PATHS TO ULTRA-HIGH EFFICIENCY (>50% EFFICIENT) PHOTOVOLTAIC DEVICES

C. B. Honsberg and A.M. Barnett
Department of Electrical and Computer Engineering, University of Delaware;
140 Evans Hall; Newark, Delaware 19716, U.S.A.
e-mail: honsberg@ece.udel.edu

ABSTRACT: A central advantage of new approaches to photovoltaic energy conversion is that the thermodynamic efficiency limit can be approached using multiple physical mechanisms and a variety of device structures. Further, these approaches have practical benefits in expanding the range of materials which can be used for energy conversion, particularly through the use of nanostructured materials. This paper shows that all the novel photovoltaic approaches can be grouped into one of five categories, and this grouping allows broad conclusions about the required physical mechanisms and the efficiency limits of practical devices to be made. Analysis show that a single solar cell faces significant challenges in exceeding 50% and instead combinations of approaches, for example combining tandems with new approaches, can utilize the advantages of each approach and provide the most immediate path to a high efficiency photovoltaic device.

Keywords: Fundamentals, High efficiency, Quantum well

1 INTRODUCTION

Theoretical efficiency limit calculations show that under ideal assumptions, many approaches can be used to approach the thermodynamic efficiency limits of solar energy conversion [1]. All of the proposed approaches can be grouped into a limited number of broad categories. Analyzing these broad categories identifies the key challenges, advantages and disadvantages of each approach. Efficiency calculations using physically realistic values for the fundamental mechanism in each of the new approaches show that the achievable efficiency for each is similar to that of a three junction tandem. However, the new approaches have practical advantages for certain wavelength regions, and hence the combination of several of the approaches into a single device allows a photovoltaic device with a “realistic” efficiency of greater than 50%.

2 APPROACHES WHICH EXCEED SHOCKLEY-QUEISSER LIMIT IN A SINGLE SOLAR CELL

The largest loss mechanism in photovoltaic energy conversion arises from the broad range of photon energies in the solar spectrum compared to those that can efficiently be converted by a solar cell. These losses are quantified by efficiency limit calculations, such as detailed balance or thermodynamic analyses. These efficiency limit calculations for *pn* junction contain several assumptions, which are: (1) the input is the solar spectrum (approximated by either a black body spectrum at a given temperature or by a digitized, measured spectrum) at a given concentration level; (2) one photon generates one electron-hole pair; (3) one quasi-Fermi level separation exists in the solar cell; (4) a constant temperature exists across the device (both lattice and carriers) and this temperature is that of the ambient, and; (5) the device is operating under equilibrium (approximated by steady state) conditions. In addition, there are several additional assumptions, such as 100% absorption of the solar spectrum and high (infinite) mobilities. However, an efficiency increase by circumventing these last two assumptions is not possible, as they are associated with loss mechanisms.

The efficiency of a single junction solar cell can be exceeded by splitting the solar spectrum in such a way that each *pn* junction only converts a narrow spectral region. Tandem or multiple junction solar cells have long used this approach by optically connecting multiple *pn* junctions in series, and a tandem solar cell with an infinite number of junctions can reach the thermodynamic efficiency limits of solar energy conversion.

While tandem solar cells can theoretically exceed 50% efficiency, tandems with large numbers of junctions face increasing complexity and materials issues, coupled with diminishing efficiency increases. Therefore, significant attention has been given to developing new approaches in which a single solar cell exceeds the efficiency of a conventional *pn* junction. In order for a solar cell approach to exceed the limit of *pn*-junction solar cell, it must circumvent one of the previous five assumptions in single junction efficiency limit calculations. Thus, while there are a large number of suggested approaches for ultra-high efficiency photovoltaics, they may be grouped according to which of the assumptions in detailed balance or thermodynamic efficiency limit calculations the approach circumvents. Therefore, the approaches to solar cell which exceed a single *pn* junction are:

1. Multiple spectrum solar cells, where the solar spectrum is changed into a different spectrum with the same total energy but a narrower spectral range;
2. Multiple absorption path solar cells, in which the absorption process is altered such that either multiple photons are absorbed to create a single electron-hole pair or alternately one photon creates multiple electron-hole pairs;
3. Multiple energy level solar cells, containing more than two single meta-stable light generated carrier populations (represented by a quasi-Fermi levels);
4. Multiple temperature solar cells, which involve the extraction of energy from variations in either carrier or lattice temperature.
5. AC solar cells, based on rectification of the electromagnetic radiation of the photon.

Each of the approaches is briefly described in the following sections and summarized in Table 1.

Table 1: Approaches to Solar Cells which exceed Shockley-Queisser limit for a single solar cell.

Approach	**Advantages/uses**	**Central Issues**	**Examples**
Multiple spectrum	• Can be implemented using low cost coatings • Can use existing solar cells (or LEDs for thermophotonics)	Efficient conversion of solar spectrum not demonstrated	Thermophotovoltaic Up and down conversion
Multiple absorption	• High impact ionization rates demonstrated with colloidal quantum dots • Suited to conversion of high energy photons	Transport of carriers not demonstrated	Impact ionization Two-photon absorption Raman absorption
Multiple energy level	• Suited to low energy photon conversion • Can capitalize on LED/photodetector devices	Demonstration of *simultaneous* radiative coupling required	Localized band (QW) Mini-band (IBSC)
Multiple temperate	Potential for high efficiencies using a single absorber material	Extraction of energy from hot carrier populations not demonstrated	Hot carriers QWs with thermal escape
AC solar cells	Potential for high efficiencies using a single absorber material	Requires THz devices	Rectenna

2.1 Multiple Spectrum Solar Cells

Multiple spectrum solar cells involve the transformation of the solar spectrum from one with a broad range of energies to one with the same power density but a narrow range of photon energies. The central advantage of these approaches, which include up and down-conversion [2,3] and thermophotonics [4], is that the transformation of the solar spectrum does not need to be included in the solar cell itself. This therefore allows an existing solar cell to exceed the Shockley-Queisser limit. This technology could be applied to any solar cell provided that power gained through spectral alternation offsets the cost of the additional optical coating or optical elements. Further, since the spectral transformation is separate from the device, electrical transport within the spectral conversion coating is not required.

The key challenge in the development of multiple spectrum solar cells is efficient optical conversion. Optical conversion is used in a variety of applications other than solar cells, including white LEDs (which down-convert UV light using phosphors) or up-conversion for optical devices. Up and down conversion approaches typically involve either nanostructured materials or dopants such as erbium. However, the conversion efficiency of the processes remains low, particularly over a broad wavelength range such as the solar spectrum. Thus, while low-cost coatings incorporating up/down conversion based on colloidal quantum dots, phosphors, or radiative defects may be economically applied to existing solar cells to raise their efficiency by several percentage points, these approaches are not suited for ultra-high efficiency.

An alternate approach to spectrum conversion is thermophotonics [4], in which the solar spectrum heats a biased LED, and a solar cell converts the output of the LED into electricity. While the theoretical efficiency of this process is 85.4%, using more realistic bias temperatures and band gaps gives an efficiency of 50%. While thermophotonics offers high efficiency with only two materials and existing devices (solar cell and LED) structures, it faces several critical challenges, including demonstration of efficient radiative emission under high temperatures for the LED.

2.2 Multiple Absorption Path Solar Cells

Multiple absorption path (MAP) solar cells involve the introduction of absorption processes in which one photon does not generate one-electron hole pair. It consists of several possible absorption process, including the absorption of multiple photons (typically two) low energy photon to create higher energy electron-hole pair, and impact ionization (also called Auger generation or multiple exciton generation), in which a single high energy photon generates multiple electron-hole pairs [5], and Raman absorption. In MAP solar cells, the absorption processes do not require meta-stable carrier populations at additional energy levels (the absorption processes are coherent) making it fundamentally different from the multiple energy level devices described below. Further, in MAP devices, unlike in multiple spectrum devices, the absorption process is integrally included as part of the device structure, and the generated electron-hole pairs must be collected, thus making transport of carriers a key issue.

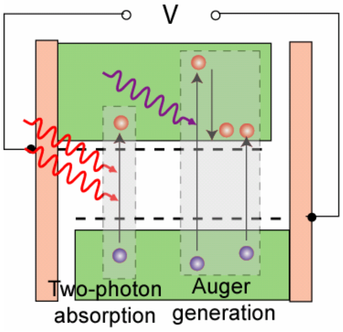


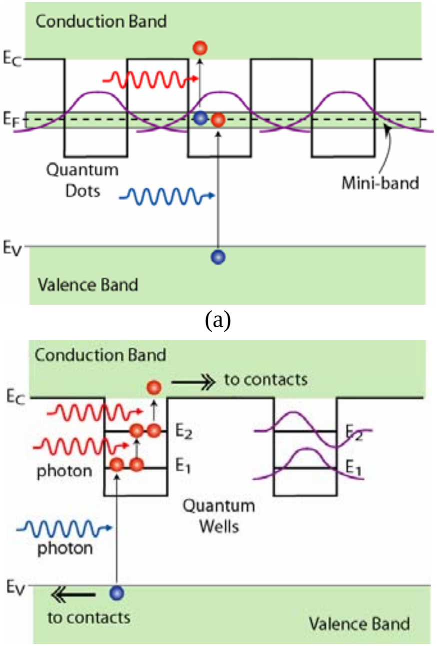
Fig 1: Absorption in multiple absorption path solar cells.

While several potential absorption processes can be used in MAP solar cells, only impact ionization (or multiple exciton generation) has demonstrated materials in which impact ionization is dominant. In bulk materials, impact ionization events represent a small fraction of the absorption events, but in nanostructured materials, the rates are substantially increased, with colloidal PbS and PbSe quantum dots showing 100% ionization [6,7]. The efficiency from a solar cell based on impact ionization depends on how many electron-hole pairs (or excitons) are generated, and a photon with energy m times the band gap should ideally generate m electron hole pairs. If the threshold energy (the minimum energy to initiate impact ionization) is $E_{th} > mEg$, the potential efficiency improvements are reduced. For example, calculations (similar to those in [6]) show that the observed impact ionization process allows efficiencies similar to those of a 2 to 3 stack tandem, even with a 100% efficient ionization processes.

Impact ionization solar cells represent a promising candidate for high efficiency as they are the only approach in which the basic physical mechanisms has been demonstrated on a scale consistent with an efficiency increase above the Shockley-Queisser limit. Furthermore, these devices offer efficient generation for the higher energy photon regions of the solar spectrum, where there are relatively few materials for conventional *pn* junctions. However, impact ionization solar cells also face substantial challenges relating to the collection of carriers.

2.3 Multiple Energy Level Solar Cells

In multiple energy level (MEL) solar cells, the mismatch between the incident energy of the solar spectrum and a single band gap is accommodated by introducing additional energy levels such that photons of different energies can be efficiently absorbed. MEL solar cells can be implemented either as localized energy levels (first suggested as a quantum well solar cell [8]) or as continuous mini-bands (also called intermediate band solar cell for the first solar cell to suggest this approach [9]). Both cases, which are shown in Figure 2, have a fundamental similarity in that they require radiatively coupled multiple light-generated quasi-Fermi levels. In theory, an arbitrary number of bands may be implemented, but in practice the need for a quasi-Fermi level in each band limits the number of band to three [10], for which the efficiency is that of a three-junction tandem solar cell. In the localized energy level approaches, each energy level may be different from that the other energy levels, but again practical constraints such as the ability to absorb all carriers in a thin region limits the ability to implement a large number of effective band gaps.



(a)

(b)

Fig 2: Implementation of multiple energy level solar cells.

The key difference between the two MEL approaches is the transport of light generated carriers. In the mini-band case, the transport must occur along the mini-bands and hence the carriers must not be able to thermalize from one band to another. To prevent thermalization, the density of states must be zero between the bands, and hence that mini-band approaches must use either quantum dots or a material which inherently has multiple bands with optimum energy spacing of the bands. In localized energy level approaches, transport is accomplished by having the carriers at each localized energy level escape by light absorption. To maintain high collection efficiency, the escape time should be faster than the recombination time. The feasibility of the escape process is demonstrated by quantum-well infrared photodetectors (QWIPs), which have high collection from intra-sub band or interband processes [11], provided that the electric field is large [12].

As with the other new approaches to ultra-high efficiency, multiple energy level devices have several advantages as well as challenges. A central challenge in the development of multiple band approaches via either mini-band or localized energy levels is the demonstration of radiative transitions between all the energy levels. While each of the transitions are used in existing devices (eg lasers, LEDs or photodetectors), simultaneous radiative coupling between all three energies needs to be demonstrated. Both approaches have a central advantage is that the lowest band gap (actually the lowest two band gaps) is not a “physical” band gap, circumventing the issues with availability and high non-radiative recombination in low band gap devices.

2.4 Multiple Temperature Solar Cells

A solar cell which contains multiple temperatures – either carrier or lattice temperatures – in a single device can use these temperature differentials to generate power. The high thermal conductivity of most semiconductors means that maintaining a lattice temperature differential is more difficult than in achieving a temperature differential between hot carriers and thermalized carriers. Multiple temperature solar cells differ from other approaches in which carriers exist above the lowest energy level for a short period of time (e.g., impact ionization of some MEL approaches) in that they require a carrier population at an elevated temperature. A thermal converter can be realized by several approaches, including band structures in which the band edges vary abruptly [13], and a device in which hot carriers are extracted through selective energy contacts after they thermalize with each other, but before they thermalize with the lattice [14]. The central issue for multiple temperature devices is that the ability to extract power from hot carrier populations has not been physically demonstrated, and hence a “practical” efficiency limit is unknown.

2.5 AC Solar Cells

A final approach which allows a single solar cell to exceed the Shockley-Queisser limit is to treat the incoming photon as an electromagnetic wave. An AC signal produced by the interaction of this wave with an antenna may be rectified by a diode. While high efficiencies have been demonstrated from similar rectenna devices [15], such efficiencies do not take into account losses such a reciprocity, which means that an antenna which receives a given wavelength must also radiate at that wavelength, and further do not incorporate the broad-band nature of the solar spectrum. Further, even if such approaches are used only for a narrow band of the lowest energy photons, the devices must operate in the Terahertz regime, representing a large technical challenge.

3 ULTRA-HIGH EFFICIENCY SOLAR CELLS

Any of the previous approaches can exceed the Shockley-Queisser limit in a single solar cell, and practical considerations limit their efficiency to about that of a three-junction solar cell, or ~ 50% at one sun and ~65% under maximum concentration. Thus, since three-junction tandems presently represent the state-of-the-art with efficiencies over 37% [16], ultra-high efficiency solar cells must use more than a single solar cell structure. This section examines how to optimally integrate multiple solar cells into a single structure.

One approach to ultra-high efficiency solar cell is to use conventional *pn* junction tandems, and Fig 3 shows the AM1.5G efficiency as a function of the number of band gaps. However, conventional tandem approaches encounter several issues as the number of *pn* junctions increases.

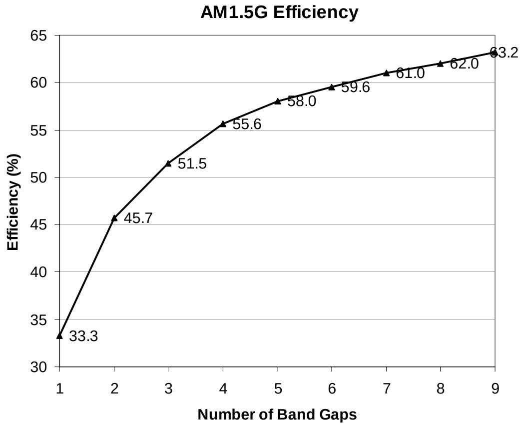


Figure 3: Efficiency *v.s.* number of band gaps.

The first well-known issue is that optimum materials, ideally lattice matched but possibly also metamorphic, must be found for each junction. While several materials and approaches are being considered and 5 and 6 metamorphic tandems have been proposed and fabricated, tandems with a large number of stacks will eventually encounter several practical problems. The first of these, which already is an issue for thermophotovoltaics, relates to the low band gap materials, particularly low band gap materials with lattice constants appropriate for inclusion in existing tandem structures. For low energy photons, MEL approaches provide several advantages. Since the lowest energy “band gap” in quantum dot (QD) or quantum well (QW) MEL solar cells is formed by difference between the energy level of the QD or QW and the barrier material, this circumvents the need for a material with a band gap below 0.7 eV. Further, MEL solar cell have practical advantages since the interband or intersubband transitions on which MEL devices rely have been demonstrated in infrared quantum well and quantum dot photodetectors and since the material choices for the solar cell are greater if only small valence band offsets are required.

A second problem encountered by tandems with a large number of band gaps is that the optimum value of the upper band gap increases as the number of stacks increases, requiring materials with band gaps above 2.4 eV. While the requirement for a high band gap does not pose an inherently fundamental problem as there are candidates materials with Eg > 2.4 eV particularly in the III-nitride material system, they involve the development of material systems not presently used in tandems. Impact ionization (or multiple exciton generation) solar cells offer the potential for both low-cost coatings as well as efficient multiple carrier generation for high energies. Consequently, impact ionization devices may offer a solution to achieving efficient high energy conversion in tandems with a large number of *pn* jucntins.

4 CONCLUSIONS

While multiple approaches to exceeding the Shockley-Queisser limit have been proposed, a single solar cell from these approaches is in practice limited to an efficiency similar to that of a three-junction solar cell. Consequently, an ultra-high efficiency solar cell will consist of multiple stacks of individual solar cells. Since each of the approaches offers potential advantages, the optimum solar cell consists of a hybrid between existing tandem and novel concept approaches.

5 ACKNOWLEDGEMENTS

The authors thank the U.S. National Renewable Energy Laboratory for their financial support through subcontract XAT-5-44277-01 administered by M. Symko-Davies and R. McConnell.

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