Role of Surface Chemistry in Photovoltaics

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Outline

I. Moore’s Law for Photovoltaics

II. Energy Bands in Heterojunctions

III. Surface Recombination in Silicon Solar Cells
Sustainability of Electricity

- Increasing sustainability requires significant PhotoVoltaic generation capacity within a decade.
- While PV has realized compound growth rates > 40% for a decade, it presently accounts for <1% of electrical generating capacity.
- Can PV reach TeraWatt production capacity in a decade – is there a Moore’s Law analog to PV?

Example: 40% growth rates
1. All new US electricity needs met by PV – within 5 years
2. New world electricity needs met by PV – within about 10 years
3. US electricity needs met by PV – within 15 years
4. World electricity needs met by PV – within 20 years
Moore’s Law Analog for PV

- Integrated circuits have had a transformational impact by increasing performance, reducing costs and integrating electronic circuitry into a wide range of systems, allowing rapid expansion in their use.
- Moore’s Law expressed the sustained, rapid growth of transistor.
- Staying on Moore’s Law requires focused, integrated projects coupled with scientific and technological innovation driven by a roadmap—e.g., voltage scaling, photolithography, high k-dielectrics, etc.
QESST Approach

- Improve efficiency, manufacturability and $/kWh for silicon, thin film, and tandem solar cells
  - **Efficiency in a manufacturable process is key metric**
- Develop advanced approaches which increase efficiency and are compatible with existing production
- Integrate with other components to increase functionality, performance and enable new applications.
II-VI ZnTe/ZnSe Thin Film Solar Cell Structures & Band Alignment
Energy conversion efficiency is the percentage of incident energy of sunlight or heat that actually ends up as electric power.

Carrier transport behavior at interface severely affects the device performance.

Suitable band offset at interface is critical for carrier transport.

Heterojunction
--- Band alignment at interface

![Diagram showing band alignment at interface with energy levels and band bending](image)
ZnTe-based Solar Cell

A promising II-VI material for TFSC:

- Wide direct band gap ($E_G > 2$ eV)
- Tunable bandgap via alloying
- Nontoxic materials
- Various growth techniques

High diffusion voltage at ZnSe/ZnTe heterojunction, $V_{oc} > 1$V is feasible

ZnTe-based Solar Cell

A promising II-VI material for TFSC:

- Wide direct band gap ($E_G$ 2.24 eV)
- Tunable bandgap via alloying
- Nontoxic materials
- Various growth techniques

High diffusion voltage at ZnSe/ZnTe heterojunction, $V_{oc} > 1V$ is feasible
Film growth

--- Close Space Sublimation/Vapor transport

Low cost --- No HV required
Reliability & Reproducibility
Scalable (compatible to roll-roll processing)

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>Source T (°C)</th>
<th>Sub T (°C)</th>
<th>Growth Rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe</td>
<td>730</td>
<td>575</td>
<td>0.1</td>
</tr>
<tr>
<td>ZnTe</td>
<td>670</td>
<td>575</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Abound Solar (formerly known as AVA Solar)
Production Prototype
(National CdTe Team Meeting April 5 and 6, 2005)
SEM cross-section image

4 um ZnTe on ZnSe/ITO/BSG glass

Energy-dispersive X-ray spectroscopy (EDS) confirmed the chemical composition of distinctive films.
**Photoemission Spectroscopy**

\[ E_B = h\nu - E_K - \Phi \]

Surface sensitive technique:
Quantitative analysis of small chemical shifts depending on the chemical environment of the atom which is ionized, allowing chemical structure and chemical identification to be determined.

![Image](http://en.wikipedia.org/wiki/File:ARPESgeneral.png)
**XPS Measurements on ZnSe Surface**

X-Ray photoelectron spectroscopy using Al-Kα source measured core level for ZnSe film surface, confirmed chemical compositions of the film surfaces.

*High-resolution surface science system PHI 5600*

Probed oxide on ZnSe surface

Binding energy of Se 3d core level for Se$^{2-}$ in ZnSe is **54.1 eV** as for Se$^{4+}$ in SeO$_2$ at **59 eV**
Surface oxide removed by sputtering or chemical etch

Prior Treatment of XPS measurement
- Ar$^+$ ion Sputtering
- Wet chemical etching
  - 40% H$_2$SO$_4$ at 50 ºC
  - 1% HCl RT

could successfully remove the oxide.
Elemental Se residual observed after etching--- Post annealing

Elemental Se is observed after etching;

Same mild anneal in-situ: inside the UHV photoemission chamber desorb it.
Fermi Level Alignment

- UPS measurement of Valence Band Maximum (VBM) at Au film surface
  \[ \rightarrow \text{Fermi Level} \]
- Aligned with all the other VBM measurements
- Assume all Fermi levels are aligned

\[
\frac{[-6.45 + (-6.66)]}{2} = -6.55 \text{ eV}
\]

Bias: -4.96 eV
Au Fermi level: -1.59 eV
UPS Measurements

Synchrotron radiation at Brookhaven National Laboratory and SSRL

Valence band (VB) structures for ZnSe and ZnTe films
Surface oxide altered valence band of ZnSe
Extrapolation of the rising edges give the valence-band maximum:
Energy Band Diagram & Device $V_{OC}$ and $J_{SC}$

As-deposited ZnSe

- $\Delta E_{vac} = 0.24\text{eV}$
- Fermi Level
- $E_{CB}$
- $E_{VB}$
- Acceptors
- Donors

Sputtered ZnSe

- $\Delta E_{vac} = 1.57\text{eV}$
- Ar$^+$ ion Sputtered Bulk
- Fermi Level
- $E_{CB}$
- $E_{VB}$
- Acceptors
- Donors

Diagram based on VB, $E_f$ (UPS) and $E_G$ (optical absorption)
Energy Band Diagram & Device $V_{OC}$ and $J_{SC}$

Solar cell parameters
AM1.5 Illumination at 25°C

<table>
<thead>
<tr>
<th>ZnSe Preparation</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{SC}$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>450</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Rapid transfer (&lt;1 min)</td>
<td>600</td>
<td>~5</td>
</tr>
<tr>
<td>Chemical Etched</td>
<td>750</td>
<td>&gt;5</td>
</tr>
</tbody>
</table>
Direct measurement of CBM
--- Inverse photoemission

Inverse photoemission is the time-reversed process of photoemission, complementary technique to measure the conduction band edge directly.

\[ PE \quad E_B = h\nu - E_K \]

\[ IPE \quad E_{(above\ EF)} = h\nu - E_K \]

http://www.physics.rutgers.edu/%7Ebart/grouphome/PE_IPE_RAB.htm
**IPES Schematic Diagram**

**Main blocks: UHV system / <10^{-7} Torr)**
- Source: electron gun
- Diffraction grating
- Position sensitive detector
- Analysis programming

Concave spherical diffraction grating

Position sensitive MCP detector
(Micro-channel plate detector)

Low energy electron gun (5-30 eV)
Thin Film Solar Cell Summary

- CSS & evaporation of sequential ZnSe/ZnTe growth demonstrated:

- Significant chemical oxidation and sensitivity to storage of ZnSe
  - Oxidation state observed by PES
  - UPS using synchrotron radiation detected band structure offsets changed by oxidation
  - Robust device baseline → minimize exposure of films to oxygen

- Film structure characterization:
  Optimize CSS grown ZnSe film → diminish lateral facets
  Refine the CSS equipment and enable better control of the ZnTe growth
  Increase grain size of ZnSe and ZnTe in evaporation growth;
  Recrystallization → post annealing
Roadmap for silicon devices

Existing State of the Art Silicon Solar Cell

Surface Passivation
Low Temperature Processes
e.g., no diffusions
New metallization processes

Thin, passivated Si Solar Cell
50 - 100 μm

Further reduced cost
Advantage: Tolerates lower material quality

Flexible Solar Cells
Concentrators

SI containing tandems

Ultra-thin high efficiency solar cells
Ultra-thin high efficiency solar cells

New photonic approaches
New physical processes
e.g., hyper-doped silicon

Si eff > 40%

Barriers

Lower cost material

New materials
e.g., organics

Heterojunctions
thin film materials
and processes

Conventional Silicon: Crystalline Silicon
Cost Reduction Opportunities, Limitations

Silicon PV cells are approaching the practical performance limit.

Bulk lifetime = 1 ms

Efficiency (%) vs. Cell thickness (μm)

1° Light in cone enters solar cell
2° Light outside cone rejected
15° 30° 90° Half angle

1000 effective SRV (cm/s)

Future Present
Dual-Junction “Limit” Results

- **III-V/Si Device**
  - Unconstrained
    - 1.72eV/1.12eV
    - 42% Efficiency
- **III-V/SiGe Device**
  - Lattice-matched
    - 1.58eV/0.84eV
    - GaAsP/SiGe
    - 40% Efficiency
GaAsP/SiGe Tandem Device

Schmeider, Diaz, Barnett, Veeco, Amber Wave

- Improved TJs, Window layers, Integration (Martin, Brianna, ….)
  - $V_{oc}$ as high as 1.32 V
  - Efficiency as high as 15.2% (AR corrected)
  - $J_{sc}$-$V_{oc}$ FF = 78%
  - Top cell ideality factor = 1.84 (Assumes n=1 in SiGe)

- Bottom cell not optimized (Xin, Dun, Anastasia, ….)
  - Low bottom cell current—Ge:Si not optimized

Generation 3 Solar Cell

- GaAsP Contact
- GaInP Window
- GaAsP Solar Cell
- GaInP BSF
- GaAsP TJs
- III-V Nucleation
- SiGe Solar Cell
- SiGe Graded Buffer
- Si Substrate

Graphs showing IV characteristics and external quantum efficiency.
Roadmap for silicon devices

- Thin, passivated Si Solar Cell
  - 50 - 100 um
  - Advantage: Tolerates lower material quality
  - Further reduced cost

- Surface Passivation
  - Low Temperature Processes
  - e.g., no diffusion
  - New metalization processes

- Existing State of the Art Silicon Solar Cell
  - Barriers
  - Lower cost material

- Flexible Solar Cells Concentrators
- Ultra-thin high efficiency solar cells
- Ultra-thin high efficiency solar cells
- Si eff > 40%

- New photonic approaches
- New physical processes e.g., hyper-doped silicon
- Nano processes and fabrication

Graphs and charts illustrate performance improvements and cost reductions over time.
Recombination Processes

- Process where an electron & a hole annihilate
- Both Carriers disappear - no collection!!
- Recombination types
  - Radiative
  - Trap-Assisted
  - Auger
  - Surface
  - Emitter

How good are the surfaces?
- Minority carrier lifetime (μs or ms)
- Surface recombination velocity (S in cm/sec)

\[
\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2S}{W}
\]
Si Passivation Schemes

Surface recombination is controlled by growing a passivation

**Moderate-to-high Temp. Techs.**
- a-Si (PECVD at 200°C)
- SiN (PECVD at 200-350°C)
- SiO₂ (Diff. Furnaces at 800-900°C)

**ROOM Temp Techs.**
- Hydrogen Fluoride (HF)
- Quinhydrone-Methanol (QHY/ME)
- Iodine-Methanol (I₂/ME)
QuinHYdrone/MEthanol Passivation

**Why QHY-ME?**
- Easy to use
- Low cost
- Important characterization tool
- Room temperature operation
- Reversible
- Ideal passivation if stable

**Procedure**
- QHY-ME = 0.01 mol/L
- Wafer cleaning: Piranha & HF
- Wafers in solution in acid resistant plastic bag
- Passivation time - 1 hour at room temp
- Measure lifetime/ Implied-Voc/ S

**Quinhydrone Structure**

**Limitations**
Lifetime not stable if sample exposed to air
Lifetime Results (QHY/ME)

**n-type Si <100>, 100 ohm-cm, 460 µm**

- **Lifetime (IN solution)**: 3.3 ms; 7 cm/s
- **Lifetime (20 mins OUT of solution)**: 2.7 ms; 8.7 cm/s

**p-type Si <100>, 3 ohm-cm, 170 µm**

- **Lifetime (IN solution)**: 1.1 ms; 21 cm/s
- **Lifetime (20 mins OUT of solution)**: 0.436 ms; 53 cm/s

Hydrogen Passivation of Silicon

- hydrocarbons
- metallic impurities
- silicon oxide layer
- ionic contamination
- particles

Premium RCA clean:
- **SC-1**: NH$_4$OH, H$_2$O$_2$, and H$_2$O at typically 80 C for 10 min
  - Removal of hydrocarbons and may cause oxidation and metal contamination.
- Immersion in HF in H$_2$O at 25 C
  - Removal of oxide and the ions dissolved in the oxide.
- **SC-2**: HCl, H$_2$O$_2$, and H$_2$O at 80 C.
  - Removes the remaining metallic contamination.
- Final HF rinse to remove oxide.

Alternative wet cleaning method:
- Hot H$_2$O$_2$ –H$_2$SO$_4$ solution (Piranha clean)
  - Cleans heavily contaminated Si wafers.
- Dilute HF/water solution.
Infrared spectra of the Si-H stretching region of H-terminated Si(111) surfaces

- a) RCA method;
- b) HF-dip method with a float zone crystal
- c) HF-dip method with n-doped crystal.

RCA clean has better surface chemistry and morphology (AFM)

<table>
<thead>
<tr>
<th>Surface Preparation</th>
<th>Charge-carrier Lifetime, ( \tau ) (( \mu )s)</th>
<th>Surface Recombination Velocity, ( S ) (cm s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCA</td>
<td>60.7±28.9</td>
<td>1002.7±577.3</td>
</tr>
<tr>
<td>HF-dip</td>
<td>169.9±14.0</td>
<td>295.3±24.4</td>
</tr>
</tbody>
</table>

But worse lifetimes!!

Chemical and electrical passivation of Si(111) surfaces

IR investigation of the C-H stretching spectral region of the 1-decene modified Si (111) surface produced by a) RCA method and b) HF-dip procedure.

IR investigation of the C-H stretching spectral region of the 1-octadecene modified Si (111) surface produced by a) RCA method and b) HF-dip procedure.

XPS Studies Si substrates after QYH/Me

First Proposed Surface Bonding from XPS

<table>
<thead>
<tr>
<th>Oxide termination</th>
<th>HF termination</th>
<th>QHY/ME treated</th>
</tr>
</thead>
</table>

IN Solution

OUT of Solution

Lifetime (IN solution) | Lifetime (24 hrs OUT of solution)
---|---
3.3 ms | 1.9 ms
Recombination center

*Quinhydrone (QHY)*

**Lifetime in solution at 1hr**

- In solution (1 hr)
- Out of solution (20 mins)
- Out of solution (1 day)
- Out of solution (3 days)

**Minority Carrier Lifetime (ms)**

- n-type

**Injection Level (cm⁻³)**

- $10^{14}$
- $10^{15}$
- $10^{16}$

**Reagents**

- p-benzoquinone $\text{C}_6\text{H}_4\text{O}_2$
- Hydroquinone $\text{C}_6\text{H}_4(\text{OH})_2$

**DDQ**
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)

2,6-dimethoxy-(1,4)-benzoquinone (DMBQ)

Acetylacetone
XPS

C

C-O

C-C

Si

Si

Si^0

SiOx

H H H

Si

C-O

C-C

Binding Energy (eV)

Binding Energy (eV)

Binding Energy (eV)

Energy (eV)

Department of Materials Science & Engineering
University of Delaware
Surface passivation of Si with hydroquinone

- Increases carrier lifetime dramatically.
- Slows oxidation rate compared to Hydrogen passivation.
- How
  - What reaction?
    - Density functional theory says BQ will not react with H-terminated Si, but will react with Si(111)7x7. What defects are important? (D. Okeeva)
    - BQ is photoactive—is light from Sinton test important in observed passivity? (L. Costello, M. Chen)
    - Are protons in MeOH important in passivity (L. Costello)?
  - Is passivating site a charge center?
  - Can we generalize it?
    - How do we make organic/Si induced junctions (N. Kotulak, ASU)
    - Can organic passivation of Si nanowires be improved (Cal Tech)
Surface Photovoltage
with Prof. Sefik Suzer, Bilkent University

Can induce shifts in surface potential (binding energy) by up to 0.5 eV with laser

• Can this induce changes in contact angle?
• Different surface chemistry (redox chemistry)?
Lifetime tester, data
Kotulak, Costello, Chen

p-type, methanol

n-type, methanol

p-type, ether

n-type, ether

Not simple redox
Protons are important
Surface chemistry is crucial in next generation solar cells!!

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