



Raising the Efficiency Ceiling in Multijunction Solar Cells

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- Global climate change and the solar resource
- Solar cell theoretical efficiency limits
 - Opportunities to change ground rules for higher terrestrial efficiency
 - Cell architectures capable of >70% in theory, >50% in practice
- Metamorphic semiconductor materials
 - Control of band gap to tune to solar spectrum
 - Dislocations in metamorphic III-Vs imaged by CL and EBIC
- High-efficiency Multijunction terrestrial concentrator cells
 - Metamorphic (MM) and lattice-matched (LM) 3-junction solar cells with >40% efficiency
 - 4-junction MM and LM concentrator cells
 - Inverted metamorphic structure, semiconductor
 bonded technology (SBT) for MJ terrestrial concentrator cells
- Concentrator photovoltaic (CPV) systems and economics











Global Climate Change



Climate and CO₂ Over the Last 400,000 Years



Vostok Ice Core Data 4 2 0 Temperature (°C) -2 -4 -6 -8 -10 45000 4000 35000 3000 25000 2000 15000 1000 5000 0

• Antarctic ice core data allows for mapping of temperature and CO₂ profiles

Years Before Present

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(J.R. Petit, J. Jouzel, Nature 399:429-436)

Climate and CO₂ Over the Last 400,000 Years

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• Clear correlation between temperature and CO₂ levels



Climate and CO₂ -Recent History





Years Before Present

- CO₂ has reached levels never before seen in measured history
- If we do nothing, we allow this rising trend to continue at our own peril







The Solar Resource



The Solar Resource





 Entire US electricity demand can be provided by concentrator PV arrays using 37%-efficient cells on:

150 km x 150 km area of land or ten 50 km x 50 km areas or similar division across US

Concentrator Photovoltaic (CPV) Electricity Generation

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Map source: http://www.nrel.gov/gis/images/map_csp_us_annual_may2004.jpg

Higher multijunction cell efficiency has a huge impact on the economics of CPV, and on the way we will generate electricity.

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Solar Cell Theoretical Efficiency



Energy Transitions in Semiconductors





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LM and MM 3-Junction Cell Cross-Section



ropcell

MidetesTunn

Middle Cell

Tunnel Junction

Bottom Cell



Lattice-Mismatched or Metamorphic (MM)

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Energy Transitions in Semiconductors





- V = voltage of solar cell
 - = quasi-Fermi level splitting = $|\phi_p - \phi_n|$
- Not all of bandgap energy is available to be collected at terminals, even though electron in conduction band has energy E_g
- Only qV = q $|\phi_p \phi_n|$ is available at solar cell terminals
- Due to difference in entropy S of carriers at low concentration in conduction band, and at high concentration in contact layers: G = H - TS



Energy Transitions in Semiconductors





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Detailed Balance Limit of Solar Cell Efficiency



- **30%** efficient single-gap solar cell at one sun, for 1 e⁻/photon
- 44% ultimate
 efficiency for
 device with
 single cutoff
 energy







- Assumptions for theoretical efficiency in Shockley and Quiesser (1961)
- Viewed from a different angle, these assumptions represent new opportunities, for devices that overcome these barriers

Assumption limiting solar cell efficiency	Device principle overcoming this limitation	
Single band gap energy	Multijunction solar cells	
	Quantum well, quantum dot solar cells	
One e⁻-h⁺ pair per photon	Down conversion	
	Multiple exciton generation	
	Avalanche multiplication	
Non-use of sub-band-gap photons	Up conversion	
Single population of each charge carrier type	Hot carrier solar cells	
	Intermediate-band solar cells	
	Quantum well, quantum dot solar cells	
One-sun incident intensity	Concentrator solar cells	









Maximum Solar Cell Efficiencies



Measured Theoretical

References C. H. Henry, solar cells W. Shockley Solar Cel J. H. Werner, Efficiency (1994)	⁴ Limiting efficiencies of ideal single and multiple energy gap terrestrial s," <i>J. Appl. Phys.</i> , 51 , 4494 (1980). and H. J. Queisser, "Detailed Balance Limit of Efficiency of <i>p-n</i> Junction Is," <i>J. Appl. Phys.</i> , 32 , 510 (1961). S. Kolodinski, and H. J. Queisser, "Novel Optimization Principles and Limits for Semiconductor Solar Cells," <i>Phys. Rev. Lett.</i> , 72 , 3851	95% 93%	Carnot eff. = $1 - T/T_{sun}$ T = 300 k Max. eff. of solar energy conversion = $1 - TS/E = 1 - (4/3)T/T_{sun}$ (F	K, T _{sun} ≈ 5800 K Henry)
R. R. King <i>et</i> Multijunct <i>Conf.</i> , Ha R. R. King et cells," <i>Ap</i> M. Green, K. (Version A. Slade, V. 0	<i>al.</i> , "Band-Gap-Engineered Architectures for High-Efficiency ion Concentrator Solar Cells," <i>24th European Photovoltaic Solar Energy</i> mburg, Germany, Sep. 21-25, 2009. al., "40% efficient metamorphic GaInP / GaInAs / Ge multijunction solar <i>pl. Phys. Lett.</i> , 90 , 183516 (4 May 2007). Emery, D. L. King, Y. Hishikawa, W. Warta, "Solar Cell Efficiency Tables 27)", <i>Progress in Photovoltaics</i> , 14 , 45 (2006). Garboushian, "27.6%-Efficient Silicon Concentrator Cell for Mass	72%	Ideal 36-gap solar cell at 1000 suns	(Henry)
Productio China, Oo R. P. Gale <i>et</i> Tandem S Florida, M J. Zhao, A. W textured r	n," <i>Proc. 15th Int'l. Photovoltaic Science and Engineering Conf.</i> , Beijing, ct. 2005. <i>al.</i> , "High-Efficiency GaAs/CulnSe ₂ and AlGaAs/CulnSe ₂ Thin-Film Solar Cells," <i>Proc. 21st IEEE Photovoltaic Specialists Conf.</i> , Kissimmee, lay 1990. /ang, M. A. Green, F. Ferrazza, "Novel 19.8%-efficient 'honeycomb' nulticrystalline and 24.4% monocrystalline silicon solar cells," <i>Appl.</i>	56% 50%	Ideal 3-gap solar cell at 1000 suns Ideal 2-gap solar cell at 1000 suns	(Henry) (Henry)
Phys. Lei 3-gap GalnF 3-gap GalnF	r, 73 , 1991 (1998). P/GaInAs/Ge LM cell, 364 suns (Spectrolab) 41.6 P/GaInAs/Ge MM cell, 240 suns (Spectrolab) 40.7	44% 43% % %	Ultimate eff. of device with cutoff E _g : 1-gap cell at 1 sun with carrier multipl (>1 e-h pair per photon) (Werner	(Shockley, Queisser) ication r, Kolodinski, Queisser)
		37%	Ideal 1-gap solar cell at 1000 suns	(Henry)
3-ga 1-gap so	p GaInP/GaAs/GaInAs cell at 1 sun (NREL) 33.8 lar cell (silicon, 1.12 eV) at 92 suns (Amonix) 27.6	% 31% 30% %	Ideal 1-gap solar cell at 1 sun Detailed balance limit of 1 gap solar c (Shockley, Queisser)	(Henry) ell at 1 sun
1-gap solar cell (GaAs, 1.424 eV) at 1 sun (Kopin) 25.1% 1-gap solar cell (silicon, 1.12 eV) at 1 sun (UNSW) 24.7%		% %		





followed by substrate removal from sunward surface

Solar Spectrum Partition for **BOEING** 3-Junction Cell



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5- and 6-Junction Cells





Ref.: U.S. Pat. No. 6,316,715, Spectrolab, Inc., filed 3/15/00, issued 11/13/01.

SPECTROLAB Photon Utilization Efficiency Description ABDEING COMPANY 3-Junction Solar Cells



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SPECTROLAB Photon Utilization Efficiency Description ABDEING COMPANY 6-Junction Solar Cells



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3-Junction Cell Efficiency Losses from 100%









Metamorphic Semiconductor Materials



Metamorphic (MM) Semiconductor Materials



- Metamorphic = "changed form"
- Thick, relaxed epitaxial layers grown with different lattice constant than growth substrate
- Allows access to subcell band gaps desired for more efficient division of the solar spectrum in multijunction solar cells
- Also called lattice-mismatched
- Misfit dislocations are allowed to form in metamorphic buffer, which typically has graded composition and lattice constant
- Threading dislocations which can propagate up into active device layers grown on buffer are minimized as much as possible



Bandgap vs. Lattice Constant







Bandgap vs. Lattice Constant





Internal QE of Metamorphic GalnAs Cells on Ge





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Cross sectional TEM Ga_{0.44}In_{0.56}P/ Ga_{0.92}In_{0.08}As/ Ge

- Low dislocation density in active cell layers in top portion of epilayer stack:
 - ~ 2 x 10⁵ cm⁻² from EBIC and CL meas.

 Dislocations confined to graded buffer layers in bottom portion of epilayer stack



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High-Resolution XRD A BOEING COMPANY High-Resolution XRD Reciprocal Space Map (RSM)



- GalnP/ 8%-In GalnAs/ Ge metamorphic (MM) cell structure
- Nearly 100% relaxed stepgraded buffer → removes driving force for dislocations to propagate into active cell layers
- 56%-In GaInP top cell pseudomorphic with respect to GaInAs middle cell

A BOEING COMPANY I.39-eV GalnAs Subcell



Growth on Ge or GaAs substrate, followed by substrate removal from sunward surface





Growth on Ge or GaAs substrate, followed by substrate removal from sunward surface




Growth on Ge or GaAs substrate, followed by substrate removal from sunward surface





Growth on Ge or GaAs substrate, followed by substrate removal from sunward surface



Dislocations in Inverted Metamorphic Cells – EBIC



1.39-eV ILM subcell

GalnAs comp. 2% In Latt. mismatch 0.1% 2.5 x 10⁵ cm⁻² Disloc. density







2.3%

5.0 x 10⁶ cm⁻²

0.97-eV

GalnAs

transparent MI

graded buffer layers

Ge substrate

50 µm



0.84-eV IMM subcell 44% In 3.1% 6.3 x 10⁶ cm⁻²

8e-9783-11

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EBIC images and dislocation density of inverted metamorphic cell test structures

Dislocations in Inverted Metamorphic Cells





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Dislocations in Inverted Metamorphic Cells





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Solar Cell Voltage



Voltage depends on non-equilibrium concentrations of electrons and holes

$$pn = n_i^2 e^{qV/kT}$$

$$n_i^2 = N_C N_V e^{-E_g/kT} \qquad pn = N_C N_V e^{-(E_g - qV)/kT} = N_C N_V e^{-qW/kT}$$
$$V = \frac{kT}{q} \ln\left(\frac{pn}{n_i^2}\right) \qquad W \equiv \left(\frac{E_g}{q}\right) - V = \frac{kT}{q} \ln\left(\frac{N_C N_V}{pn}\right)$$

• Bandgap-voltage offset $W \equiv (E_g/q) - V$ is a useful parameter for gauging solar cell quality, especially when dealing with semiconductors of many different bandgaps

 Basically a measure of how close electron and hole quasi-Fermi levels are to conduction and valence band edges SPECTROLAB

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Band gap - Voltage Offset (Eg/q) - Voc



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High-Efficiency Multijunction Cells



LM and MM 3-Junction Cell Cross-Section





contact AR n⁺-GalnAs TOPCEIL n-AllnP window n-GaInP emitter p-GalnP base MidetoTum p-AlGaInP BSF p++-TJ n++-TJ L Middle Cell n-GaInP window n-GalnAs emitter p-GalnAs base p-GalnP BSF p-GalnAs Tunnel Junction step-graded buffer p++-TJ Cell n++-TJ Bottom nucleation n+-Ge emitter p-Ge base and substrate contact

Lattice-Matched (LM) Lattice-Mismatched or Metamorphic (MM)



Metamorphic (MM) 3-Junction Solar Cell





• Metamorphic growth of upper two subcells, GalnAs and GalnP







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Metamorphic (MM) 3-Junction Solar Cell





 Metamorphic GalnAs and GalnP subcells bring band gap combination closer to theoretical optimum



Record 40.7%-Efficient Concentrator Solar Cell





Concentrator cell light I-V and efficiency independently verified by J. Kiehl, T. Moriarty, K. Emery – NREL R. R. King, Stanford Photonics Research Center Symposium, Stanford, CA, Sep. 14-16, 2009 SPECTROLAB

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New World Record 41.6% Multijunction Solar Cell



Ref.: R. R. King et al., 24th European Photovoltaic Solar Energy Conf., *Hamburg, Germany, Sep. 21-25, 2009.*

• 41.6% efficiency demonstrated for 3J lattice-matched Spectrolab cell, a new world record

- Highest efficiency for any type of solar cell measured to date
- Independently verified by National Renewable Energy Laboratory (NREL)

 Standard measurement conditions (25°C, AM1.5D, ASTM G173 spectrum) at 364 suns (36.4 W/cm²)

• Lattice-matched cell structure similar to C3MJ cell, with reduced grid shadowing as planned for C4MJ cell

 Incorporating high-efficiency 3J metamorphic cell structure + further improvements in grid design
 → strong potential to reach 42-43%

champion cell efficiency

Concentrator cell light I-V and efficiency independently verified by C. Osterwald, K. Emery – NREL



- At peak 41.6% efficiency \rightarrow 364 suns, Voc = 3.192 V, FF = 0.887
- Efficiency still >40% at 820 suns, at 940 suns efficiency is 39.8%
- Diode ideality factor of 1.0 for all 3 junctions fits V_{oc} well from 100 to 1000 suns



0 L A B41.6% Solar CellA BOEING COMPANYLIV Curves vs. Concentration



- At peak 41.6% efficiency \rightarrow 364 suns, Voc = 3.192 V, FF = 0.887
- Series resistance causes drop in V_{mp} above 400 suns, V_{oc} continues to increase
- Efficiency still >40% at 820 suns, at 940 suns efficiency is 39.8%

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Best Research Cell Efficiencies





Chart courtesy of Larry Kazmerski, NREL

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Inverted Metamorphic (IMM) 3-Junction Cell



Bottom ~1-eV GaInAs subcell is inverted and metamorphic (IMM)

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• Upper two GaInAs and GaInP subcells are inverted and lattice matched (ILM)

Inverted Metamorphic (IMM) *Second* 3-Junction Cell

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 Raising band gap of bottom cell from 0.67 for Ge to ~1.0 eV for IMM GaInAs raises theoretical 3J cell efficiency



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4-Junction Lattice-Matched Cell





- Current density in spectrum above Ge cell 4 is divided 3 ways among GalnAs, AlGa(In)As, GalnP cells
- •Lower current and I²R resistive power loss



0.67-eV Ge cell 4 and substrate

4-Junction Cell



 Lowering band gap of subcells 2 and 3, e.g., with MM materials, gives higher theoretical 4J cell efficiency

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• Light I-V curves for 3-junction upright MM (40.7%), 3J lattice-matched (41.6%), 3J lattice-matched at 822 suns (39.1%), and 4J lattice-matched cell (36.9%)



Wafer bonding for multijunction solar cells

Low band gap cells for MJ cells using high-quality, lattice-matched materials

 Epitaxial exfoliation and substrate removal

 Formation of latticeengineered substrate for later MJ cell growth

 Bonding of high-band-gap and low-band-gap cells after growth

 Electrical conductance of semiconductor-bonded interface

 Surface effects for semiconductor-tosemiconductor bonding





6-Junction Solar Cells







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Concentrator Photovoltaic (CPV) Systems and Economics



Concentrator PV Systems with Multijunction Cells



- •1 football field of ~ 17% solar cells at 1-sun produces ~ 500 kW.
- By using MJ cells (> 35%) at concentration of 500 suns, same power is produced from smaller semiconductor area (or the football field produces 500 MW).



Combination of high efficiency & 500X concentration boosts output per semiconductor area by a factor of 1000.

MJ cells are replaced by less expensive optics and common materials.

Leads to reduced cost of energy despite paying extra for tracking & cooling.







III-V MJ cells give
 56% measured
 improvement in
 module efficiency
 relative to Si
 concentrator cells

Courtesy of Solar Systems Pty. Ltd., Australia



Balance of System Costs



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Economics for Device Physicists



Continuity equation:

$$\frac{\partial \rho}{\partial t} = qG - qR - \nabla \cdot J$$

...in \$\$ rather than charge carriers:



Terrestrial PV System Cost



R. R. King et al., 3rd Int'l. Conf. on Solar Concentrators (ICSC-3), Scottsdale, AZ, May 2005

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Summary



- Urgent global need to address carbon emission, climate change, and energy security concerns \rightarrow renewable electric power can help
- Theoretical solar conversion efficiency
 - Examining built-in assumptions points out opportunities for higher PV efficiency
 - Multijunction architectures, up/down conversion, quantum structures, intermediate bands, hot-carrier effects, solar concentration \rightarrow higher η
 - Theo. solar cell η > 70%, practical η > 50% achievable

Metamorphic multijunction cells have begun to realize their promise

- Metamorphic semiconductors offer vastly expanded palette of band gaps
- 40.7% metamorphic GaInP/ GaInAs/ Ge 3J cells demonstrated
- First solar cells of any type to reach over 40% efficiency
- New world record efficiency of 41.6% demonstrated
 - Highest efficiency yet measured for any type of solar cell
 - 41.6% efficiency independently verified at NREL (364 suns, 25°C, AM1.5D)
- Solar cells with efficiencies in this range can transform the way we generate most of our electricity, and make the PV market explode