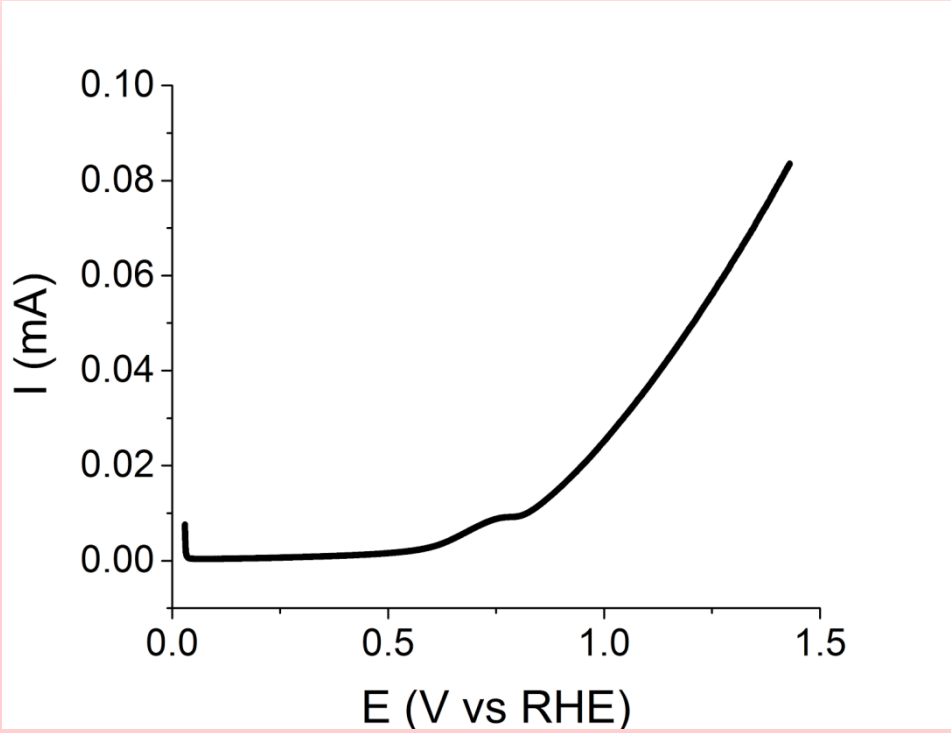
Preliminary PEC of NiO/Ta_3N_5/TiN/n-Si

OCV



- V_{ph} is observed but is very low (20mV).

Illuminated LSV



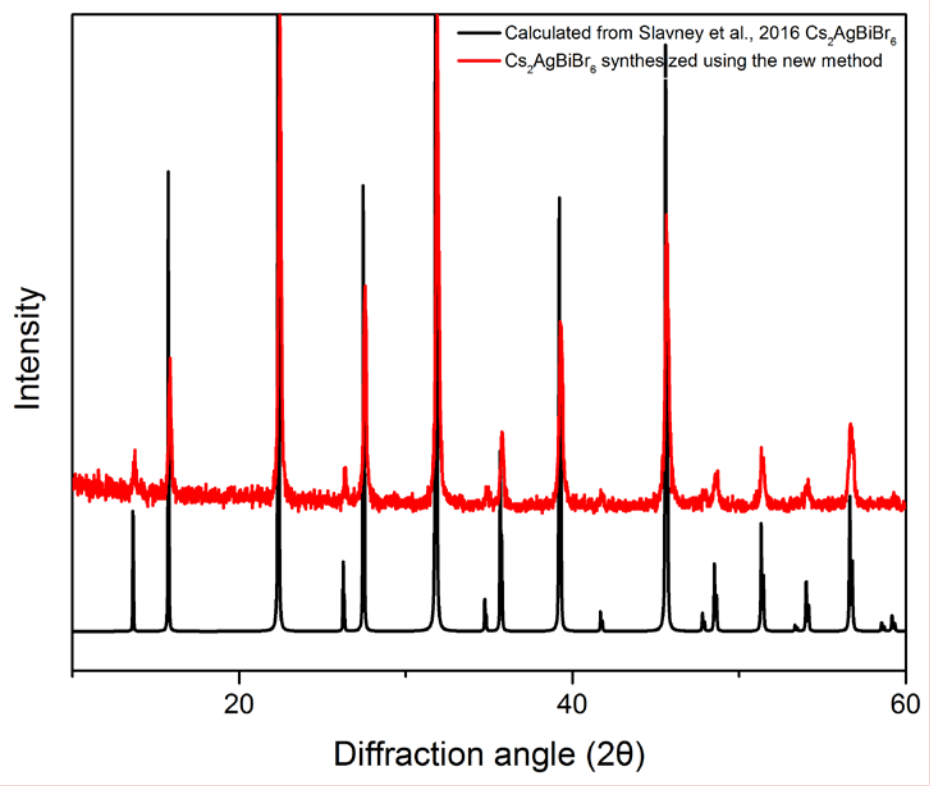
- At increasing potentials an anodic current is observed.

Half-cells are unstable due to photocorrosion. Optimization of the passivation layer (thickness and post-anneal) and experiments to thoroughly evaluate each layer's contribution to the PEC properties are in progress.

Accomplishments:
Photoanode device

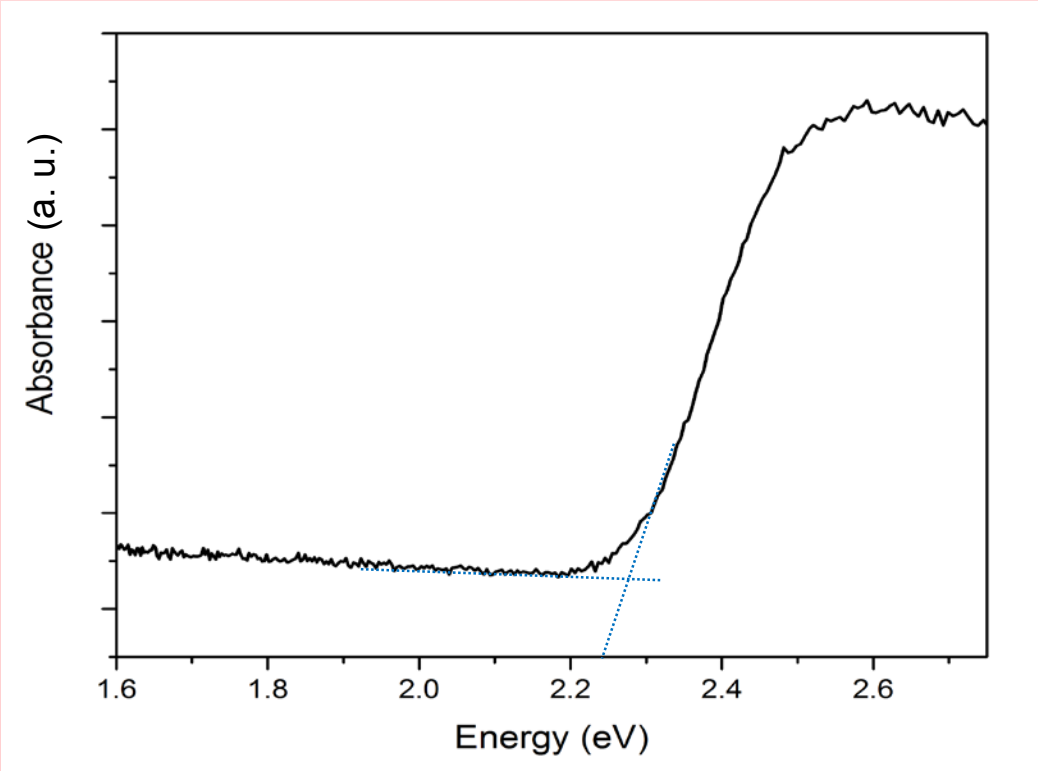
Double perovskite halide ($Cs_2AgBiBr_6$) synthesized as photoabsorber

PXRD



- Bulk powders match those reported previously. Large crystals are formed during solution synthesis.

Optical properties



- Bandgap is ~ 2.3eV from UV-visible diffuse reflectance, in line with other reports.

Accomplishments:
Photoanode device

Spin-coated thin films of $Cs_2AgBiBr_6$

Development of a solution processing route

Precursor solution **Spin-coating solution** **Precipitated crystals**

Yield 72%

- Excess solution decanted & the crystals are washed with ethanol

Fabricated film

- Triple layered spin-coated $Cs_2AgBiBr_6$ films on top of ZnO/FTO.

Conclusions

Photocathode

- Successful formation of the polycrystalline NiP_2 thin film (~ 17 nm) with TiN passivation interlayer on a silicon photoabsorber. Other Ni_xP_y options open.
- Developed TiN passivation interlayer to prevent thermal diffusion of Si during phosphidation reaction that forms NiP_2, yielding a non-diffusing interface.
- Metallic NiP_2 and TiN layers did not significantly interfere with light absorption of silicon photoabsorber thereby obtaining similar *Jsc* to bare Si (PV measurement).
- The half cell device demonstrated high activity in both acid (pH 0) and base (pH 14). Low 145 mV overpotential was required vs. ref. Pt catalyst in acid.
- The developed device was stable for over 25 h without failure.

Photoanode:

- A route to thin films of Ta_3N_5 on Si for tandem photoabsorber applications has been identified.
- NiO passivation layer is conductive and transparent promoting its use in the photoanode, though preliminary PEC data needs more understanding.
- Spin-coated $Cs_2AgBiBr_6$ has been demonstrated as a low-cost, scalable candidate for the wide bandgap photoabsorber in a tandem PEC.

Full project summary

Full cell. FY2017. In progress.

Photocathode half-cell. FY2017.

Photoanode half-cell. FY2017. In progress.

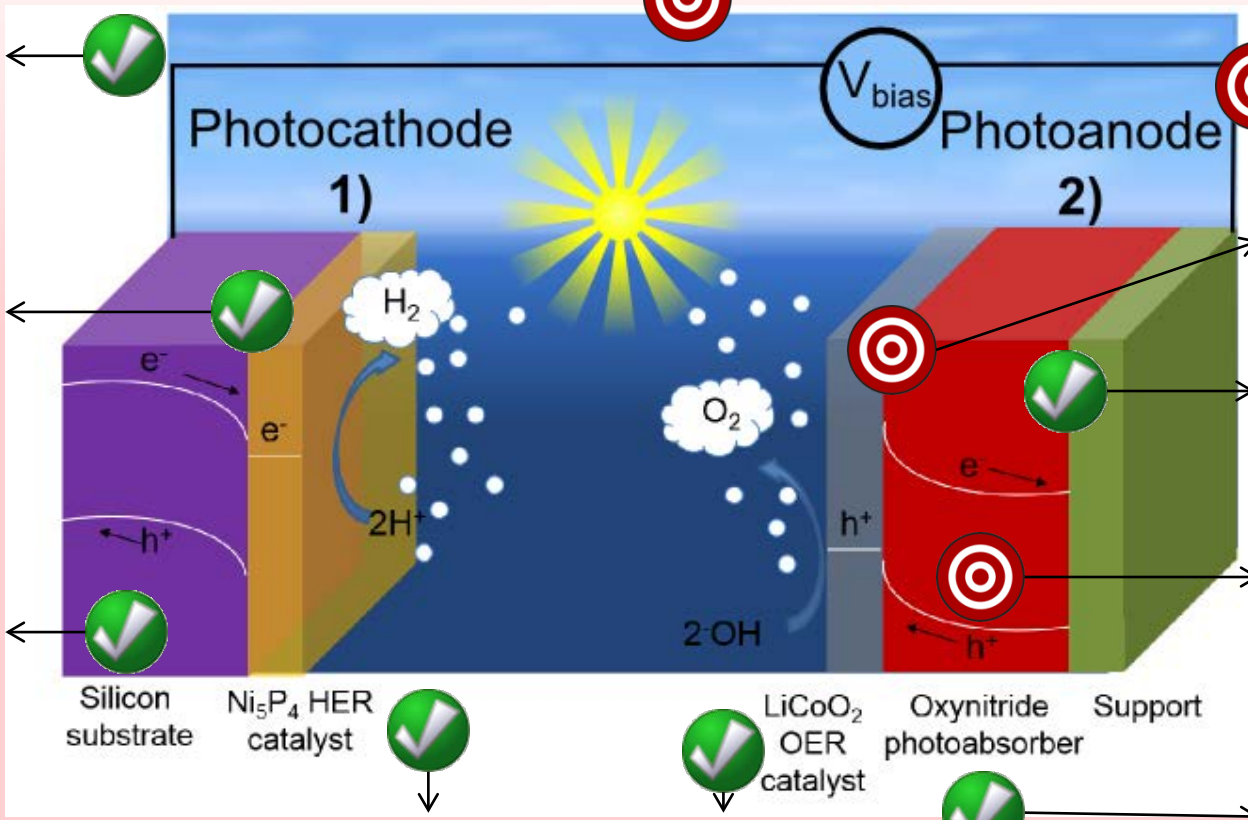
Catalyst/Photoabsorber Interface. FY2017. In progress.

TiN passivation layer. FY2017.

Photoabsorber/Si interface. FY2016.

Gradient doping. FY2017. In progress.

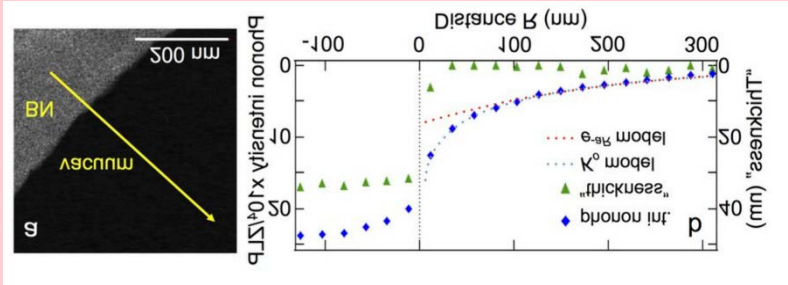
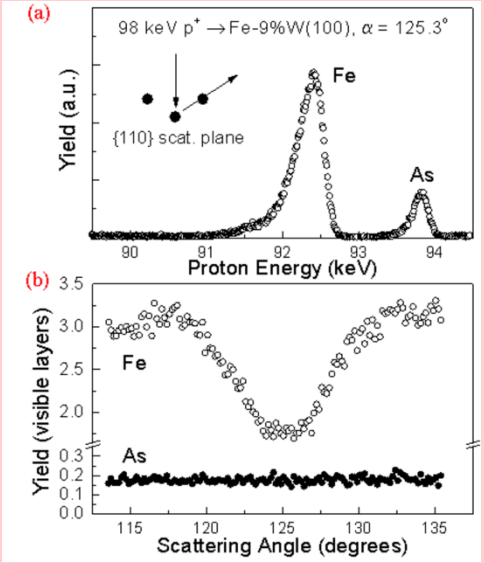
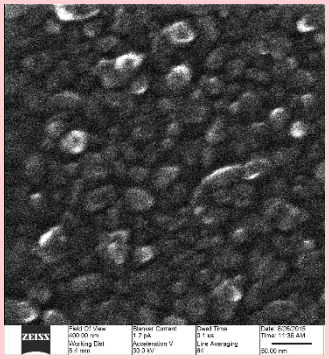
Gradient doped Si. FY2016-7.



HER and OER as a thin film. FY2016.

Photoabsorber synthesis, bulk and thin film. Oxynitrides in FY2015, others ongoing

- <u>Key FY2017 technical results</u>:
  - A stable (>25h in acid with no significant change to operating current 10% gain in the first 10 hours due to activation; base has same stability but instead a 10% loss in operating current in the first 10 hours), highly active (145mV overpotential for HER at 10mA/cm^2 vs Pt in 0.5M H_2SO_4) photocathode utilizing a TiN passivation layer was fabricated and characterized.
  - Scalable low-temperature routes to wide bandgap absorbers ($SrNbO_2N$, Ta_3N_5, $Cs_2AgBiBr_6$) that can be fabricated upon silicon (low bandgap photoabsorber) were identified and investigated with the intent to optimize the interfacial chemistry on route to a full tandem device

Relating to EMN HydroGEN

- <u>Looking for colloborators that have these capabilites:</u>
  - Wide and/or narrow band gap semiconductors
  - Diurnal testing
  - In-situ e-chem analysis techniques
- <u>Things our team has and can collaborate with:</u>
  - Thin film HER and/or OER catalyst integration with your device
  - Characterization
    - “ultra”-Scanning Tunneling Electron Microscope (STEM)
      - Sub-nm scale
      - Vibration, plasmon, interband-transition and core-shell transition spectra capable
    - Medium Energy Ion Scattering (MEIS)
      - High-resolution-surface-“Rutherford backscatter technique”
    - Helium Ion Microscopy (HeIM)
      - High resolution even for an untreated semiconductor