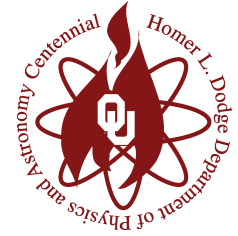




Narrow-Gap Semiconductors for High Efficiency Next-Generation Photovoltaics

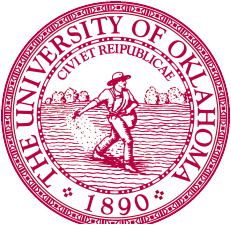


Ian R. Sellers

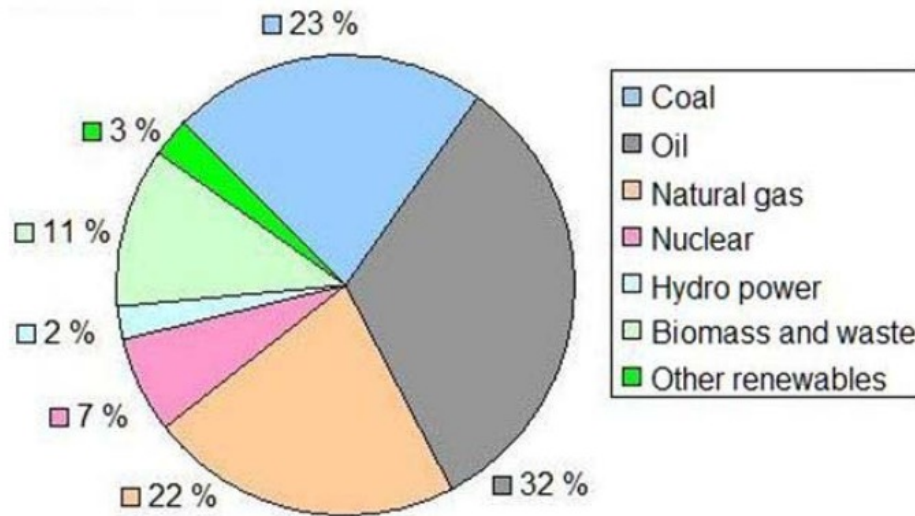
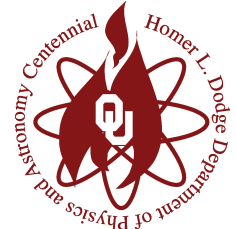
*Dept. Physics & Astronomy
University of Oklahoma*



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

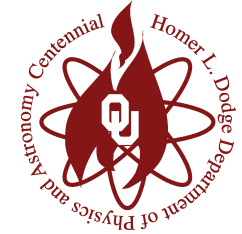


The Energy Problem



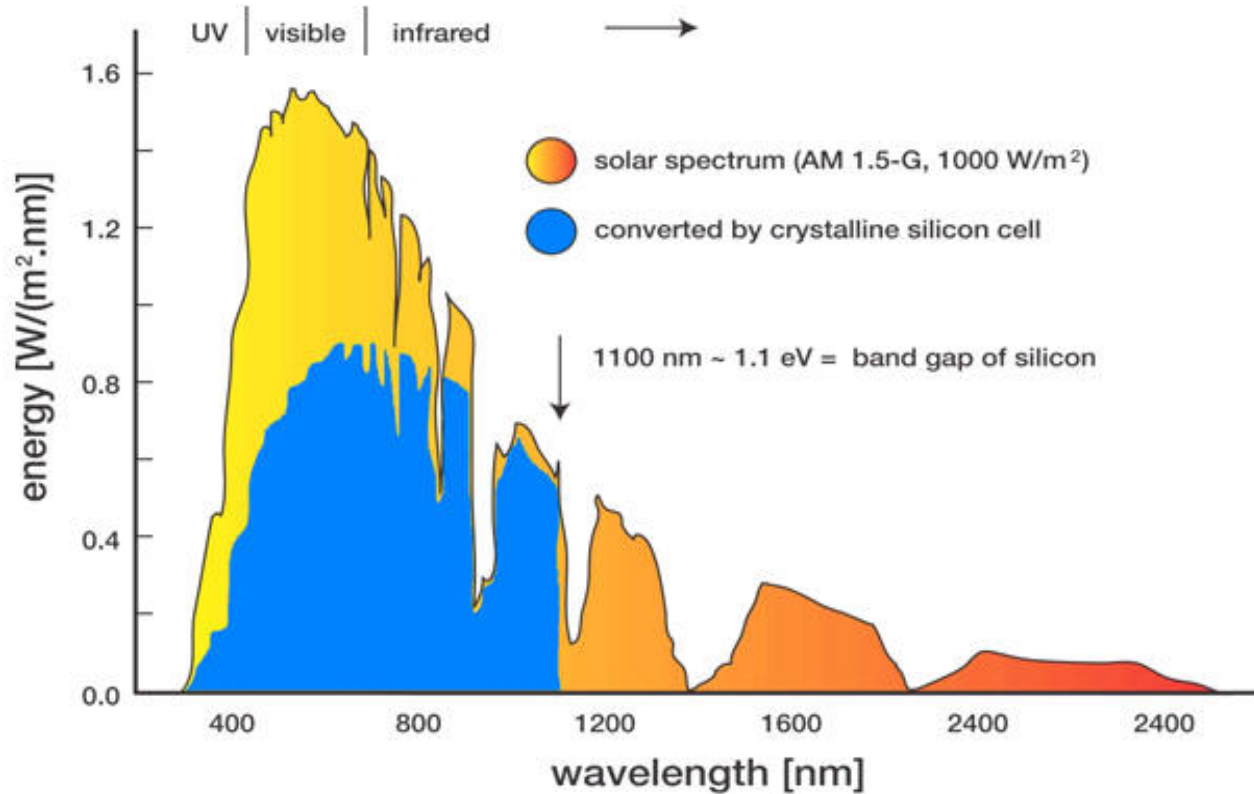
- Need for alternative sources of energy
- Currently PV less 3% of energy market
- UK has an 80% reduction in CO₂ emissions target → all technologies *will need* to play a role...

- Solar radiation is a 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?

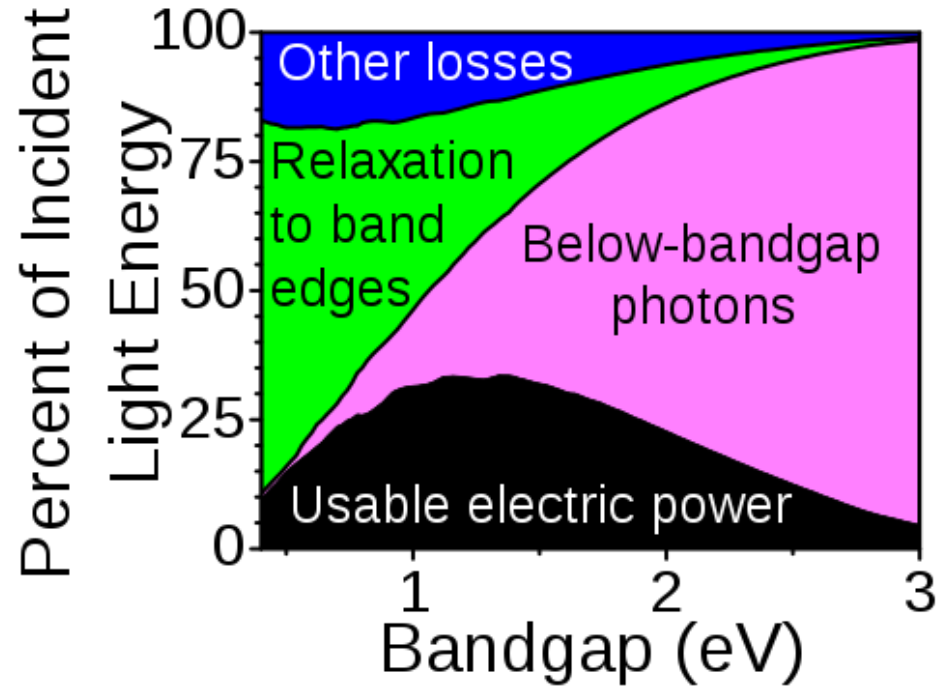
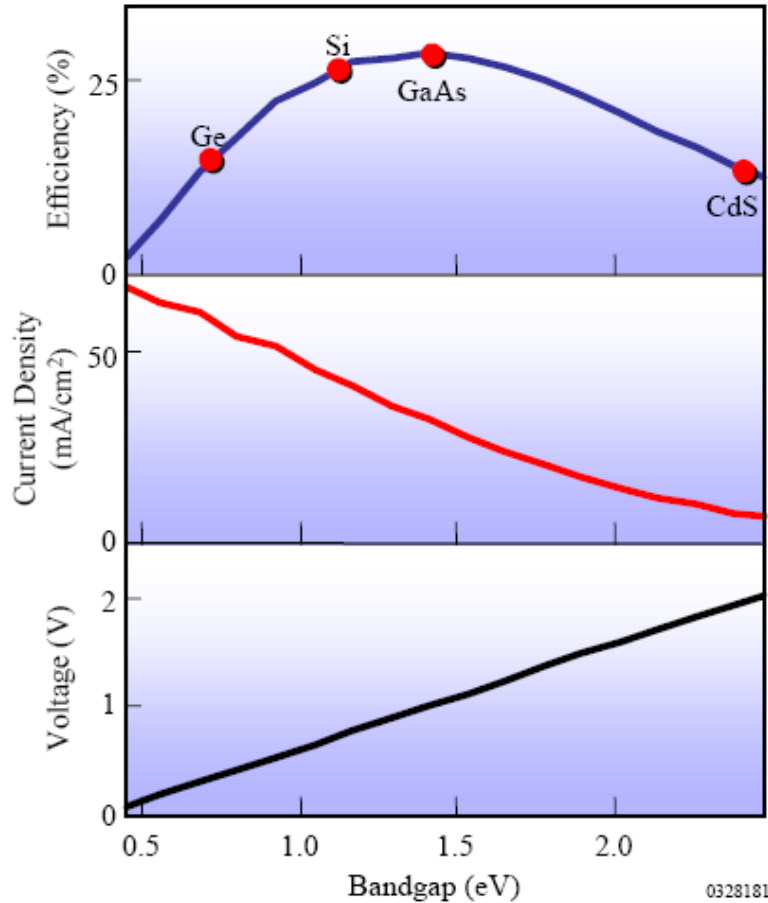
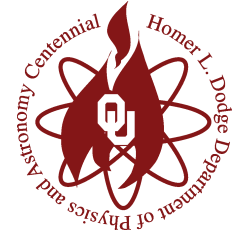
Maybe..... but not quite yet!



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

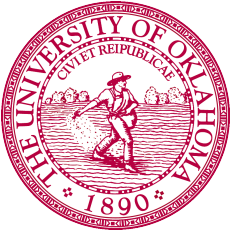


Photovoltaics: Current Issues

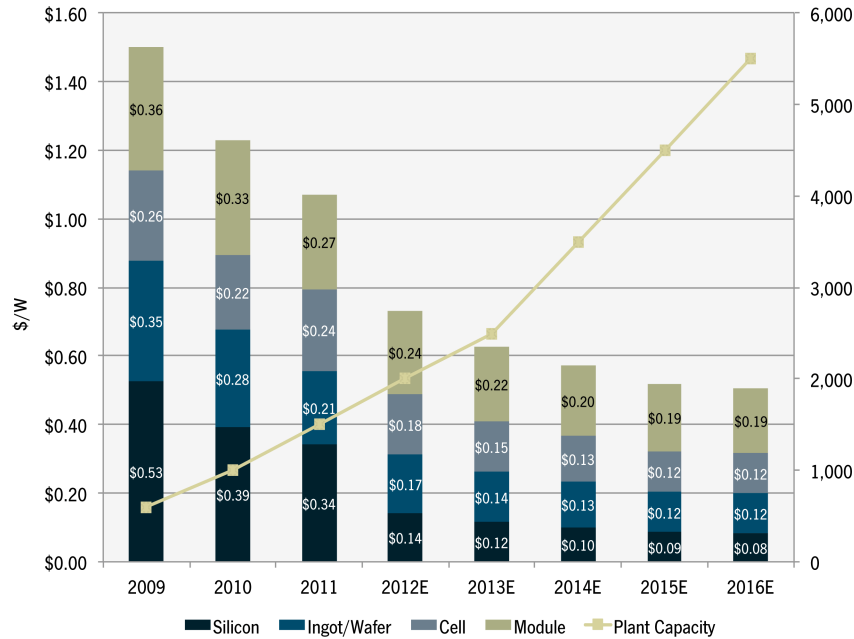
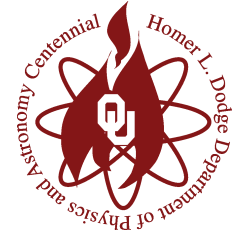


Hirst & Ekins-Daukes, *Prog. PV.* **19**, 286 (2011)

Significant amount of energy is lost!

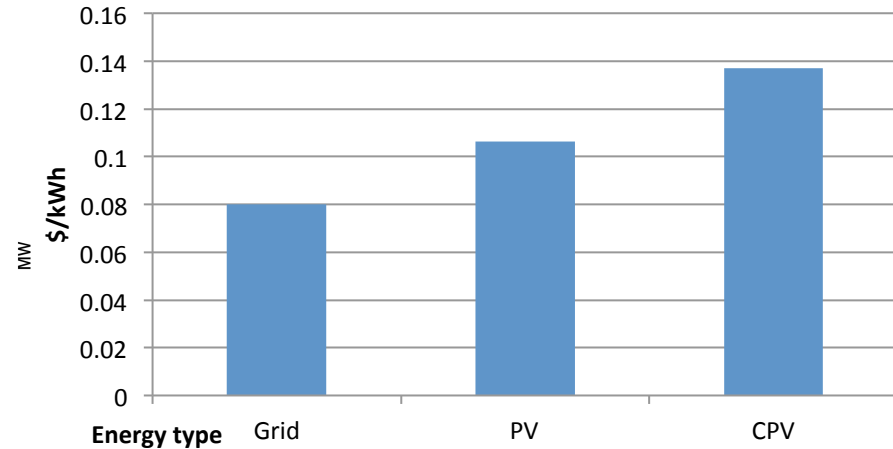


Cost of Photovoltaics: Economics



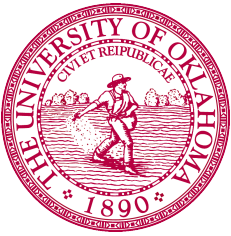
Source: Greentech Media.

Cost of Energy, \$/kWh

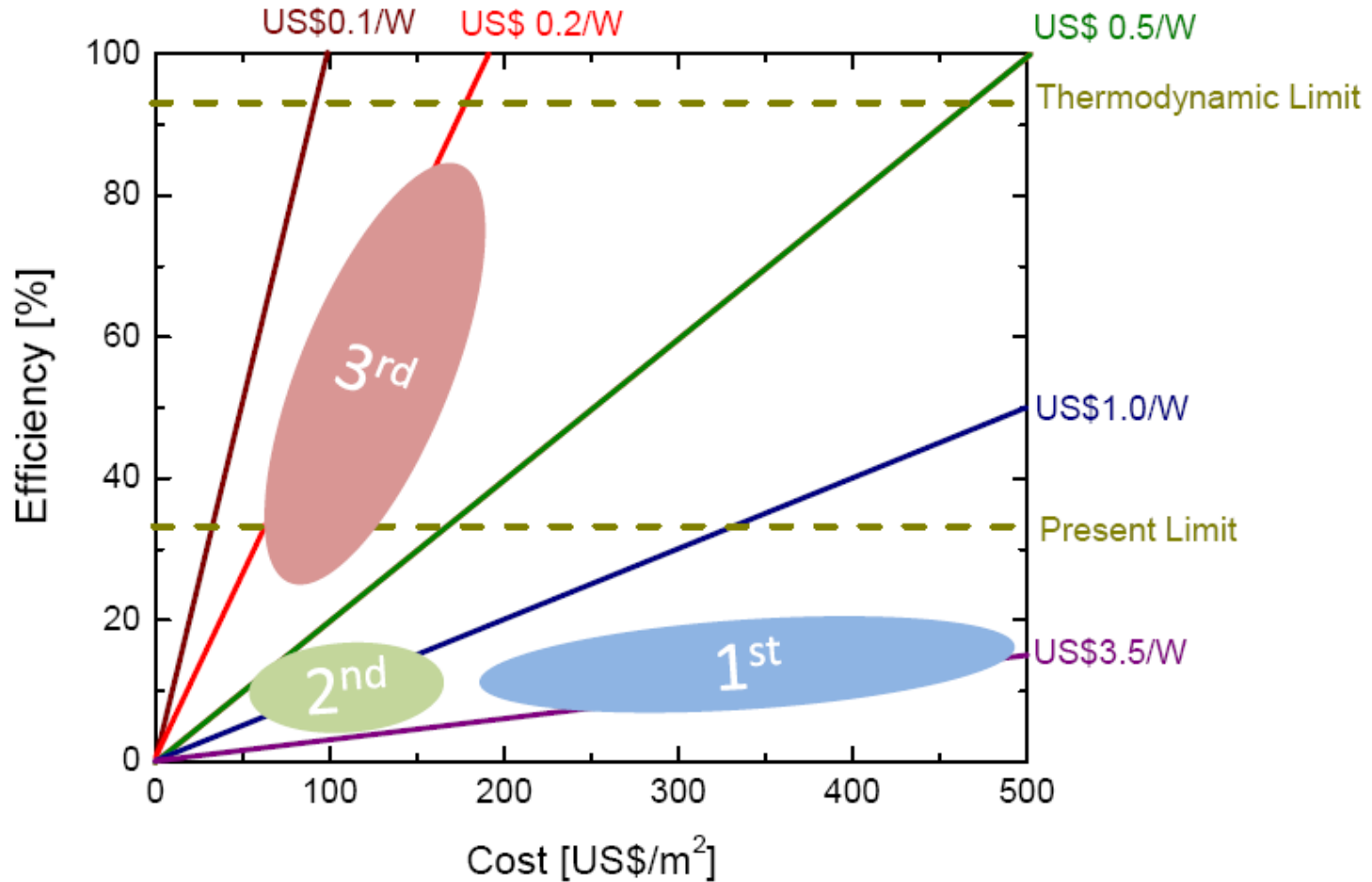
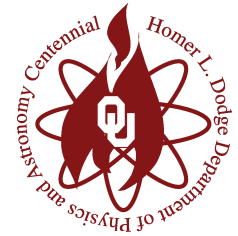


Source: Average US Energy Costs. Data: Barbose 2012, Kurtz 2012, US EIA

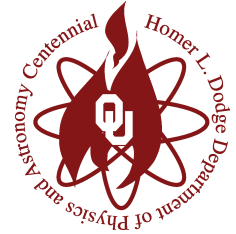
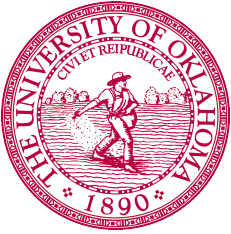
Solar prices continue to fall but so do other forms of “new” energy!



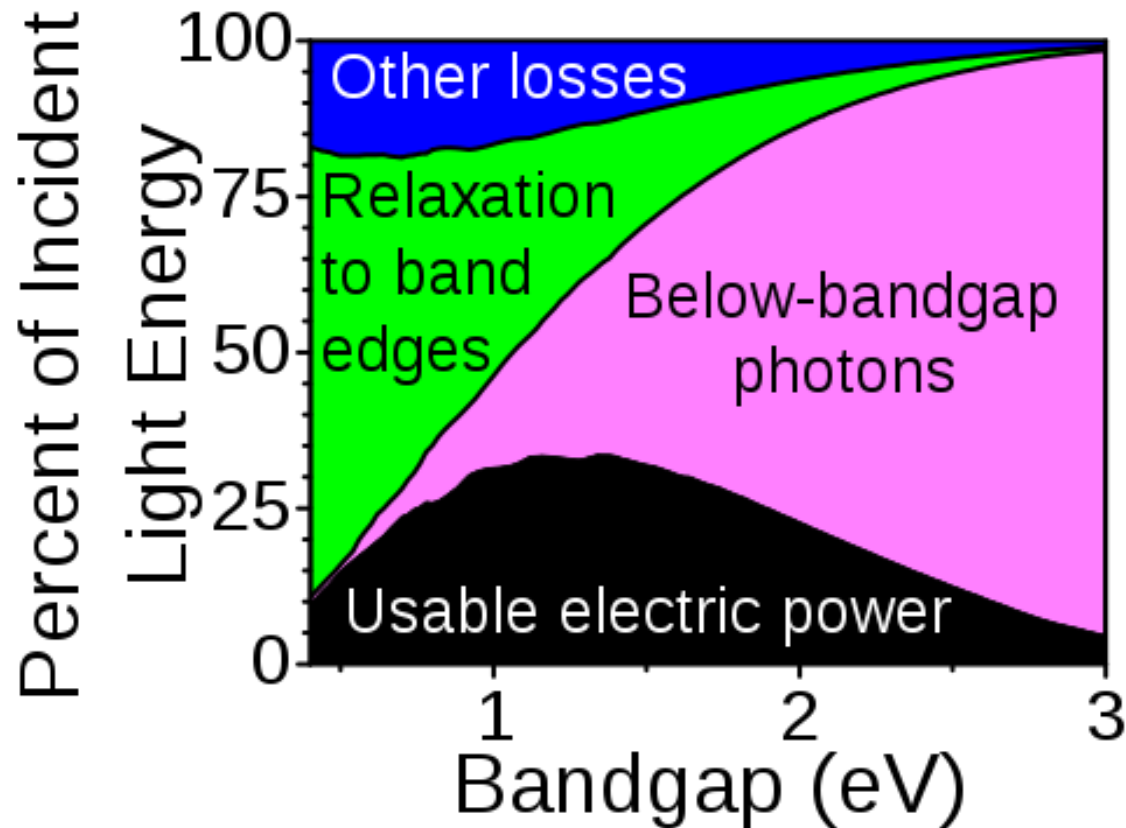
Third Generation Photovoltaics



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



Improving Efficiency

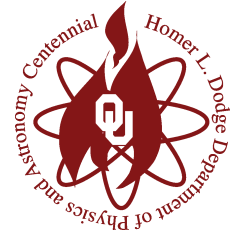


Hirst & Ekins-Daukes, *Prog. PV.* **19**, 286 (2011)

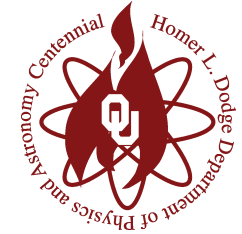
86.7% of the sun's energy is available of conversion!



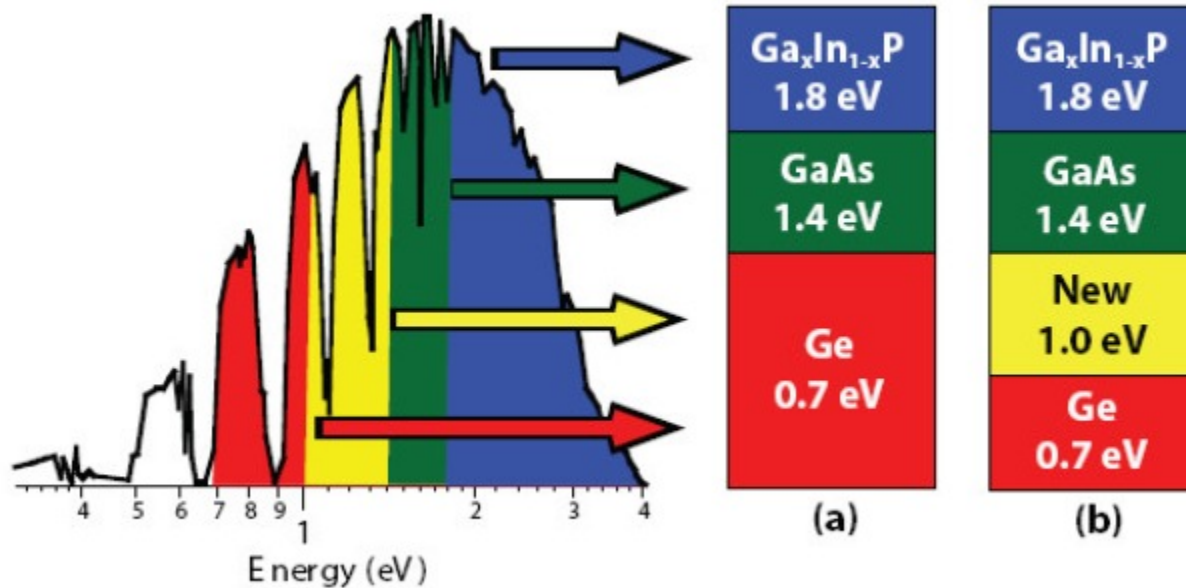
Third-Generation Technologies



- Multi-junction Solar Cell
- Intermediate-Band Solar Cells
- Hot Carrier Solar Cells and Multi-exciton Generation



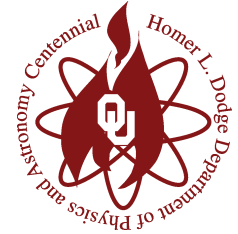
Multi-Junction Solar Cells



- **Stack individual semiconductors to absorb different region of solar spectrum**
 - **Used in space applications**



Multi-Junction Solar Cells: Utilities?

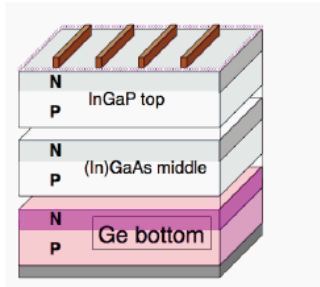


Big push to use MJSCs at utility scale: solar power stations



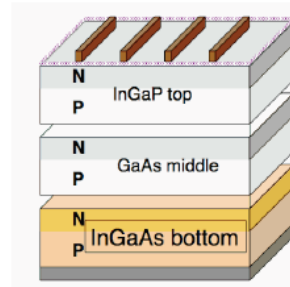
- Increase in efficiency have been predicted to have big effect on economics in CPV
- Have been so success in improving efficiency of MJ systems: metamorphic growth, GaInNAs

Conventional Cell Structure

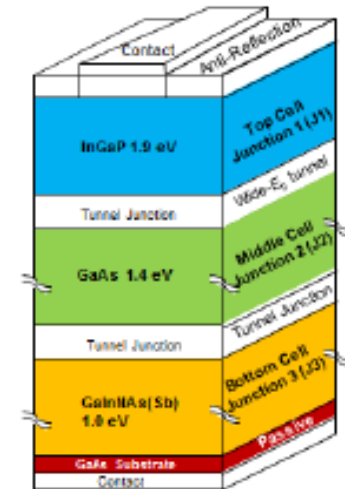


InGaP: Indium Gallium Phosphide
 (In)GaAs: (Indium) Gallium Arsenide
 Ge: Germanium

New Cell Structure



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

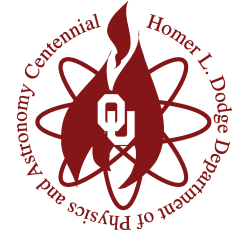


Sharp: 44.4% (302 suns)

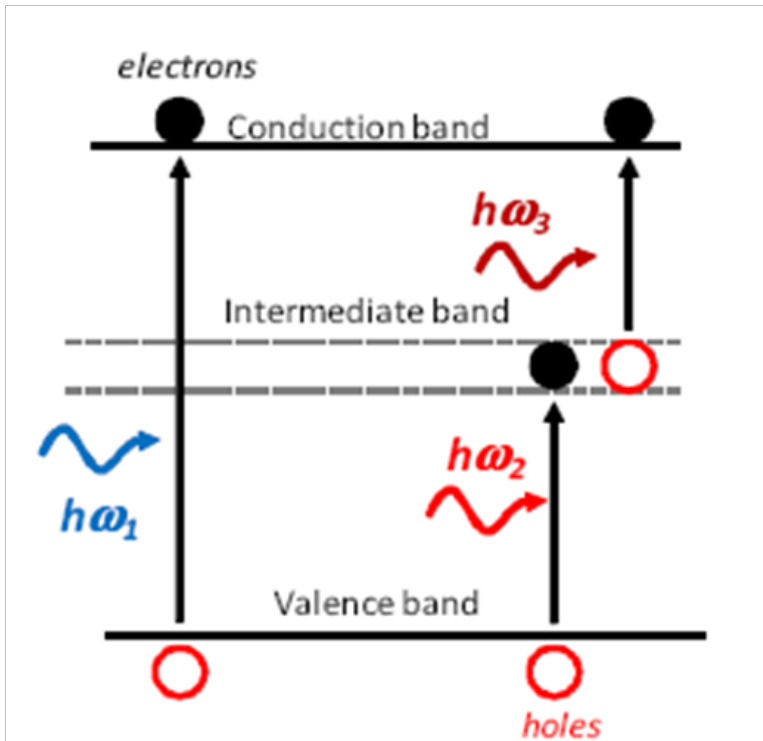
Solar Junction: 43.5% (500 suns)



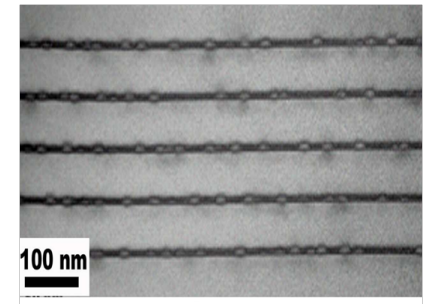
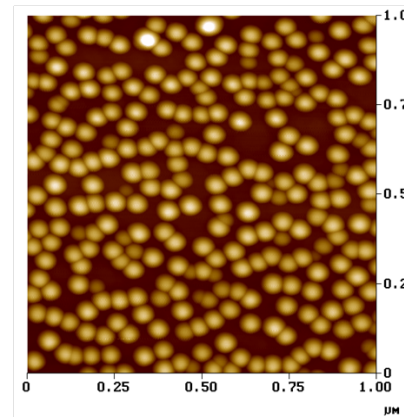
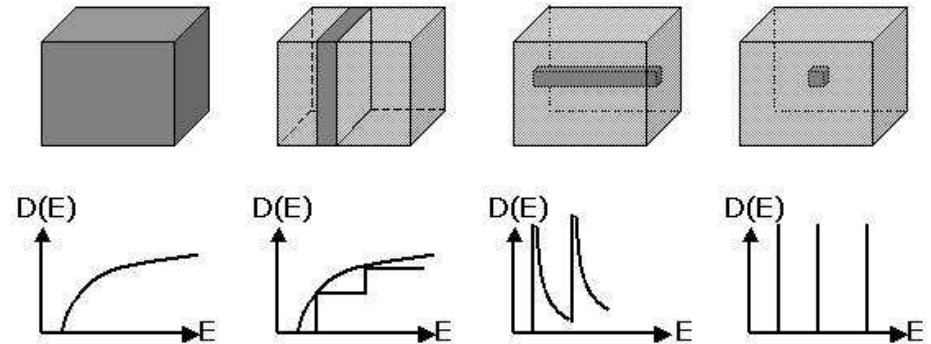
Intermediate Band Solar Cells



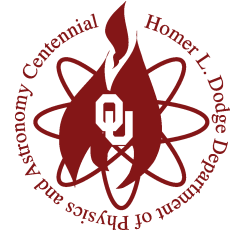
Intermediate Band Solar Cell



Luque & Marti. *Adv. Mat.* **22**, 160 (2010)

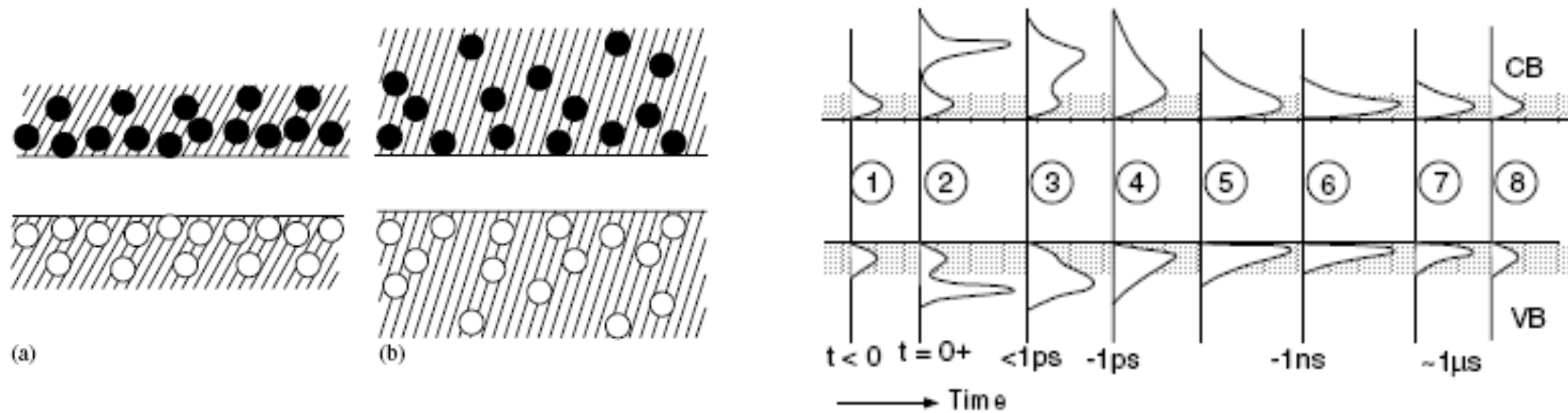


H. Y. Liu , I. R. Sellers et al. *Appl. Phys. Lett.* **85**, 704 (2004)



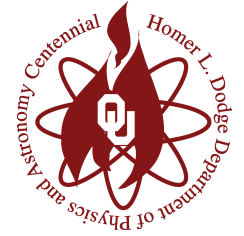
Harnessing “hot” carriers

Hot carrier solar cells



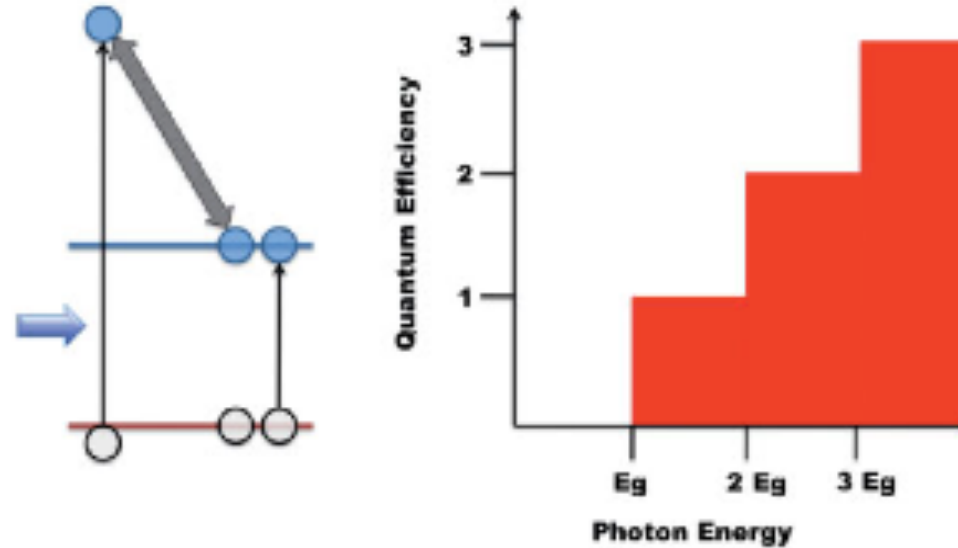
Source: “Third Generation Photovoltaics,” M. A. Green, Springer 2006

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



Harnessing “hot” carriers

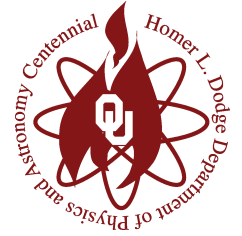
Multi-exciton Generation



Brown & Wu. Laser & Photon Rev. 3, 394 (2009)



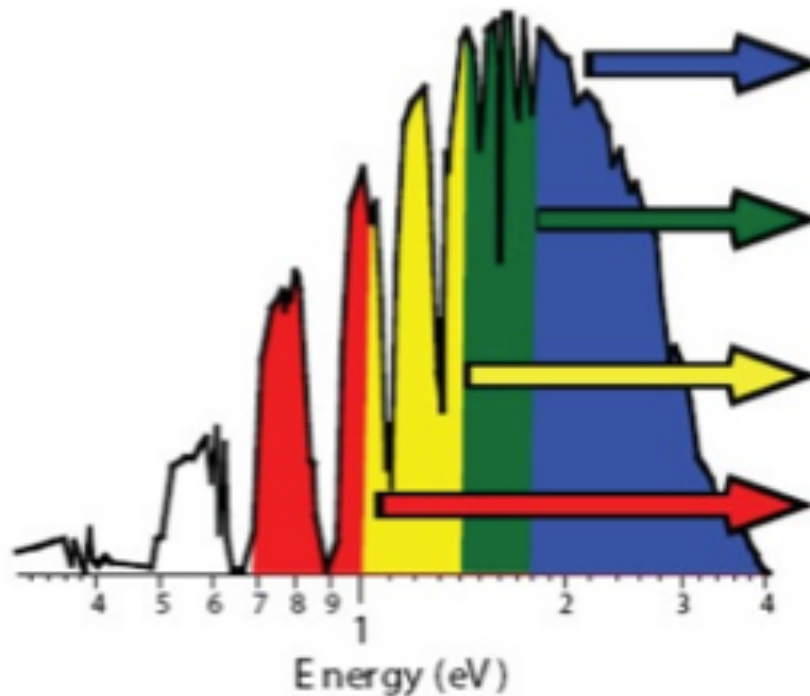
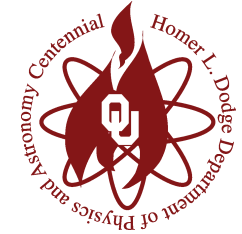
Third-Generation Technologies



- Multi-junction Solar Cell
- Intermediate-Band Solar Cells
- Hot Carrier Solar Cells and Multi-exciton Generation



3G PV: Harnessing the solar spectrum



Hot Carriers

2, 3x E_g - MEG

ΔE_{IC} - IBSC

Fundamental Gap
 $\sim 0.7\text{eV}$

To harness the solar spectrum effectively Energy-gap is lowered slightly to $\sim 0.7\text{eV}$



Narrow-Gap Semiconductors

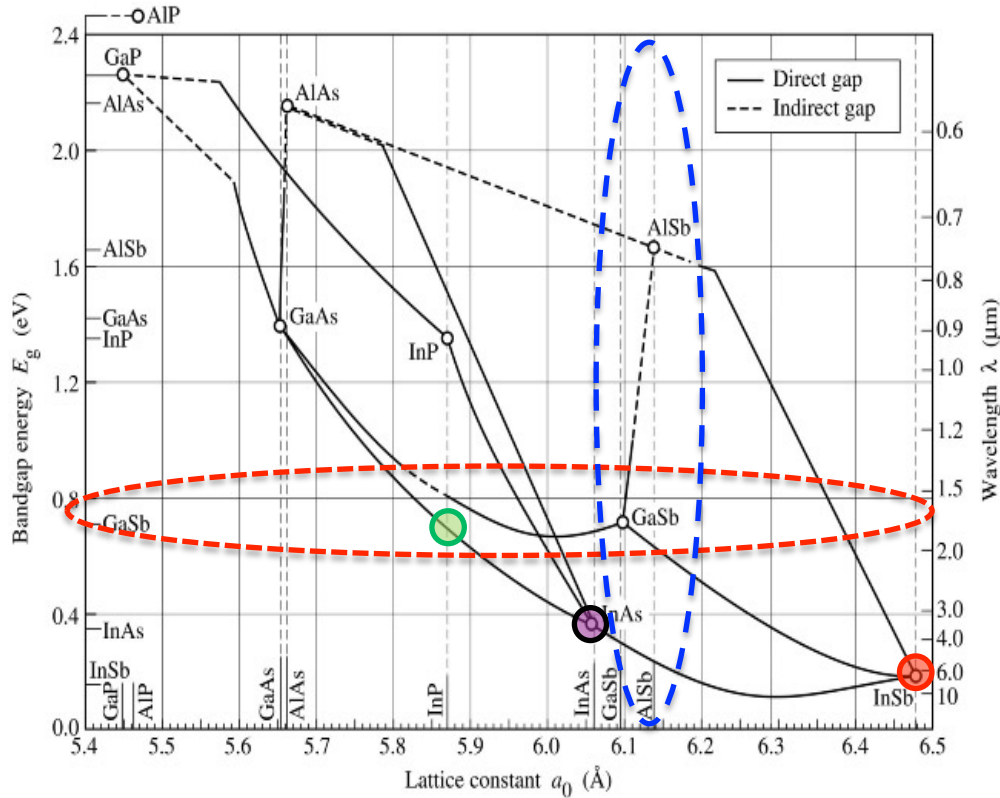
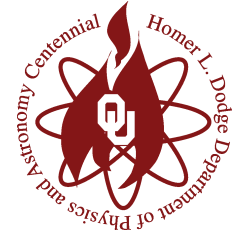
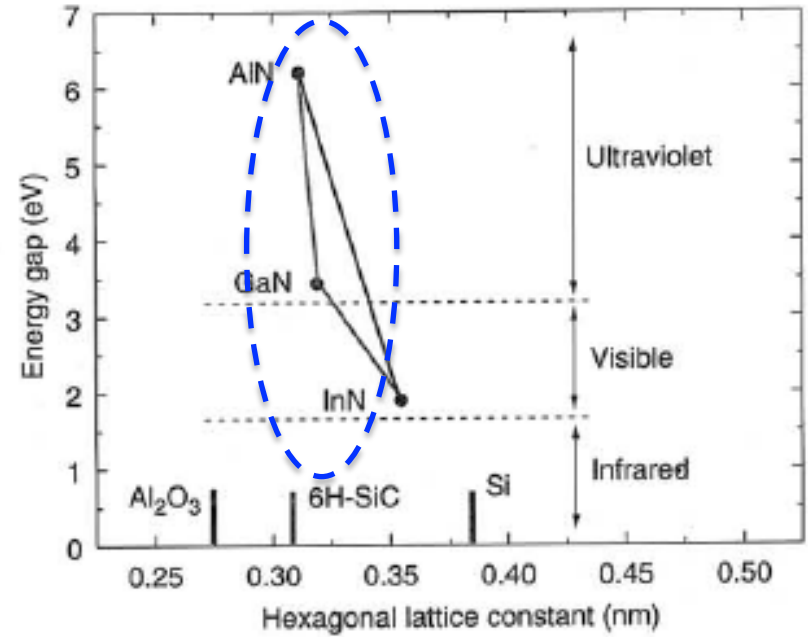
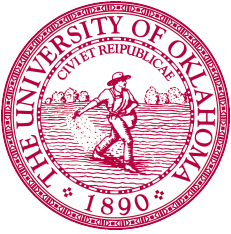


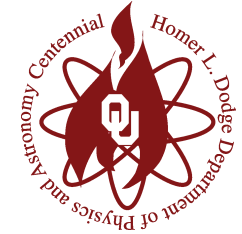
Fig. 7.6. Bandgap energy and lattice constant of various III-V semiconductors at room temperature (adopted from Tien, 1988).



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



QD Intermediate Band Solar Cells



PRL 97, 247701 (2006)

PHYSICAL REVIEW LETTERS

week ending
15 DECEMBER 2006

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

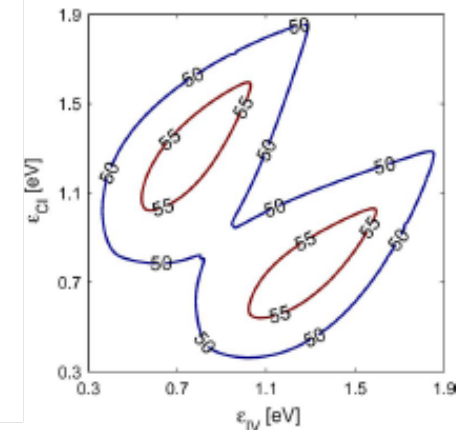
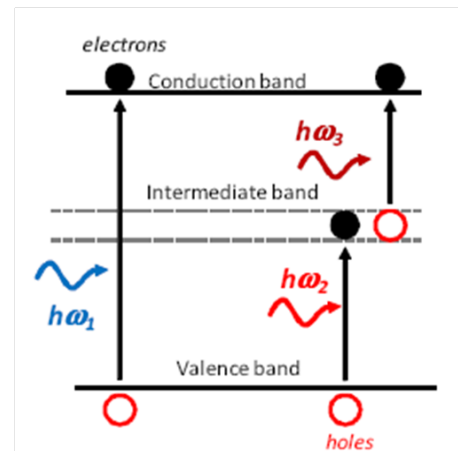
Production of Photocurrent due to Intermediate-to-Conduction-Band Transitions: A Demonstration of a Key Operating Principle of the Intermediate-Band Solar Cell

A. Martí,¹ E. Antolín,¹ C. R. Stanley,² C. D. Farmer,² N. López,¹ P. Díaz,² E. Cánovas,¹ P. G. Linares,¹ and A. Luque¹

¹Instituto de Energía Solar, Universidad Politécnica de Madrid, E.T.S.I. Telecomunicación, Ciudad Universitaria s/n Madrid, Madrid 28040, Spain

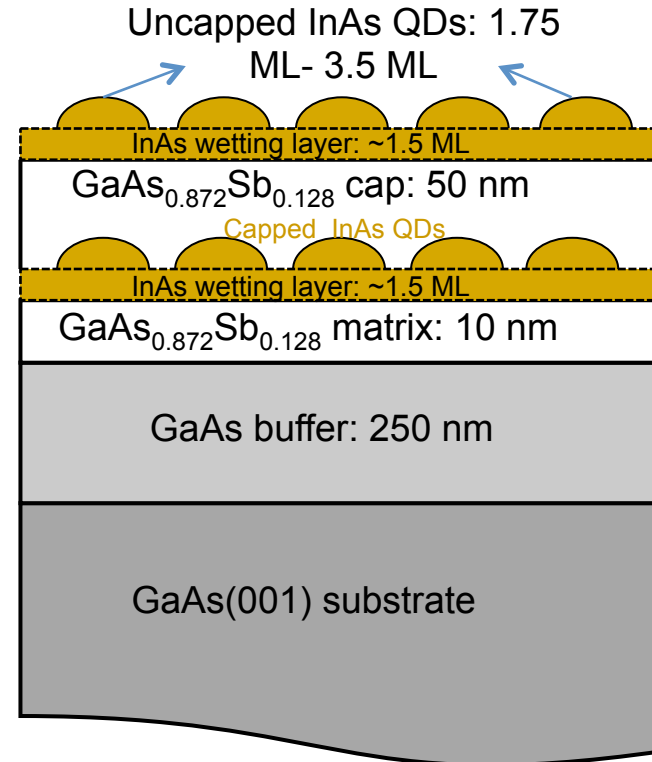
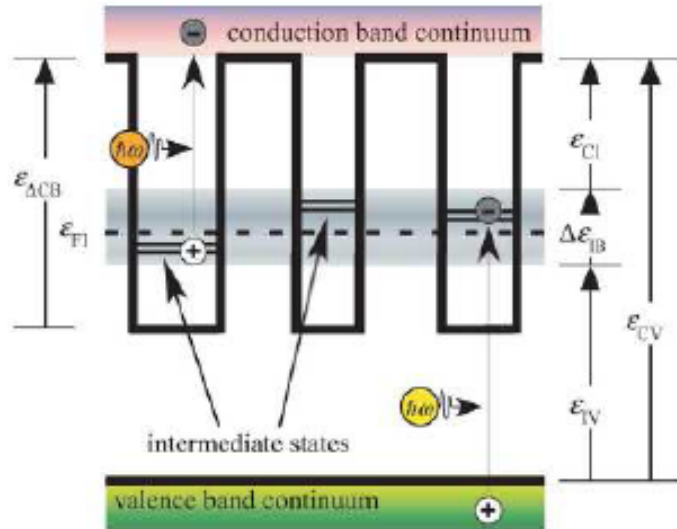
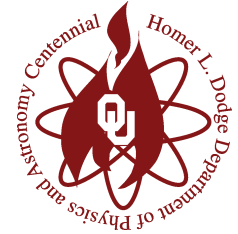
²Department of Electronics and Electrical Engineering, University of Glasgow, Glasgow, G12 8QQ, United Kingdom
(Received 15 August 2006; published 13 December 2006)

We present intermediate-band solar cells manufactured using quantum dot technology that show for the first time the production of photocurrent when two sub-band-gap energy photons are absorbed simultaneously. One photon produces an optical transition from the intermediate-band to the conduction band while the second pumps an electron from the valence band to the intermediate-band. The detection of this two-photon absorption process is essential to verify the principles of operation of the intermediate-band solar cell. The phenomenon is the cornerstone physical principle that ultimately allows the production of photocurrent in a solar cell by below band gap photon absorption, without degradation of its output voltage.





QD Intermediate Band Solar Cells



Levy & Honsberg . *IEEE Trans. Elect. Dev.* 55, 706 (2008)

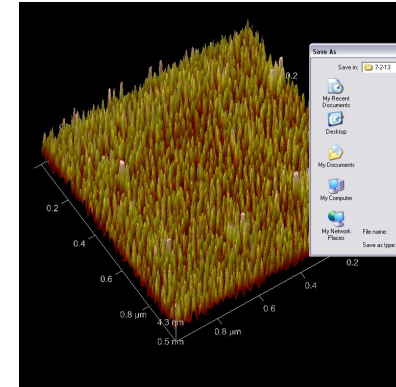
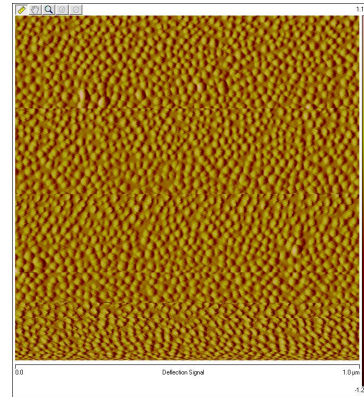
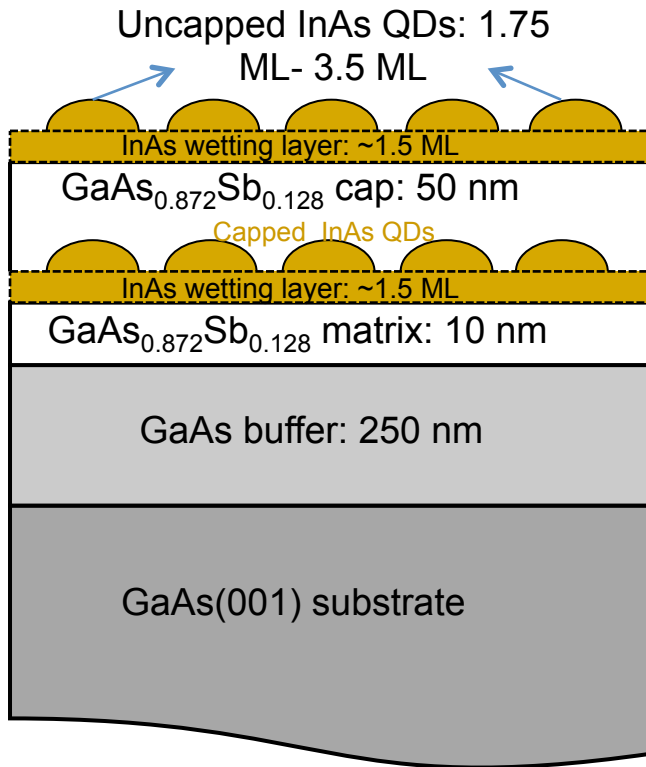
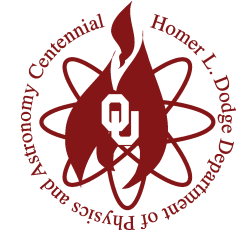
InAs QD/GaAs_{0.86}Sb_{0.14}As

Predicted PCE > 50%

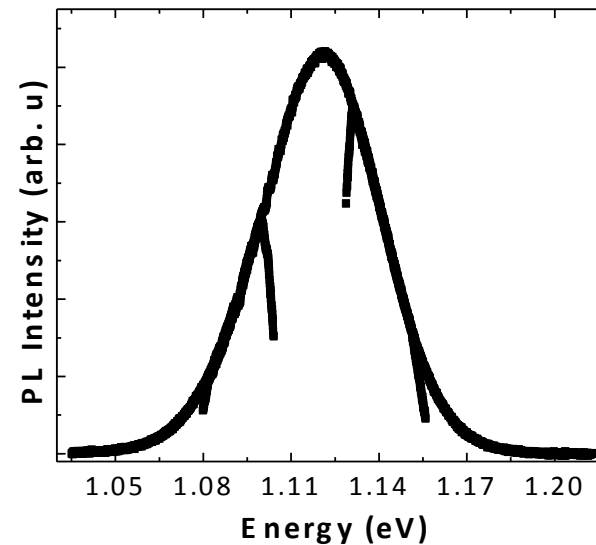
Full GaAsSb matrix structure

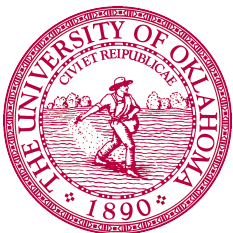


QD Intermediate Band Solar Cells

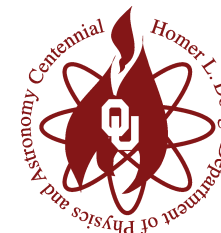


QD Densities $> 10^{11} \text{cm}^{-2}$





Multi-Exciton Generation



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

Octavi E. Semonin,^{1,2} Joseph M. Luther,² Sukgeun Choi,¹ Hsiang-Yu Chen,¹ Jianbo Gao,^{2,3} Arthur J. Nozik,^{1,4*} Matthew C. Beard^{1*}

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 $114 \pm 1\%$ 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. Oshero², Y. Golan², C. Delerue³, G. Allan³ and M. Bonn^{1*}



LETTER

pubs.acs.org/NanoLett

Perspective on the Prospects of a Carrier Multiplication Nanocrystal Solar Cell

Gautham Nair, Liang-Yi Chang, Scott M. Geyer, and Mouni G. Bawendi*

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



PERSPECTIVE

pubs.acs.org/JPCLETT

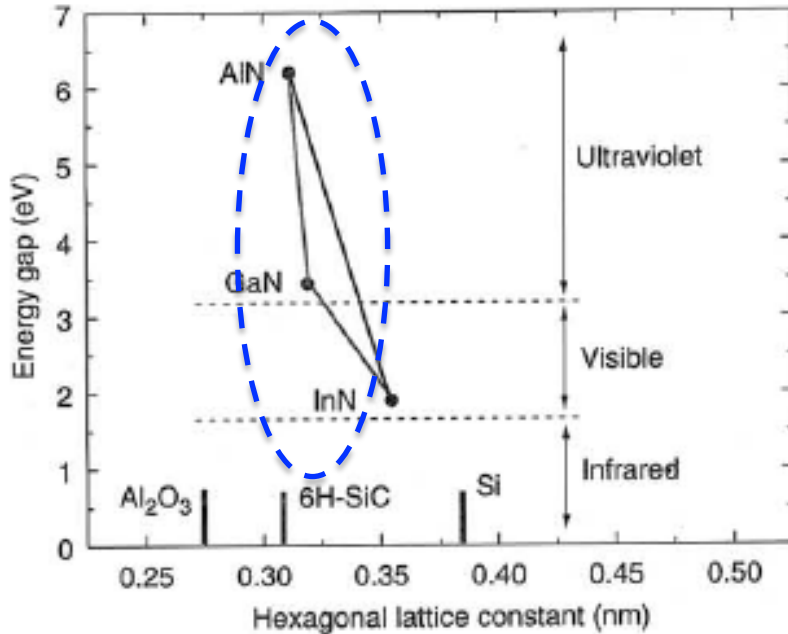
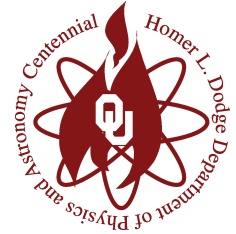
Multiple Exciton Generation in Semiconductor Quantum Dots

Matthew C. Beard*

Chemistry and Materials Research Center, The National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401, United States



Narrow-Gap Semiconductors: InN



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

Appl. Phys. Lett., Vol. 75, No. 21, 22 November 1999

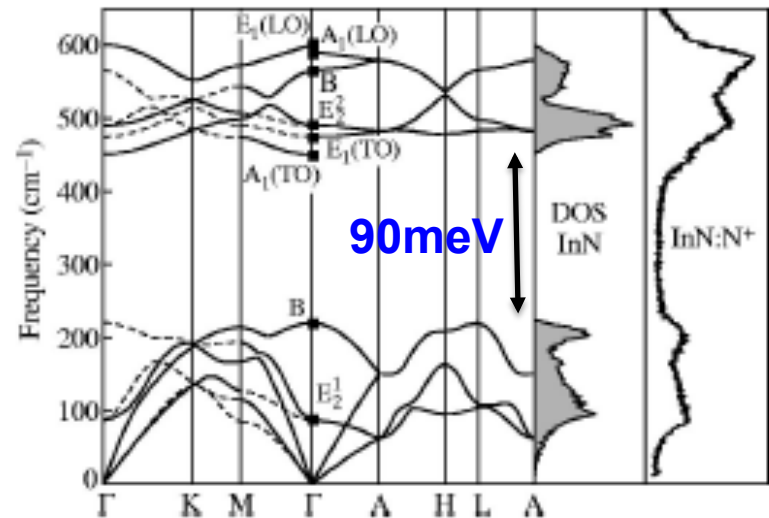


FIG. 4. Calculated phonon dispersion curves and phonon DOS function for hexagonal InN. The disorder-induced Raman spectrum obtained at 7 K for N⁺-implanted InN is also shown.

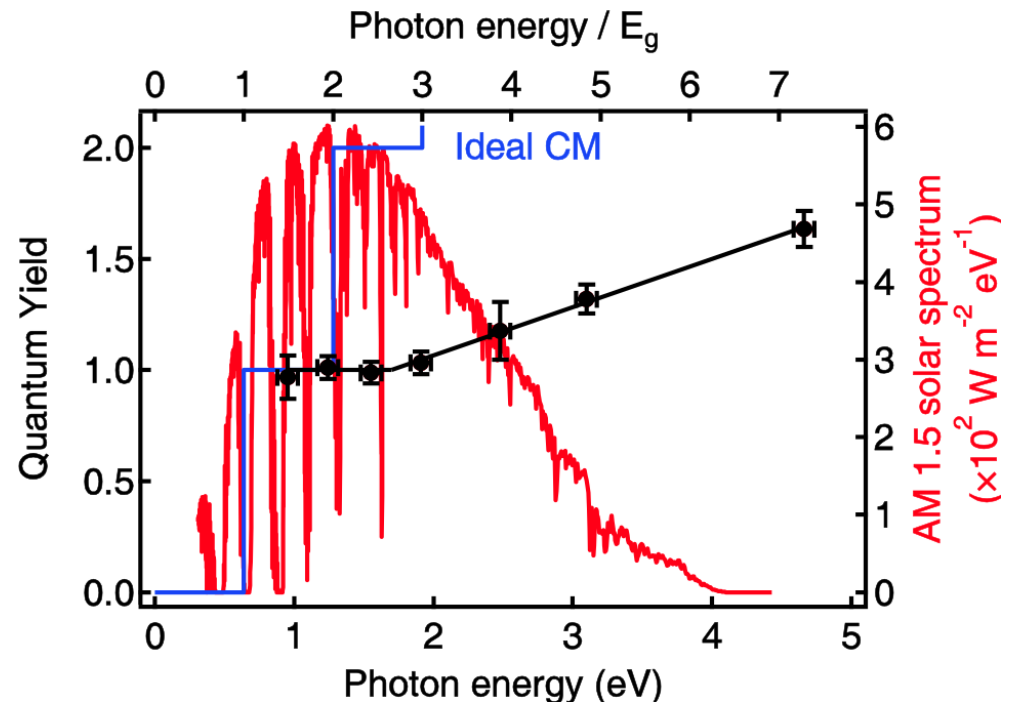
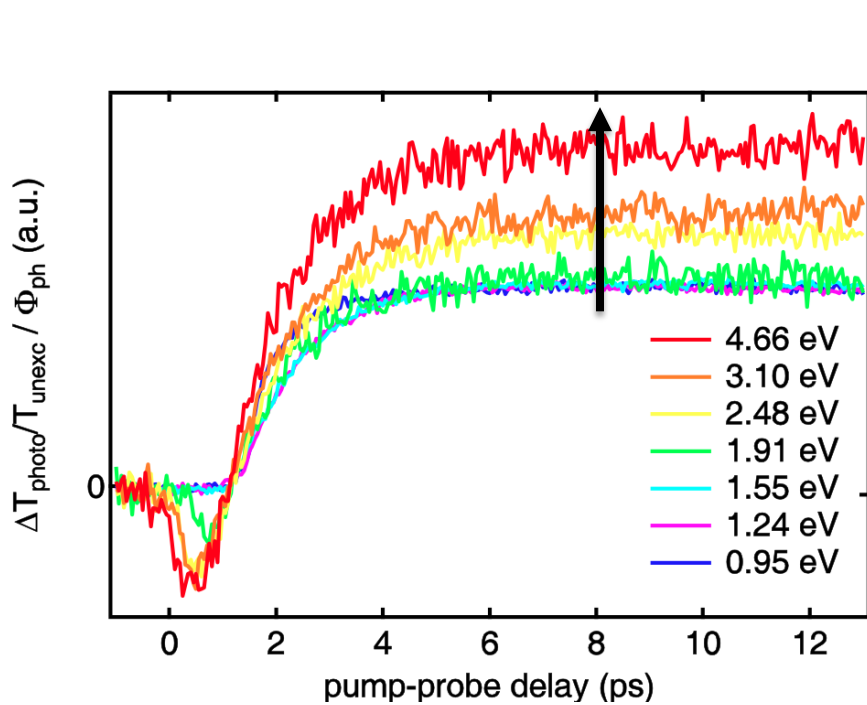
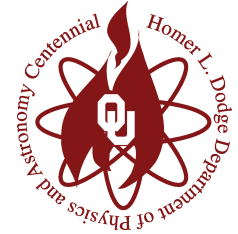
Davydov *et al* (1999)

Extremely attractive “phononic” properties optimum Energy gap!



Evidence of MEG in InN

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

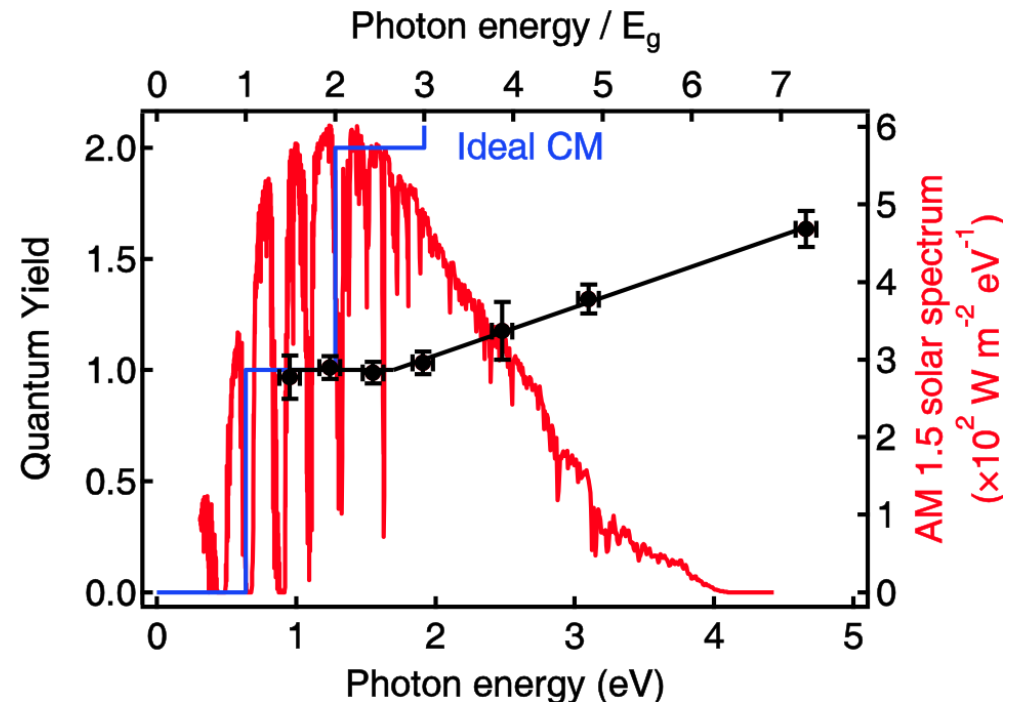
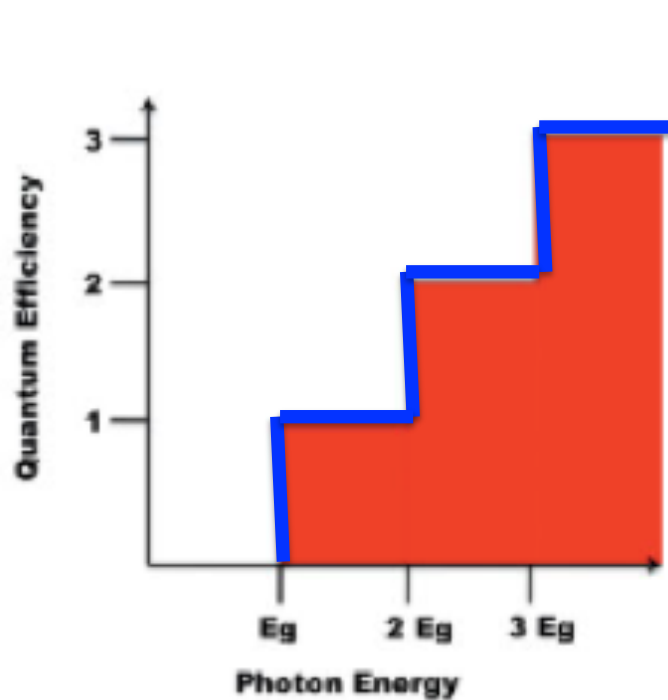
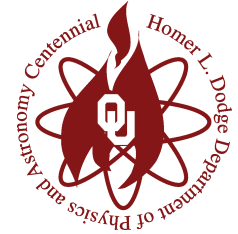


$$\sigma(\omega) = N \times e \times \mu(\omega) = N \times \frac{e^2 \tau_s}{m^*} \times \frac{1}{1 - i\omega\tau_s}$$



Evidence of MEG in InN

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

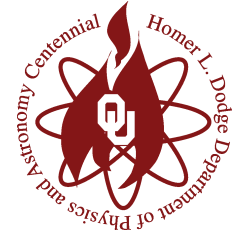


Impact Ionization seen in InSb, Si, PbS, and PbSe, and now InN!

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,a)} 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

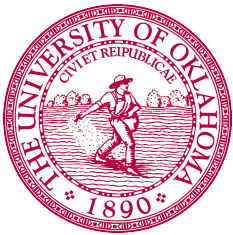
¹*ARC Photovoltaics Centre of Excellence, The University of New South Wales, Sydney 2052, Australia*

²*Department of Physics and Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, Republic of China*

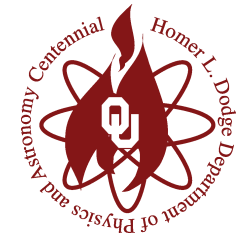
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The performance of an InN based hot carrier solar cell with a bulk InN absorber has been evaluated using an innovative approach that takes into account absorber energy-momentum dispersion relations, energy conservation, Auger recombination and impact 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



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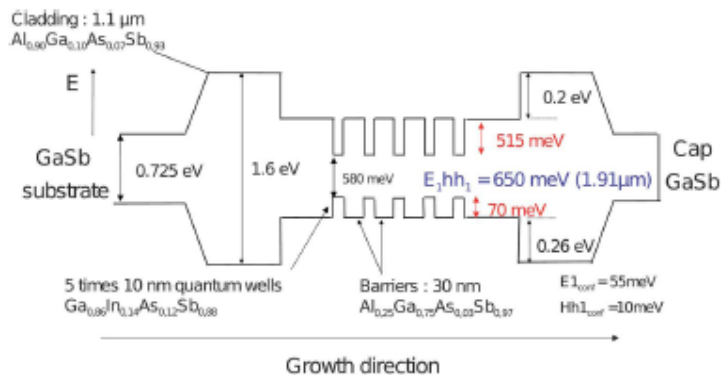
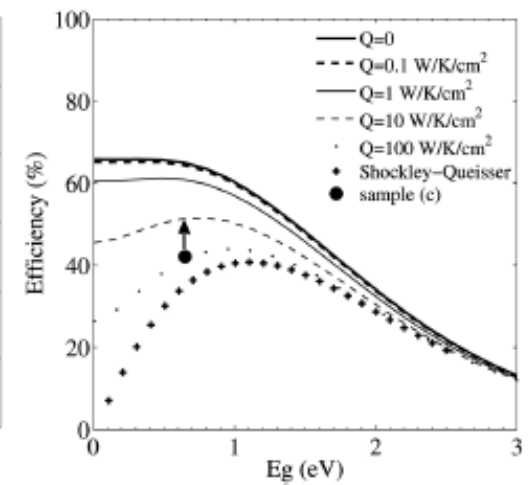
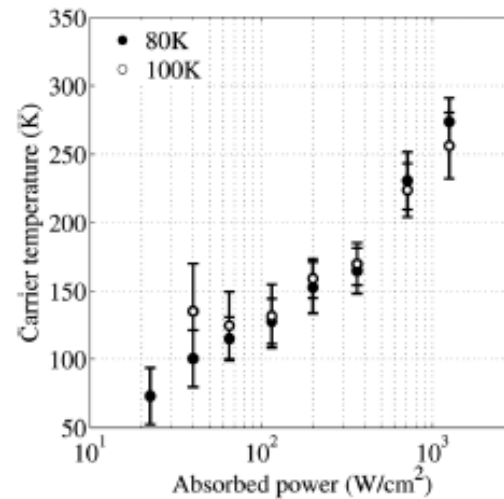
PAPER

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

A. Le Bris,^{a,b,c} L. Lombez,^{a,b,c} S. Laribi,^{a,b,c} G. Boissier,^d P. Christol^d and J.-F. Guillemoles^{a,b,c}

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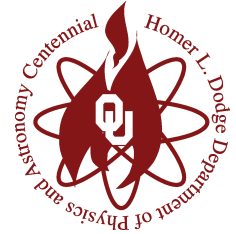
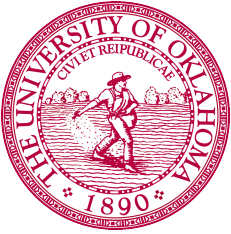
GaSb-based heterostructures are tested as candidates for a hot carrier solar cell absorber. Their thermalisation properties are investigated using continuous wave photoluminescence. Non-equilibrium carrier populations are detected at high excitation levels. An empirical expression of the power lost by 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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J.A.R. Dimmock, S. Day, M. Kauer, K. Smith & J. Heffernan
SHARP, Oxford, United Kingdom
An Offset Tunneling Structure for a Hot Carrier Photovoltaic Cell



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**

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