Narrow-Gap Semiconductors for High Efficiency Next-Generation Photovoltaics

Ian R. Sellers
Dept. Physics & Astronomy
University of Oklahoma

• Introduction: the energy problem, photovoltaics……
• Current status of PV: state of the art, economics etc.
• Next Generation PV: where next? Third-Generation PV

Photovoltaics Materials & Device Group, University of Oklahoma: http://www.nhn.ou.edu/~sellers/group/index.html
The Energy Problem

- Need for alternative sources of energy
- Currently PV less 3% of energy market
- UK has an 80% reduction in CO2 emissions target → all technologies will need to play a role...

- Solar radiation is an non-polluting abundant source of free energy
- Photovoltaics describes a technology in which the energy of the sun is absorbed and converted to electricity using semiconductor technology
- Currently this PV market is dominated by silicon technology but is expensive and relatively inefficient (~ 3-4 $/W and 14-18%)
Photovoltaics: The solution?

Maybe...... but not quite yet!

Shockley-Queisser limit predicted max efficiency ~ 30% (J. Appl. Phys. 1961)
Photovoltaics: Current Issues

Significant amount of energy is lost!

Hirst & Ekins-Daukes, Prog. PV. 19, 286 (2011)

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**Cost of Photovoltaics: Economics**

### Cost of Energy, $/kWh

<table>
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</thead>
<tbody>
<tr>
<td>Grid</td>
<td>$0.36</td>
<td>$0.33</td>
<td>$0.34</td>
<td>$0.27</td>
<td>$0.24</td>
<td>$0.18</td>
<td>$0.15</td>
<td>$0.13</td>
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<tr>
<td>PV</td>
<td>$0.26</td>
<td>$0.26</td>
<td>$0.26</td>
<td>$0.27</td>
<td>$0.24</td>
<td>$0.22</td>
<td>$0.20</td>
<td>$0.19</td>
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<tr>
<td>CPV</td>
<td>$0.26</td>
<td>$0.26</td>
<td>$0.26</td>
<td>$0.27</td>
<td>$0.24</td>
<td>$0.22</td>
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Solar prices continue to fall but so do other forms of “new” energy!

Source: Greentech Media.

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Third Generation Photovoltaics

Source: M. A. Green, “Third Generation Photovoltaics,” Springer 2006

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Improving Efficiency

86.7% of the sun’s energy is available for conversion!

Hirst & Ekins-Daukes, Prog. PV. 19, 286 (2011)

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Third-Generation Technologies

• Multi-junction Solar Cell

• Intermediate-Band Solar Cells

• Hot Carrier Solar Cells and Multi-exciton Generation
Multi-Junction Solar Cells

- Stack individual semiconductors to absorb different region of solar spectrum
  - Used in space applications
Multi-Junction Solar Cells: Utilities?

Big push to use MJSCs at utility scale: solar power stations

- Increase in efficiency have been predicted to have big effect on economics in CPV
- Have been so successful in improving efficiency of MJ systems: metamorphic growth, GaInNAs

**Conventional Cell Structure**

- InGaP: Indium Gallium Phosphide
- (In)GaAs: Indium Gallium Arsenide
- Ge: Germanium

**New Cell Structure**

- InGaP: Indium Gallium Phosphide
- GaAs: Gallium Arsenide
- InGaAs: Indium Gallium Arsenide

**Sharp:** 44.4% (302 suns)

**Solar Junction:** 43.5% (500 suns)

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Intermediate Band Solar Cells

Intermediate Band Solar Cell


Harnessing “hot” carriers

Hot carrier solar cells

- Carrier thermalize on picosecond timescale
- Efficient carrier extraction requires thin absorbers good “phononic” properties...
- Energy selective contacts

Harnessing “hot” carriers

Multi-exciton Generation

Third-Generation Technologies

- Multi-junction Solar Cell
- Intermediate-Band Solar Cells
- Hot Carrier Solar Cells and Multi-exciton Generation
3G PV: Harnessing the solar spectrum

**Fundamental Gap**

To harness the solar spectrum effectively, the energy gap is lowered slightly to \( \sim 0.7 \text{eV} \).
Narrow-Gap Semiconductors

Y. S. Park, Optoelectronics Rev. 9, 117 (2001)

Fig. 7.6. Bandgap energy and lattice constant of various III-V semiconductors at room temperature (adopted from Tien, 1988).
QD Intermediate Band Solar Cells

InAs/Ga(Al)As QDSCs
- Hubbard et al. APL 2008
- Guimard et al. APL 2010
- Zhou et al. APL
- Sablon et al. APL, Nano Lett. 2010
- Tutu et al. JAP 2012
- Willis et al. SOLMAT 2012
- Marti et al. PRL 2006

GaSb/(In)GaAs QDSCs
- Laghumavarapu et al. APL 2007, PVSEC 2013
  Huffaker Group...

GaAs/InAs QDs/GaAsSb
- Honsberg Group ASU..
- Sellers, Santos OU
QD Intermediate Band Solar Cells


InAs QD/GaAs$_{0.86}$Sb$_{0.14}$As

Predicted PCE > 50%

Uncapped InAs QDs: 1.75 ML - 3.5 ML

GaAs$_{0.872}$Sb$_{0.128}$ cap: 50 nm

Capped InAs QDs

GaAs$_{0.872}$Sb$_{0.128}$ matrix: 10 nm

GaAs buffer: 250 nm

GaAs(001) substrate

Full GaAsSb matrix structure
QD Intermediate Band Solar Cells

**Uncapped InAs QDs:** 1.75 ML - 3.5 ML

**InAs wetting layer:** ~1.5 ML

**GaAs\textsubscript{0.872}Sb\textsubscript{0.128} cap:** 50 nm

**InAs wetting layer:** ~1.5 ML

**GaAs\textsubscript{0.872}Sb\textsubscript{0.128} matrix:** 10 nm

**GaAs buffer:** 250 nm

**GaAs(001) substrate**

**QD Densities:** $>10^{11}$ cm$^{-2}$

**PL Intensity (arb. u.) vs Energy (eV):**

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Multi-Exciton Generation

Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell

Octavi E. Semoen,1,2 Joseph M. Luther,3 Sukgeun Choi,2 Hsiang-Yu Chen,1 Jianbo Gao,2,3 Arthur J. Nozik,3,4* Matthew C. Beard1

Multiple exciton generation (MEG) is a process that can occur in semiconductor nanocrystals, or quantum dots (QDs), whereby absorption of a photon bearing at least twice the bandgap energy produces two or more electron-hole pairs. Here, we report on photocurrent enhancement arising from MEG in lead selenide (PbSe) QD-based solar cells, as manifested by an external quantum efficiency (the spectrally resolved ratio of collected charge carriers to incident photons) that peaked at 114 ± 1% in the best device measured. The associated internal quantum efficiency (corrected for reflection and absorption losses) was 130%. We compare our results with transient absorption measurements of MEG in isolated PbSe QDs and find reasonable agreement. Our findings demonstrate that MEG charge carriers can be collected in suitably designed QD solar cells, providing ample incentive to better understand MEG within isolated and coupled QDs as a research path to enhancing the efficiency of solar light harvesting technologies.

Beard, Nozik et al. Science 334, 1530 (2011)

Most recent work in the colloidal QDs: some related work in PbS bulk: what about epitaxial III-V’s?

Assessment of carrier-multiplication efficiency in bulk PbSe and PbS

J. J. H. Pijpers1, R. Ulbricht1, K. J. Tielrooij1, A. Osherov2, Y. Golan3, C. Delehuy1, G. Allen3 and M. Born1

Perspective on the Prospects of a Carrier Multiplication Nanocrystal Solar Cell

Gaitham Nair, Liang-Yi Chang, Scott M. Geyser, and Moungi G. Bawendi*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02143, United States

Photovoltaics Materials & Device Group, University of Oklahoma: http://www.nhn.ou.edu/~sellers/group/index.html
Narrow-Gap Semiconductors: InN

Y. S. Park, Optoelectronics Rev. 9, 117 (2001)

Davydov et al (1999)

Extremely attractive “phononic” properties optimum Energy gap!
Evidence of MEG in InN

Jensen, Sellers, Bonn et al, APL 101, 222113 2012

\[ \sigma(\omega) = N \times e \times \mu(\omega) = N \times \frac{e^2 \tau_s}{m^*} \times \frac{1}{1 - i\omega \tau_s} \]

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Evidence of MEG in InN

Jensen, Sellers, Bonn et al, APL 101, 222113 2012

Impact Ionization seen in InSb, Si, PbS, and PbSe, and now InN!

At OU we are also assessing the possibility of InAs, InSb, and GaSb......
Hot Carrier Solar Cells

Effects of non-ideal energy selective contacts and experimental carrier cooling rate on the performance of an indium nitride based hot carrier solar cell

P. Aliberti,¹ ¹a) Y. Feng,¹ S. K. Shrestha,¹ M. A. Green,¹ G. Conibeer,¹ L. W. Tu,² P. H. Tseng,² and R. Clady³

¹ARC Photovoltaics Centre of Excellence, The University of New South Wales, Sydney 2052, Australia
²Department of Physics and Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, Republic of China
³School of Chemistry, The University of Sydney, Sydney 2006, Australia

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The performance of an InN based hot carrier solar cell with a bulk InN absorber has been evaluated using an innovative approach that takes into account absorber energy-momentum dispersion relations, energy conservation, Auger recombination and impact ionization mechanisms simultaneously. The non ideality of the energy selective filters has also been included in the model. In order to obtain practical achievable values of conversion efficiency, the actual thermalisation velocity of hot carriers in InN has been measured using time resolved photoluminescence. Results of the computations shown limiting efficiencies of 24% for 1000 suns and 36.2% for maximal concentration. © 2011 American Institute of Physics. [doi:10.1063/1.3663862]
Hot Carrier Solar Cells

Energy & Environmental Science

Thermalisation rate study of GaSb-based heterostructures by continuous wave photoluminescence and their potential as hot carrier solar cell absorbers†

A. Le Bris,∗∗† L. Lombet,∗∗† S. Lazibi,∗∗† G. Beissier,∗‡ P. Christof‡ and J.-F. Guilleminot‡∗∗

Received 9th October 2011, Accepted 15th December 2011
DOI: 10.1039/c2ee02943c

GaSb-based heterostructures are tested as candidates for a hot carrier solar cell absorber. Their thermalisation properties are investigated using continuous wave photoluminescence. Non-equilibrium carrier populations are detected at high excitation levels. An empirical expression of the power law by thermalisation is deduced from the incident power dependent carrier temperature. The experimentally determined thermalisation rate is then used to simulate the potential efficiency of a hot carrier solar cell, showing a significant efficiency improvement compared to a fully thermalised single p-n junction of similar bandgap.

28th EU PVSEC, Paris 2013

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Summary

• Photovoltaics is genuine contender to address global energy needs

• The viability of this technology on a utilities scale requires novel solutions and a new generation of devices operating at high efficiency without prohibitive cost increases

• 3rd Generation PV using narrow-gap semiconductors (and the development new architectures and (nano)structures from them) offers exciting possibilities for high-efficiency solar cells.

• Although high-risk, groups around the World have demonstrated the potential of third generation PV, which although challenging, offers the potential for a paradigm shift in solar cell operation and performance

sellers@ou.edu