II.C.4 High Efficiency Tandem Absorbers for Economical Solar Hydrogen Production

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Subcontractors

- University of Nevada Las Vegas, Las Vegas, NV (XGB-2-11673-01)
- University of Hawaii, Honolulu, HI (XGJ-5-52227-01)

Project Start Date: October 2014
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop a semiconductor-based, solar-driven water splitting photoelectrochemical (PEC) device with greater than 20% solar-to-hydrogen (STH) efficiency and several thousand hours of stability under normal operating conditions
- Incorporate components that can be fabricated cost-effectively and are straightforward to scale up such that a plant scaled to 50,000 kg H_2 per day can achieve an estimated production cost of $1 to $2 per kilogram hydrogen using only sunlight and water as feedstocks
- Demonstrate a prototype photoreactor that produces 3 L of standard hydrogen within an 8-hour period under moderate solar concentration (~10x)

Fiscal Year (FY) 2015 Objectives

- Design tandem III-V semiconductor structures with lower bandgaps than $GaInP_2$/GaAs, 1.8 eV and 1.4 eV, respectively, that have the potential to push the boundaries on achievable STH efficiencies
- Demonstrate 15% STH at short circuit, establishing a new efficiency record
- Demonstrate surface modification for passivation against corrosion improves durability for lower bandgap III-V semiconductor electrodes at high current densities

Technical Barriers

This project addresses the following technical barriers from Section 3.1 (Hydrogen Production) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan:

(AE) Materials Efficiency – Bulk and Interface

(AF) Materials Durability – Bulk and Interface

(AG) Integrated Device Configurations

(AI) Auxiliary Materials

Technical Targets

This project is a materials discovery investigation to identify a single semiconductor material that meets the technical targets for efficiency and stability. The 2015 technical targets from the MYRDD Plan PEC hydrogen production goals in Table 3.1.8.A are the following:

- 15% STH conversion efficiency
- 900-hour replacement lifetime (1/2 year at 20% capacity factor)
- \$300/m^2 PEC electrode cost

FY 2015 Accomplishments

- We exceeded 400 hours of stability by testing a N_2^+ ion implanted and flash PtRu sputtered p-GaAs electrode for 468 hours at -15 mA/cm^2.
- We digested N_2^+ and PtRu sputtered GaAs and $GaInP_2$ samples in aqua regia and used inductively coupled plasma mass spectrometry to get quantitative data on loading and distribution. We discovered the distribution across the wafer surfaces is fairly uniform and the ion treatment is a significant source of PtRu. The total loading of PtRu nanoparticles, if they were compacted into a continuous thin film, is between 1–2 nm.
- Working with the University of Nevada, Las Vegas, one of our surface validation partners, we discovered more recently N_2^+ ion implanted and flash PtRu treated samples have less nitride incorporated and much greater PtRu loadings, which may be leading to less effective surface stabilization. We are amending treatment parameters to achieve surfaces with similar nitride and PtRu loadings to those found in our initial

samples, which had the greatest yield of stable electrodes to date.

- We worked with the Jaramillo group at Stanford to extend the durability of p-$GaInP_2$ coated with MoS_2 from a few hours to over 150 hours by changing deposition parameters.
- We designed and fabricated an electrochemical cell with short optical pathlength to minimize absorption of infrared photons by water.
- We collected our first results of a lowered bottom bandgap junction inverted metamorphic multijunction (IMM) cell and were able to generate a higher photocurrent density than $GaInP_2$/GaAs tandems. The voltage of the IMM cell was insufficient for unbiased water splitting, which we plan to address by incorporating a buried junction. This configuration with a buried junction should result in a new water splitting efficiency record.
- We filed a provisional patent on IMM cells for high efficiency water splitting.

INTRODUCTION

Photoelectrolysis cells combine a light harvesting system and a water splitting system into a single, monolithic device. The catalyzed surface of a semiconductor is the light harvesting component as well as one part of the water splitting system with the balance consisting of a spatially separated counter electrode. Discovering a semiconductor system that can efficiently and sustainably collect solar energy and direct it towards the water splitting reaction could provide renewable and economically competitive fuel for the hydrogen economy.

The goal of this work is to develop a semiconductor material set or device configuration that (1) splits water into hydrogen and oxygen spontaneously upon illumination without an external bias, (2) has an STH efficiency of at least 15% with a clear pathway to exceed 20%, and (3) can ultimately be synthesized via high volume manufacturing techniques with a final hydrogen production cost below $2/kg.

APPROACH

All proven zero-bias PEC devices with STH over 1% rely on two, series-connected semiconductor junctions (tandem cell) to increase the majority-carrier potential at the counter electrode [1–4], providing sufficient potential difference, or photovoltage, for water splitting (Figure 1). Tandem devices also overcome the band alignment challenge common to PEC materials. For maximum efficiency, the currents in series-connected devices must be equal, creating the requirement of current matching. The maximum current generated by a semiconductor can be calculated by assuming unity quantum yield for every above-bandgap photon in the solar spectrum. Using the accepted lower heating value efficiency equation [5], 20% STH corresponds to a short circuit current density (J_{sc}) of 16.26 mA/cm^2 under AM1.5G (1 sun). The largest

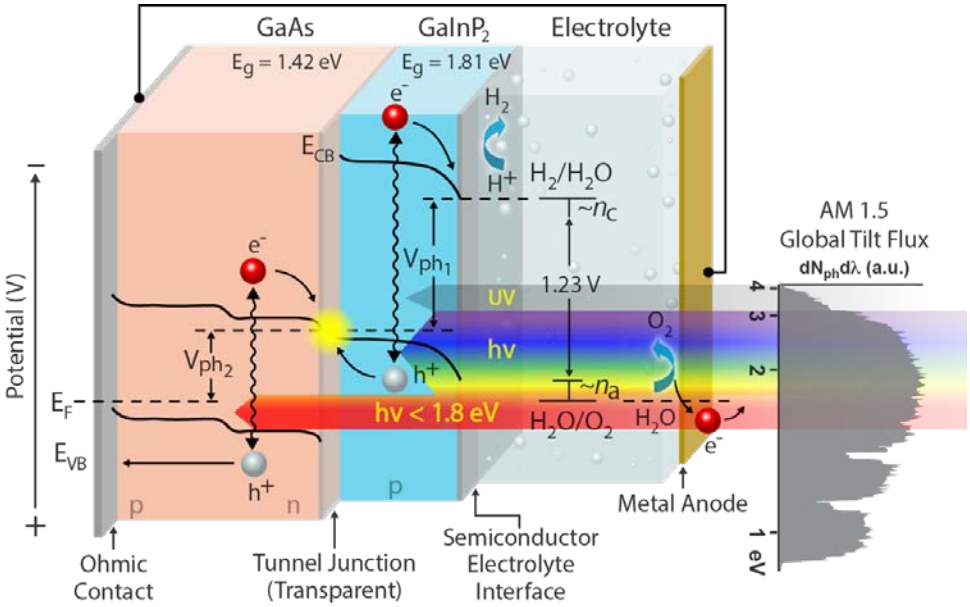

FIGURE 1. Energy-level diagram and spectral splitting of a tandem configuration photoelectrolysis cell. Photons with energies below the bandgap of the top junction pass through and generate an electron/hole pair in the bottom junction, which provides the holes with sufficient oxidative potential to perform water oxidation in this example.

bottom-cell bandgap that can be used and still achieve 20% STH is 1.41 eV. However, quantum yields are never 100% and semiconductors are not true step function devices. Therefore, to realistically achieve STH values in excess of 20%, we must use lower top-cell and bottom-cell bandgap combinations, which guides our selection of potential tandem materials. An additional variable that can be used to match the currents is the thickness of the top cell—a thinner cell will allow more photons through to the bottom cell. This gives us some additional flexibility in the bandgaps that we can use. The lower limit of useable bandgaps is ~0.8 eV [6], dictated by the penetration depth through water. We will focus on III-V semiconductors, which exhibit the highest conversion efficiencies among all photoabsorber materials, and design tandem junctions to maximize the spectrally split device current, while achieving sufficient voltage to drive the maximum current through the device. We plan to initially focus on conventional III-V metal organic vapor phase epitaxy to demonstrate maximum possible efficiencies and then port successful device structures to emerging synthesis techniques, such as spalling, epitaxial lift-off, or hydride vapor phase epitaxy, that have the potential to meet low cost absorber targets. We plan to improve the stability of III-V semiconductor water splitting electrodes by a variety of surface protecting modifications that include nitridation/sputtering, atomic layer deposition of oxides/nitrides, and thin coatings of MoS_2.

RESULTS

Over 400 Hours of Stability at Operating Conditions for Surface Protected p-GaAs

Our first attempt at achieving over 400 hours of durability on a nitrogen ion bombarded and PtRu sputtered p-GaAs electrode held at a constant (photo)current of -15 mA/cm^2 was unsuccessful. The applied bias was initially stable, but after 70 hours the bias gradually increased and the electrolyte yellowed. After about 170 hours, the semiconductor surface had a noticeable film and its ability to generate photocurrent under bias was greatly diminished. The performance of the semiconductor was restored by removing the film on its surface via sonication in methanol. We hypothesized the Triton X-100 surfactant was responsible for the yellowing and electrode fouling, which we confirmed experimentally by performing electrolysis on two platinum electrodes in an H-cell separated by a glass frit. Without surfactant, large bubbles build up on the semiconductor electrode surface and hasten degradation, so omitting it from durability electrolytes is not practical. We exceeded 400 hours of stability on p-GaAs operating at -15 mA/cm^2 by periodically stopping the experiment and replacing the electrolyte with fresh 3 M H_2SO_4 with 1 mM Triton X-100 either every day during weekdays or after 60 hours over weekends. The semiconductor electrode still exhibited fouling but it was not as severe as the uninterrupted 170-hour test described above. The electrolytes appeared yellow after only 24 hours of testing, after 60 hours the bubbles were noticeably larger and had a greater tendency to adhere to the sample surface than they did in a fresh solution. Without surfactant, a treated electrode failed in less than 24 hours.

The surface ion implantation and sputtering treatment shows the ability to protect the surface of p-GaAs for over 400 hours of operation (Figure 2) as demonstrated by a negligible loss in light-limited photocurrent magnitude. The illumination intensity from a 250 W tungsten light source was set using a silicon reference cell calibrated to AM1.5 G. One noticeable difference between pre and postdurability chopped light current density-voltage (J-V) curves is that the catalytic activity of the surface treatment appears to be lost during the durability testing. This is evidenced by the more negative onset of photocurrent for both the post 25-hour J-V and post 468-hour J-V. It is unclear whether this is due to the PtRu catalyst particles being deactivated by the cathodic fouling discussed above or due to physical detachment of the particles from the surface through etching or some other mechanism.

Demonstration of Novel III-V Structures for Improved Water Splitting Efficiency

We evaluated the first IMM cell designed for PEC water splitting. The new devices are described as “inverted”

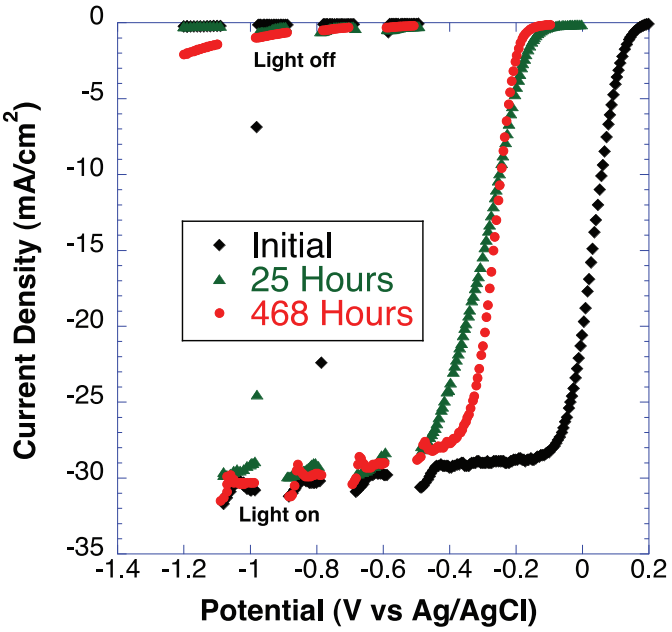

FIGURE 2. Chopped light J-V analysis in 3 M H_2SO_4 with 1 mM Triton X-100 before (black), after 25 hours (green), and after 468 hours (red) of galvanostatic testing at -15 mA/cm^2. Illumination was provided by a 250 W tungsten source set to AM1.5 G with a Si reference cell. The electrolyte was replaced every weekday to minimize fouling of the semiconductor by decomposed surfactant.

because the wider bandgap (top) junction, which is lattice-matched to the GaAs substrate, is grown first. A tunnel junction is then grown followed by a carefully engineered transparent buffer layer that grades the lattice constant to the lattice mismatched, "metamorphic" lower bandgap (bottom) junction. High quality multijunction structures can be realized because the transparent graded buffer layer moderates the strain induced by the lattice mismatch between the layers [7]. Additionally, the bandgaps of top and bottom absorbers are easily tailored by varying the III-V alloy compositions, allowing optimization of the device performance (current, voltage) with respect to water splitting requirements, with high precision. Our first modification to the $GaInP_2$/GaAs tandem aims to lower the bottom absorber bandgap, targeting 1.2 eV, by incorporating indium. This increases the overall fraction of the solar spectrum absorbed and makes the device, theoretically, top junction limited based on the current matching requirement (Figure 3).

The first characterization of the IMM cell was with incident photon-to-current efficiency, which revealed that the InGaAs cell was of high quality, and demonstrated values as good as GaAs, approaching the limit of reflection (~70% for our cell). We also took two-terminal J-V measurements, against a highly catalytic IrO_x anode, to determine the water splitting efficiency (Figure 4). Compared with the standard $GaInP_2$/GaAs tandem (green) line, the IMM cell (orange) exhibited an increased light-limited photocurrent density, but had a reduced onset voltage, making it unable to split water at zero bias. Our strategy to improve the onset is based on making a buried junction at the semiconductor surface. The black dashed line in Figure 4 had additional p-GaAs and i-$GaInP_2$ layers on the surface and demonstrates how this would lead to an improvement. These layers were included in the growth as etch-stop and window layers that are used for solid-state devices and were inadvertently left on after processing. Our hypothesis is that the i-$GaInP_2$ layer increased the voltage, but the p-GaAs layer acted as a filter and reduced the photocurrent of the device. We are currently testing various modifications of these layers, including thinning and entirely removing the p-GaAs layer, to determine the configuration that gives us the most voltage with minimal or no current loss. Improving the voltage (i.e., shifting the orange curve to the right) should allow us to exceed 15% STH, and set a new bar for unassisted photoelectrolysis efficiency. In order to surpass 20% STH, we will need to include an antireflective surface and possibly reduce the top bandgap from 1.8 eV to 1.7 eV. We are currently looking at both of these pathways to improving efficiency.

CONCLUSIONS AND FUTURE DIRECTIONS

- Surface passivation of III-Vs could provide sufficient durability to these high-efficiency materials to meet technical targets for efficiency and semiconductor absorber replacement schedule. We have exceeded 400 hours of stability at -15 mA/cm^2 with N_2^+ implantation and PtRu sputtering on GaAs and exceeded 150 hours of durability at -10 mA/cm^2 with MoS_2 films on $GaInP_2$. We plan to continue optimizing these surface modifications as well as exploring atomic layer deposition of thin oxide and nitride layers to demonstrate 900 hours of stability,

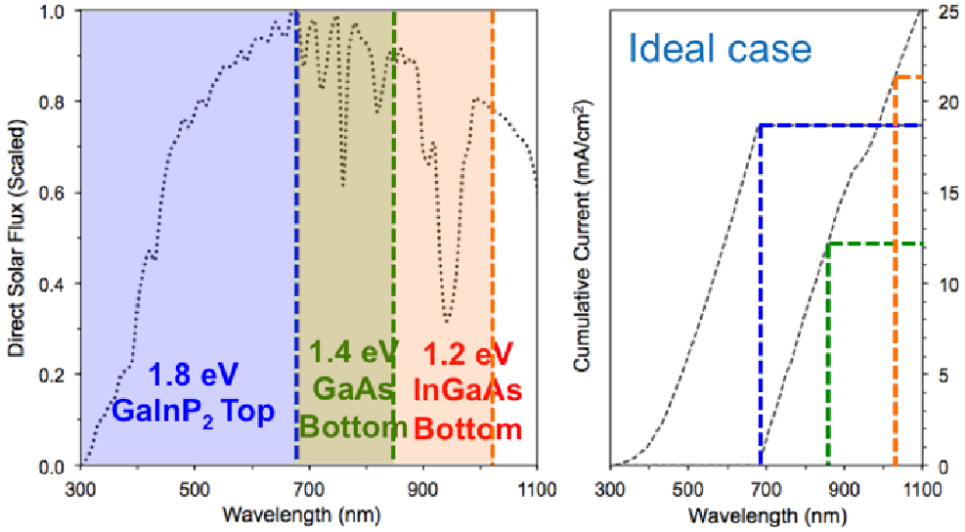

FIGURE 3. The portion of the direct solar spectrum that each semiconductor junction utilizes is depicted on the left. The right image depicts the integrated thermodynamic (no loss) limit of each junction and shows that using $GaInP_2$/GaAs will limit the overall current in these series connected tandems to about 12 mA/cm^2 due to the GaAs junction. Incorporating InGaAs will make the device top junction ($GaInP_2$) limited and increase the overall device current (and efficiency).

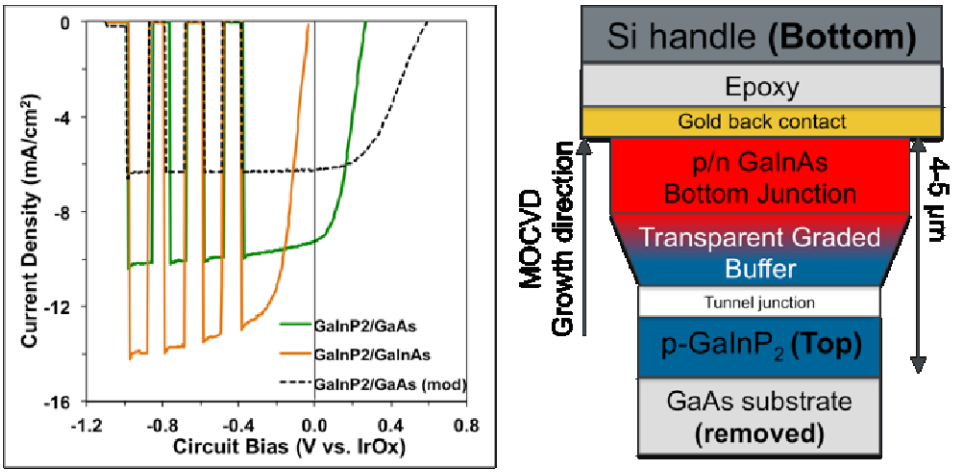

FIGURE 4. Current density vs. circuit bias for a standard tandem (green), an IMM tandem with a 1.2 eV bottom cell bandgap (orange), and a standard tandem with additional GaAs and $GaInP_2$ layers (black, dashed). These measurements were made in 3M H_2SO_4 with the surfactant Triton X-100 under AM1.5 G illumination. The cartoon on the right shows the layered structure of the IMM device.

which corresponds to a 6-month replacement schedule while operating at a 20% capacity factor.

- Lowering the bandgap of the bottom junction in a tandem device is a viable strategy to improving the photocurrent and exceeding 15% STH efficiency, assuming sufficient voltage can be maintained. In order to meet STH efficiency targets of 20% and beyond, antireflection strategies will have to be considered for the photoelectrode surface. We plan to investigate antireflection in parallel with lowered top and bottom bandgap IMM tandems.
- In order to meet PEC hydrogen production targets of <$2/kg, significant reductions in semiconductor synthesis costs must be realized in addition to improved efficiency and durability. We plan to synthesize, or obtain where necessary, semiconductor configurations that use alternative substrates, such as III-V(N) on Si, in addition to those that use synthesis techniques that re-use substrates (spalling, epitaxial lift-off) and evaluate their capacity to meet efficiency and stability targets. We also plan to model the viability of photoreactors that use higher optical concentrations as a possible way to make hydrogen cost less sensitive to those of the semiconductor absorber.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Pending Patent: "Stable Photoelectrode Surfaces and Methods," Publication number US20140332374A1.

FY 2015 PUBLICATIONS & PRESENTATIONS

1. "Enabling a Sustainable Energy Future Through Hydrogen," Science Undergraduate Laboratory Internship Seminar, Golden, CO. October 22, 2014. (Deutsch*) Invited*

2. "Semiconductor Materials for Photoelectrolysis: Requirements, Challenges and Opportunities," Colorado School of Mines MRS Chapter Seminar, Golden, CO. November 20, 2014. (Deutsch) *Invited*

3. "Photoluminescence Response of p-$GaInP_2$ Photocathodes to Vapor and Solution Ambient," American Vacuum Society, 61st Meeting, Baltimore, MD. November 10, 2014. (Young)

4. "Challenges in Photoelectrochemical Water Splitting," University of Arkansas, Little Rock, AR. December 8, 2014 (Turner) *Invited*

5. "Frontiers, Opportunities and Challenges for a Hydrogen Economy," TU Darmstadt, Darmstadt, Germany. February 24, 2015. (Turner) *Invited*

6. "Direct Conversion Photoelectrochemical Systems for Hydrogen Production from Sunlight and Water," Ovshinsky Award Session – A Legacy of Energy Technologies, 2015 American Physical Society March Meeting, San Antonio, TX. March 3, 2015. (Turner) *Invited*

7. "Challenges in photoelectrochemical water splitting materials," 249th American Chemical Society Meeting, Denver, CO. March 22, 2015. (Turner) *Invited*

8. "Solar Water Splitting and the Hydrogen Economy," ACS Committee on Science: Transitioning between Academic Research into Practical Use: Solar-Energy and Advanced Materials, 249th American Chemical Society Meeting, Denver, CO. March 23, 2015. (Turner) *Invited*

9. "Semiconductor materials for efficient photoelectrochemical water splitting: The PEC working Group," 249th American Chemical Society meeting, Denver, CO. March 23, 2015. (Wang) *Invited*

10. "High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production," RE3 Workshop, Louisville, KY. March 24, 2015. (Deutsch) *Invited*

11. "High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production," Materials Research Society Spring Meeting. San Francisco, CA. April 6, 2015. (Deutsch) *Invited*

12. "Sunlight Absorption in Aqueous Electrolytes and Inverted Metamorphic III-V Growth – a Pathway to Direct Solar Water Splitting with Highest Efficiencies," Materials Research Society Spring Meeting. San Francisco, CA. April 8, 2015. (Döscher)

13. "Developing a monolithic GaAs|GaAs tandem photovoltaic|p hotoelectrochemical device," Materials Research Society Spring Meeting. San Francisco, CA. April 9, 2015. (Young)

14. "Materials and Structures for Efficient Photoelectrochemical Water Splitting," Materials Research Society Spring Meeting. San Francisco, CA. April 10, 2015. (Wang)

15. "Tandem devices design for PEC water splitting: The impact of sunlight absorption in aqueous electrolytes and the role of inverted metamorphic III-V epitaxy," University of California-Davis, Davis, CA. April 13, 2015. (Döscher) *Invited*

16. "Direct solar water splitting at high efficiency: Impact of sunlight absorption in aqueous electrolytes and advanced III-V tandem design strategy," 1st International Solar Fuels Conference, Uppsala, Sweden. April 30, 2015. (Döscher)

17. "High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production," 227th Meeting of the Electrochemical Society, Chicago, IL. May 25, 2015. (Deutsch) *Invited*

18. "Materials for Efficient Photoelectrochemical Water Splitting: The PEC Working Group," 227th Meeting of the Electrochemical Society, Chicago, IL. May 25, 2015. (Wang)

19. "Hydrogen from Photoelectrochemical Water Splitting: What's it Gonna' Take?," 227th Meeting of the Electrochemical Society, Chicago, IL. May 25, 2015. (Turner) *Invited Plenary*

20. "Corrosion analysis of p-GaInP2 photocathodes: Comparison of oxygen and argon-sparged electrolyte," 227th Meeting of the Electrochemical Society, Chicago, IL. May 27, 2015. (Young)

21. "High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production," DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington, DC. June 11, 2015. (Deutsch)

22. "Tandem devices design for photoelectrochemical water splitting: The impact of sunlight absorption in aqueous electrolytes and the role of inverted metamorphic III-V epitaxy," TU Clausthal, Kolloquium, Clausthal-Zellerfeld, Germany. June 25, 2015. (Döscher) *Invited*

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