New Concepts and Materials for Solar Energy Conversion

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http://emat-solar.lbl.gov/
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The Energy Challenge

- With a projected global population of 12 billion by 2050 coupled with moderate economic growth, the total global power consumption is estimated to be ~28 TW. Current global use is ~13 TW.
- To cap CO₂ at 550 ppm (twice the pre-industrial level), most of this additional energy needs to come from carbon-free sources.
- A comprehensive approach is required to address this difficult and complex issue facing humankind.
Solar Energy Potential

- Theoretical: $1.2 \times 10^5$ TW solar energy potential
  (1.76 $\times 10^5$ TW striking Earth; 0.30 Global mean)
  - Energy in 1 hr of sunlight $\leftrightarrow$ 14 TW for a year
- Practical: $\approx 600$ TW solar energy potential
  (50 TW - 1500 TW depending on land fraction etc.; WEA 2000)
  Onshore electricity generation potential of $\approx 60$ TW (10% conversion efficiency):
- Photosynthesis: 90 TW
Energy Production by Source

Renewable Energy Sources

- **94.2 Quadrillion BTU**
- **7.0 Quadrillion BTU**

www.eia.doe.gov/fuelrenewable.html
Courtesy of Renewable Energy Annual website
There is a growing consensus that continued use of carbon based fuels for energy production will irreversibly change the planet’s climate.
Energy dilemma

Fossil fuels
Abundant, inexpensive energy resource base
Potentially destructive to environment and survival of humankind

Renewable Energy Sources
Safe and environmentally friendly
Still relatively expensive, cumbersome technology
Needs major scientific/technological/cost breakthroughs
Why should one work on renewable energy?
Global Warming and CO₂ Emission

Over the 20th century, human population quadrupled and energy consumption increased sixteenfold. Near the end of the last century, a critical threshold was crossed, and warming from the fossil fuel greenhouse became a dominant factor in climate change.

Hoffert, DOE workshop
To make money


- Biofuels: 2007 - 25, 2017 - 81
- Wind Power: 2007 - 30, 2017 - 83
- Photovoltaic: 2007 - 20, 2017 - 74
- Fuel Cells: 2007 - 2, 2017 - 16
- Total: 2007 - 77, 2017 - 264

JEl May 2008, Clean Edge, Inc.
To do exciting multidisciplinary science

Intersection of physics, chemistry and material science
Solar Energy Utilization

Fuels

CO₂
Sugar
H₂O
O₂

Photosynthesis

Semiconductor/Liquid Junctions

H₂O

Electricity

Light

Fuel

Electricity

Fuels

O₂
H₂
e

Semiconductor/Liquid Junctions

Photovoltaics

Adapted from Nathan S. Lewis, 1998
1. Thermalization loss
2. Junction loss
3. Contact loss
4. Recombination loss

- Dark and light I-V curves
- \( V_{\text{open-circuit}} \)
- \( I_{\text{short-circuit}} \)
- Maximum power \( P_m \)
- Fill factor (squareness)
  \[ FF = \frac{P_m}{V_{\text{open-circuit}} \times I_{\text{short-circuit}}} \]
How to improve the power conversion efficiency?

Each of the cells efficiently converts photons from a narrow energy range.

Band gaps are selected for optimum coverage of the solar energy spectrum.

Strict materials requirements
Complex, expensive technology

The intermediate band serves as a “stepping stone” to transfer electrons from the valence to conduction band.

Photons from broad energy range are absorbed and participate in generation of current.
Best Research-Cell Efficiencies

Current record - 43.5%
### Three-Junction Solar Cells

#### Structure of Triple-Junction (3J) Cell

<table>
<thead>
<tr>
<th>AR Coating</th>
<th>Front Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>n^+ (In)GaAs</td>
<td></td>
</tr>
<tr>
<td>n^+ AlInP [Si]</td>
<td></td>
</tr>
<tr>
<td>n^+ InGaP [Si]</td>
<td></td>
</tr>
<tr>
<td>p InGaP [Zn]</td>
<td></td>
</tr>
<tr>
<td>p AlInP [Zn]</td>
<td></td>
</tr>
<tr>
<td>p^++ AlGaAs [C]</td>
<td></td>
</tr>
<tr>
<td>n^+ InGaP [Si]</td>
<td></td>
</tr>
<tr>
<td>n^+ AlInP [Si]</td>
<td></td>
</tr>
<tr>
<td>n^+ (In)GaAs [Si]</td>
<td></td>
</tr>
<tr>
<td>p (In)GaAs [Zn]</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>n^+ InGaP [Si]</td>
<td></td>
</tr>
<tr>
<td>n^+ (In)GaAs [Si]</td>
<td></td>
</tr>
<tr>
<td>n^+ GaAs : 0.1µm</td>
<td></td>
</tr>
<tr>
<td>p Ge Substrate</td>
<td></td>
</tr>
<tr>
<td>Back Contact</td>
<td></td>
</tr>
</tbody>
</table>

#### Tunnel Junctions
- **InGaP Top Cell**
- **InGaAs Middle Cell**
- **Buffer Layer**
- **Ge Bottom Cell**

#### Key Points
- **Efficiencies up to 41%**
- **Six different elements**
- **Three different dopants**
- **Practically used:**
  - 3-junction cells
- **Research:**
  - 4 to 5 junctions

Could this be simplified?
Group III-Nitrides before 2002

![Graph showing Band Gap Energy vs. Lattice Constant for various materials including AlN, BN, diamond, GaN, ZnO, 6H-SiC, InN, Al₂O₃, MgO, Si, GaAs, GaP, InP, ZnS, MgS, and CdSe.]
Fundamental Bandgap of Wurtzite InN

- MBE-grown high-quality InN
- All characteristic band gap features lie near 0.7 eV
- No energy gap is observed around 2 eV
In$_{1-x}$Ga$_x$N Alloys

- Small bowing parameter in In$_{1-x}$Ga$_x$N: $b = 1.43$ eV
- The bandgap of this ternary system ranges from the infrared to the ultraviolet region!
Full solar spectrum nitrides

- The direct energy gap of $\text{In}_{1-x}\text{Ga}_x\text{N}$ covers most of the solar spectrum
What is unusual about InN?

- InN has electron affinity of 5.8 eV, larger than any other semiconductor.
- Extreme propensity for native n-type conduction and surface electron accumulation for InN and In-rich $\text{In}_x\text{Ga}_{1-x}\text{N}$.
Integration of InGaN with Si

Conduction Band

Valence Band

Eg = 1.1 eV

Eg ~ 1.7-1.8 eV

No barrier for e-h recombination
Band diagram of In$_{46}$Ga$_{54}$N/Si

- **In$_{46}$Ga$_{54}$N**
  - p-type
  - $Na=1e18$
  - n-type
  - $Nd=5e19$

- **Si**
  - p-type
  - $Na=1e17$
  - n-type
  - $Nd=1e17$

Energy, relative to $E_F$ (eV)

Depth from Surface (Angstroms)
Two-junction hybrid solar cell

\[ \text{In}_{.46}\text{Ga}_{.54}\text{N} \quad \text{Si} \]

Diagram showing energy levels (E) for a two-junction hybrid solar cell with In$_{.46}$Ga$_{.54}$N and Si.
Two-junction hybrid solar cell

In$_{46}$Ga$_{54}$N

Si
Two-junction solar cell
Two-junction hybrid solar cell

In$_{46}$Ga$_{54}$N

Si

E

h$^+$
e$^-$
h$^+$
e$^-$
Two-junction hybrid solar cell

In$_{46}$Ga$_{54}$N

Si

$E$

$e^-$ $e^-$ $e^-$

$h^+$ $h^+$ $h^+$

$h^+$ $h^+$ $h^+$

$e^-$ $e^-$ $e^-$

$h^+$ $h^+$ $h^+$
Two-junction hybrid solar cell

In_{0.46}Ga_{0.54}N

Si

e-e-e-

h+h+h+
Two-junction hybrid solar cell

\[ V_{oc,\text{cell}} = V_{oc,\text{InGaN}} + V_{oc,\text{InGaN}} \]
**InGaN/Si tandem**

- Optimum top cell bandgap for a dual junction tandem solar cell with a Si bottom cell: 1.7~1.8 eV
- Thermodynamic efficiency limits (1x sun AM1.5G) Si single junction: 29%, with additional top cell: 42.5%

Adding InGaN top cell boosts a 20% efficient Si cell into more than 30% efficient tandem cell!

No tunnel junction needed
InGaN/Si MJ efficiency estimates

Calculated 300 K AM1.5 direct efficiency of a 2J InGaN/Si tandem solar cell.

The maximum efficiency is 35% using InGaN with a bandgap of 1.7 eV (In$_{0.5}$Ga$_{0.5}$N).

**Assumed InGaN parameters**

$\mu_e = 300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

$\mu_h = 50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

$m_e = 0.07m_0$

$m_h = 0.7m_0$

The surface recombination velocities assumed to be zero.
GaN-Si tandem cell

**GaN/Si hybrid tandem**

Not current matching!
Top cell greatly restricts the current
Eg = 3.4 eV → max. Jsc = 0.6 mA/cm²
(1 sun, 100% QE)

Illumination: 1x AM1.5G plus 325 nm HeCd laser
Voc = 2.5 V, Jsc = 7.5 mA/cm², fill factor = 61%

**Demonstration of GaN-Si tandem**
(developed with funding by RSLE)

External Quantum Efficiency

Clear evidence for tandem PV action
Intermediate band solar cells

Multi-junction solar cell

- Each cell converts photons from a narrow energy range.
- Band gaps are selected for optimum coverage of the solar spectrum.
- Strict materials requirements.
- Complex, expensive technology.

Intermediate band solar cells

- The intermediate band serves as a "stepping stone" to transfer electrons from the valence to conduction band.
- Photons from broad energy range are absorbed and participate in generation of current.
Intermediate band cell

Sun

n-type

p-type

n+
Intermediate band cell

Sun
Intermediate band cell
Intermediate band cell
Intermediate band cell

The intermediate band cell acts as a up-converter for low energy photons

Two small energy photons produce single electron-hole pair contributing to large $V_{oc}$
Intermediate Band Solar Cells (IBSCs)

Concept first proposed in early 1960’s but no practical demonstrations

63.2%!

- Simple, one junction design
- Higher efficiency limits
- No material suitable for IBSC
- QD arrays used to demonstrate IB transition
Engineering *Electronic Band Structure* for Solar Energy Applications

- Alloying materials with distinctly different electronegativities and/or atomic radii, e.g. III-N_x-V_{1-x}, II-O_x-VI_{1-x}
- Band edges are strongly affected by anticrossing interaction between localized and extended states
- Such highly mismatched alloys (HMAs) are difficult to synthesize

![Chemical Elements Table](image)

![Band Diagram](image)
Highly Mismatched Alloys: conduction band anticrossing

A highly mismatched alloy (HMA) is formed when anions are partially replaced with distinctly different isovalent elements

- Drastic decrease in bandgap with N incorporation
- Changes in transport properties due to modified conduction band
- Formation of an intermediate band

Conduction band anticrossing

e.g. As-rich GaNAs, Te-rich ZnOTe
Multiband in Dilute Nitride HMA

Dilute nitride HMA (GaN$_x$As$_{1-x}$, $x \sim 0.02$)

- BIB-AlGaAs blocking layers to isolate the IB from the charge collecting contacts
- UIB- no blocking layers, IB acts as the conduction band

Dilute Nitride HMA IBSC

Demonstrates the principle of IBSC with a three band dilute nitride material.

Issues: optimize N concentration
       more efficient carrier collection
       doping level in absorber layer
ZnOTe synthesized using O implantation followed by pulsed laser melting

External Quantum Efficiency clearly shows a photocurrent with excitations to the intermediate band

T. Tanaka et. al., Jpn. J. Appl. Phys. 50 (2011) 082304
Band Anticrossing in HMAs

- Localized level above CBE and interaction with CB
  - GaAs(N), ZnSe(O), CdTe(O)

- Localized level below CBE and interaction with CB
  - GaAsP(N), ZnTe(O)

- Localized level above VBE and interaction with VB
  - GaN(As), ZnSe(Te), ZnS(Se), GaN(Bi)

- Localized level below VBE and interaction with VB
  - GaAs(Bi), GaAs(Sb), Ge(Sn)
Photoelectrochemical Cells (PECs)

Material requirements

- Band gap must be at least 1.8-2.0 eV but small enough to absorb most sunlight
- Band edges must straddle Redox potentials
- Fast charge transfer
- Stable in aqueous solution

\[ 2h \nu + H_2O \rightarrow H_2(g) + \frac{1}{2} O_2 (g) \]
Semiconductors for PECs

Sources
Semiconductors for PECs: III-nitrides

Sources

8/17/2010
Semiconductors for PECs: oxides

Sources
Band Structure Engineering: GaNAs

- Allying materials with distinctly different electronegativities and/or atomic radii
- Band edges are strongly affected by anticrossing interaction between localized and extended states
Interpolation of BAC of alloys with a limited composition range:
- Bandgap reaches a minimum at $x \sim 0.8$ with a minimum band gap of 0.7 eV
- Drastically different from values predicted by virtual crystal approximation or using a single-bowing-parameter fitting.

Growth of $\text{GaN}_{1-x}\text{As}_x$ alloys with large composition is challenging due to the miscibility gap for the Ga-N-As system.
Band Gap: Composition Dependence

- Band gap of GaNAs covers most of the solar spectrum
- Films deposited on different substrates follow the same trend
- Experimental data follow the trend of the BAC interpolation.
- Amorphous alloys (0.15<x<0.8) can be utilized for low cost solar cell applications
- Can these materials be doped?
Strong Optical Absorption

- Sharp absorption edges
- Band gap decreases with As content
- The monotonic shift of absorption edge suggests random alloys with no phase separation
- All light absorbed by a thin film.
Conduction and valence band bowing

Soft x-ray absorption (CB) and emission (VB) spectroscopy

- $E_g$ reduction due to movements of both CB and VB edges
- CB and VB shifts in crystalline/amorphous GaNAs alloys follows the trend of the BAC model
Highly Mismatched Oxides
Summary

- New solar concepts are developed based on the progress in understanding of the electronic structure of complex semiconductor systems.
- Highly mismatched semiconductor alloys allow for electronic band structure engineering through an independent control of the conduction and the valence band offsets.
- Better understanding of the properties of surfaces and interfaces of the dissimilar materials essential for the new concepts of high efficiency solar and photoelectrochemical cells.
Extremely High Hole Concentration

Controlled heavy p-type doping of amorphous GaAs could have significant consequences for the whole group III-nitride based semiconductor industry.