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Approach

The US DOE PEC Working Group approach towards efficient and durable solar H₂ production

- **Approach 1:** Stabilization of High Efficiency Crystalline Material Systems
- **Approach 2:** Enhanced Efficiency in Thin-Film Material Systems
- **Approach 3:** Development of 3rd Generation Materials and Structures

**DOE Targets:**
- >1000h @ STH > 8% (2013)
- Projected PEC Cost: $2 - 4/kg H₂

**MVS/HNEI program**

**Efficiency**

**Durability**

[Diagram showing the approach with interlinked strategies and DOE targets]
Overview

Timeline

Phase 1:
- Project start date: 9/1/2007
- Project end date: 12/31/2010

Passed go/no go evaluation in Nov, 2010

Phase 2:
- Project start date: 1/1/2011
- Project end date: 12/31/2012

Budget

- Total project funding
  - DOE share: $2,970,172
  - Cost share: $820,000
- Funding received FY11: $686k
- Planned funding FY12: $556k

Barriers

- Challenges for photoelectrochemical hydrogen production technologies:
  - Y: Materials Efficiency
  - Z: Materials Durability
  - AB: Bulk Materials Synthesis
  - AC: Device Configuration Designs

Partners

- Collaborators:
  Hawaii Natural Energy Institute (HNEI)
  National Renewable Energy Laboratory (NREL)
  University of Nevada at Las Vegas (UNLV)

- Project Lead: MVSystems, Inc.
Our goal: Develop a monolithic hybrid PEC device powered by MVS’ low-cost a-Si-based tandem solar cell.

Project Objectives:
- Solar-to-hydrogen efficiency: 5%
- Durability: 500-hrs (by the end of Phase II)
# Relevance - Milestones

<table>
<thead>
<tr>
<th>Material/Device</th>
<th>Durability*</th>
<th>Device Efficiency (STH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous Silicon Carbide (a-SiC)</td>
<td>8mA/cm²</td>
<td>310hrs @ 1mA/cm²</td>
</tr>
<tr>
<td>Tungsten Oxide (WO₃)</td>
<td>3.6mA/cm²</td>
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<td>I-III-VI₂ (Copper Chalcopyrite-based)</td>
<td>20mA/cm²</td>
<td>420hrs @ 4mA/cm²</td>
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- **Goal ->** 4mA/cm²
- **Material Photocurrent**
  - Amorphous Silicon Carbide (a-SiC): 8mA/cm²
  - Tungsten Oxide (WO₃): 3.6mA/cm²
  - I-III-VI₂ (Copper Chalcopyrite-based): 20mA/cm²

- **Material/Device Durability**
  - Amorphous Silicon Carbide (a-SiC): 310hrs @ 1mA/cm²
  - Tungsten Oxide (WO₃): 600hrs @ 1.5mA/cm²
  - I-III-VI₂ (Copper Chalcopyrite-based): 420hrs @ 4mA/cm²

- **Device Efficiency (STH)**
  - Amorphous Silicon Carbide (a-SiC): 2.5%STH
  - Tungsten Oxide (WO₃): 3.1%STH
  - I-III-VI₂ (Copper Chalcopyrite-based): 4.34%STH

- **Achievement Status**
  - Amorphous Silicon Carbide (a-SiC): >100% Achieved
  - Tungsten Oxide (WO₃): >100% Achieved
  - I-III-VI₂ (Copper Chalcopyrite-based): >100% Achieved

*Test conditions in slide #24.*
<table>
<thead>
<tr>
<th>Relevance – Barriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB: Synthesis</td>
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<tr>
<td>a-SiC</td>
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<tr>
<td>Entire PEC device fabricated with low-cost PECVD in an cluster tool identical to those used in PV industries.</td>
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<td>AC: Device design</td>
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<tr>
<td>- Achieved:</td>
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<tr>
<td>- Barriers:</td>
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<tr>
<td>Z: Durability</td>
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<td>- Achieved: (so far tested)</td>
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<tr>
<td>Y: Efficiency</td>
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<tr>
<td>- Achieved:</td>
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<td>- Barriers:</td>
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Approaches

Synergetic work on 3 different material classes

1) All 3 hybrid PEC devices will use the same a-Si tandem solar cell “engine”
   --> each improvement on the solar cell design benefits to the entire program

2) Both photo-anodes and photo-cathodes are evaluated under one program
   --> Discovery on new surface catalysts can be implemented to new counter electrodes

3) All 3 material classes performances are evaluated in the same laboratory
   --> all tests are performed under identical experimental conditions facilitating comparison

3 major tasks to achieve STH efficiency > 5%

a-SiC: improve interface energetics and kinetics with appropriate surface treatment
   - decrease overpotential

Metal oxides: identify stable compounds with appropriate band gap (2.0-2.2 eV)
   - improve transport properties with elemental doping

I-III-VI$_2$: lower valence band edge via Cu and Se (partial) substitution
   - decrease overpotentials and increase bandgap from 1.6 to 1.9 eV
Part I

Amorphous Silicon Carbide (a-SiC)
Presenter: Jian Hu, MVSystems, Inc

Part II

Metal Oxide Compounds
Presenter: Nicolas Gaillard, Hawaii Natural Energy Institute

Part III

I-III-VI$_2$ (Copper Chalcopyrite-based)
Presenter: Nicolas Gaillard, Hawaii Natural Energy Institute
All a-SiC films, photoelectrodes, solar cells and the PEC hybrid devices were fabricated in the cluster tool PECVD/Sputtering System, designed and manufactured by MVSystems, Inc.

Main deposition parameters:

- RF power: 10-20 W
- Excitation frequency: 13.56 MHz
- Pressure: 300-550 mTorr
- SiH₄ flow rate: 20 sccm
- CH₄ flow rate: 0-20 sccm
- H₂ flow rate: 0-100 sccm
- Substrate temperature: 200°C

http://www.mvsystemsinc.com

Amorphous and/or nano-crystalline Si solar cells in conjunction with the photo-electrode as the driver for a-SiC, WO3 and I-III-VI₂ PEC.
Progress: Comparison with a Solid-State Configuration

- STH efficiency of hybrid PEC cell should be >4% base on solid state version (right)
- Low current in hybrid PEC cell (left)
- Charge carrier extraction problem at the a-SiC/electrolyte interface
**Progress:** Surface Modification – by methylation (CH$_3$-termination)

Addressing efficiency with catalytic surface treatment

**Surface treatment procedure:**
- Step 1: Eliminate SiO$_x$ from a-SiC surface (via HF etch)
- Step 2: H-termination by immersing the sample into NH$_4$F
- Step 3: Treated with CH$_3$-containing species
- Step 4: Coated with Ti nano-particles

**J$_{sc}$ increase after CH$_3$/Ti treatment**

- J$_{sc}$ = 1 mA/cm$^2$
- 1.2% STH efficiency

[ Data measured by NREL ]
Progress: Surface Modification – Use of Ru Nanoparticles

Addressing efficiency with catalytic surface treatment

- Ru alloys (i.e. Ru-Ni) with high HER catalytic activity demonstrated
- Ru nanoparticles with activity comparable with Pt recently reported (*)

Ru nanoparticle coating (HNEI)

PV/a-SiC hybrid device

STH efficiency of ~2.5% is achieved

$V_{FB}$ increased by 0.5V with Ru n.p.


(*) Data measured by HNEI
Future Work (a-SiC PEC electrode)

⇒ Catalytic activity of a-SiC PEC hybrid devices greatly improved with Ti-CH$_3$ or Ru surface treatments

- Improvement of photocurrent in the hybrid PEC cell.
  a. Refine surface treatment processes and further reduce over-potential: expected $J_{ph} > 3$ mA/cm$^2$ and STH efficiency $> 3\%$.
  b. Improve performance of a-Si tandem solar cell and PV/a-SiC photoelectrode triple junction device:
     expected $FF > 0.7$ and $J_{ph} > 4$ mA/cm$^2$ @1.5V.

- Durability tests.
  - Perform more durability test up to $\geq 500$ hours.
Part I

Amorphous Silicon Carbide (a-SiC)

Presenter: Jian Hu, MVSystems, Inc

Part II

Metal Oxide Compounds

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Part III

I-III-VI\textsubscript{2} (Copper Chalcopyrite-based)

Presenter: Nicolas Gaillard, Hawaii Natural Energy Institute
Progress: New metal oxides with $E_G = 2.0-2.2\text{eV}$

**CuWO$_4$ fabricated with co-sputtering process**

- Band-gap $\approx 2.2\text{ eV}$ ($\text{STH}_{\text{theor.}} = 13\%$)

**Transport properties must be addressed!**

- 0.4 mA/cm$^2$ under AM1.5G illumination

**Addressing efficiency**

- 0.33M H$_3$PO$_4$ / AM1.5$_G$

**Band structure derived from MS and UV-VIS**

**Ideal surface energetics**

- AM1.5$_G$
- 0.33M H$_3$PO$_4$ (pH 1.35)

CuWO$_4$ fabricated by spray-pyrolysis

Process:
- **Precursors**: Cu(ac)+AMT
- **Temperature**: 275°C
- **Uniformity**: ± 5% (1 inch$^2$)
- **Annealing**: 500°C

**CuWO$_4$ stability in various pH**

Stability demonstrated for 24 hrs (so far tested)

Progress: New metal oxides with $E_G = 2.0$-$2.2$eV

Addressing efficiency

Porous CuWO$_4$ thin film $\Rightarrow$ high surface area

0.7 mA/cm$^2$ under AM1.5$_G$ illumination
**Progress:** New metal oxides with $E_G = 2.0-2.2$ eV

**Improving CuWO$_4$ transport properties with CNT**

$\rightarrow$ 1 mA/cm$^2$ achieved with CuWO$_4$/CNT nanocomposites

$\rightarrow$ Compatible with hybrid concept (CNT absorb only 2.5%)
Progress: new monolithic integration for hybrid PEC device

Main barrier: a-Si solar cells performances degraded after long exposure to heat

**Issue**

Effect of heat exposure on (WO₃ filtered) a-Si tandem solar cell performances

**Solution**

Bifacial integration

→ Bifacial monolithic integration demonstrated
→ WO₃ samples clearly underperformed in this test
→ New hybrid device being tested
⇒ Theoretical STH limit with WO$_3$ is approx. 6%. All attempts to reduce $E_G$ have been unsuccessful.

⇒ With a band gap of 2.2 eV, CuWO$_4$ is a serious candidate for low cost PEC hydrogen production, with potentially 13% STH efficiency.

CuWO$_4$ transport properties have been identified as main limitation

Plans to achieve higher efficiency:

1. Other solar absorber/charge collector architectures will be studied (Stanford).
2. Improvements could be also achieved with elemental doping (NREL).
Part I

Amorphous Silicon Carbide (a-SiC)
Presenter: Jian Hu, MVSystems, Inc

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I-III-VI$_2$ (Copper Chalcopyrite-based)
Presenter: Nicolas Gaillard, Hawaii Natural Energy Institute
**Progress:** bulk modifications of CGSe baseline

**Addressing “Efficiency”**

**Barriers:**
1. Bandgap (1.65 eV) currently too small
2. Overpotential too high

Addressing both barriers by lowering valence band-edge with substitution of Ag and/or Sulfur

**Bandgap:**
- CuGaSe$_2$ = 1.65eV (baseline)
- AgGaSe$_2$ up to 1.85eV
- CuGaS$_2$ up to 2.43eV

*Highlight in yellow is the voltage region where completed devices typically operate.*

The graph shows the JV characteristics of three different materials in the I-III-VI$_2$ material class tested in 0.5M H$_2$SO$_4$ under AM1.5G illumination.
Progress: STH efficiency with co-planar integration

Addressing “Device design”

Barrier: Low band gap (1.65eV) materials currently produced require innovative device design

Solution: Large photocurrent produced by materials in this class allow co-planar PV-PEC integration

4.34% STH achieved! (AM1.5 1-sun)

- 3 a-Si PV cells
- CGSe_2 PEC
- Outdoor Standalone (no external voltage):
  - 3.53mA/cm^2 = 4.34%STH
- Surpasses old record while using much cheaper materials

Load-Line Analysis

V = 1.78V
J = -3.64mA/cm^2
Eff. = 4.48%STH

a-Si triple-PV

3 PV + PEC serial device
Future Work (I-III-VI$_2$ hybrid photoelectrode)

- Coplanar Device utilizing 3 PV cells of suitable performance can surpass 5% STH.
- Lowering the valence band to increase $E_g$ and decrease overpotential is THE key to high performance chalcopyrite-based PEC hybrid devices.

Lower overpotential $\Rightarrow$ fewer PV cells required $\Rightarrow$ diminishes photocurrent division

Higher band gap: buried PV cell approach possible (synergy with ongoing research in PV industry towards tandem CIGSe-based PV cells)
Future Work (Novel Inverted Monolithic Stack)

- Progress at MVSystems utilizing higher-bandgap a-SiC (~2.0eV) in PV applications
- Lowering I-III-VI$_2$ bandgap much easier than raising it
- Device development underway, possibility of 8-10%STH efficiency
- Highly dependent on voltage characteristics when fabrication proceeds

Step 1: Coplanar PV cells (~2.0eV) with ~1.4eV CIGSe$_2$ PEC

- 2.0eV a-SiC PV expected transmission
- 1.4eV CIGSe$_2$ PEC expected QE
- Filtered QE (CIGSe$_2$ PEC)

Step 2: Inverted Monolithic Integration

- Higher Bandgap PV
- Slight Lower Bandgap PEC
**a-SiC photoelectrode:**
- Under AM1.5G @1mA/cm², in pH2 buffer solution.
- No dark current increase for 310 hours

**WO₃ photoelectrode:**
- Under AM1.5G @1.6V vs. SCE in pH2.
- High corrosion resistance of tungsten oxide in acidic solution for up to 600 hrs.

**CGSe photoelectrode:**
- Under AM1.5G @1.7V (4mA/cm²), in 0.5M H₂SO₄ for 420 hours total
- Sealant and illumination issues may have led to degradation
Collaborations

– **US Department of Energy PEC working group**: Leading task force on WO$_3$, I-III-VI$_2$ and a-SiC photoelectrodes

– **National Renewable Energy Laboratory**: collaboration to perform theoretical research and advanced morphological analysis of new materials.

– **University of Nevada at Las Vegas**: collaboration to analyze the surface energy band structure of new photoelectrode materials.

– **University of California in Santa Barbara**: collaboration on surface treatment for catalytic purposes.

– **Stanford University**: collaboration on surface treatment for catalytic purposes.

– **Helmholtz Centre Berlin**: New alloy composition (sulfurization) fabrication, material/device theory

– **International Energy Agency/HIA/Annex 26**: collaboration with international institutes and universities including EMPA (Swiss) and University of Warsaw (Poland).
**Project summary**

**a-SiC photoelectrode:**
- Durability of hybrid PV/a-SiC cell: 310 hours
- Photocurrent density (in solid state version): >4 mA/cm² (possible STH efficiency >5%)
- Photocurrent density in pH2 electrolyte: 2.0 mA/cm² (or STH efficiency of ~2.5%)

Future work: enhance surface catalysis and improve a-Si tandem solar cell (FF, Jsc)

**Metal oxides photoelectrode:**
- Durability of WO₃ sputtered material: 600 hrs.
- CuWO₄ (2.2 eV) is a promising PEC material, \( J_{\text{photo}} \times 10 \) over the past year.
- Bifacial monolithic integration demonstrated. Compatible with CGSe systems.

Future work: improve CuWO₄ transport properties (new architectures and/or doping)

**I-III-VI₂ photoelectrode:**
- Durability of CGSe PEC cell: 420 hrs
- Photocurrent density of PEC film: 20 mA/cm² (offers novel device integration)
- Photocurrent density of coplanar hybrid device: 3.53 mA/cm² (4.34% STH efficiency)

Future work: develop robust sulfurization process (↗ \( E_G \)) and create CIGSe with lower \( E_G \)
Technical Back-Up Slides
Solid state device has a barrier at the a-SiC/ITO interface.

Hence current density is low (~4mA/cm²) and FF is low. Despite this, we can still get 4mA/cm², which could translate to STH >5%.

Removal of barrier will improve the solid state device substantially.
**a-SiC**: Surface methylation and nanoparticles

Surface methylation (CH₃) and nanoparticle coating

- a-SiC(i), ~100nm
- a-Si(i), 80nm
- a-Si(i), 360nm
- SnO₂
- Glass

(\(\text{CH}_3\)-termination (methylation) prevents oxidation)

Photocurrent enhanced (i.e., from 5 to 25 mA/cm² in n-Si electrode* )

500-hr durability test on hybrid PV/a-SiC device

- Under AM1.5G @1mA/cm², in pH2 buffer solution.

- Hybrid PV/a-SiC device after 500-hrs (initial results)
  - Surface morphology changed
  - Investigation underway (ie by EDS)

  - Photocurrent remains largely unchanged with improved fill-factor
  - Dark current increase @>-1V

[ Data measured by NREL ]
a-SiC: Hybrid PV/a-SiC PEC Device - Simulation Results

- Energy band diagram for hybrid PV/a-SiC PEC device

- Calculated photocurrent and STH efficiency for 3 different configurations:

<table>
<thead>
<tr>
<th>Photo-electrode</th>
<th>Eg (eV)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>PV cell configuration</th>
<th>Filtered Available</th>
<th>Voc (V)</th>
<th>STH (%) Possible</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-SiC:H (1)</td>
<td>2</td>
<td>8.85</td>
<td>0.6</td>
<td>a-Si/a-Si</td>
<td>7.1</td>
<td>1.9</td>
<td>8.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(100 nm)</td>
<td>(p-i)</td>
<td>(620nm/132nm)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>a-SiC:H (2)</td>
<td>2</td>
<td>8.85</td>
<td>0.6</td>
<td>nc-Si/a-Si</td>
<td>8.85</td>
<td>1.5</td>
<td>10.89</td>
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<tr>
<td></td>
<td></td>
<td>(100 nm)</td>
<td>(p-i)</td>
<td>(1.5µm/244nm)</td>
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<tr>
<td>a-SiC:H (3)</td>
<td>2</td>
<td>12</td>
<td>&gt;1</td>
<td>nc-Si</td>
<td>12.0</td>
<td>0.6</td>
<td>14.7</td>
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<tr>
<td></td>
<td></td>
<td>(250 nm)</td>
<td>(p-i-n)</td>
<td>(1.5µm)</td>
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**Progress:** reduction of WO₃-based material bandgap

**Improving CuWO₄ transport properties with CNT**

1. Various CNT:CuWO₄ w.t. %
2. Spray on SnO₂:F substrate
3. Annealing @ 500°C in air

→ 1 mA/cm² achieved with CuWO₄CNT nanocomposites
→ Compatible with hybrid concept (only 2.5% transmission loss)
Progress: reduction of WO$_3$-based material bandgap