NANOSTRUCTURED SOLAR CELLS FOR HIGH EFFICIENCY PHOTOVOLTAICS

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ABSTRACT

The use of nanostructures in photovoltaics offers the potential for high efficiency by either using new physical mechanisms or by allowing solar cells which have efficiencies closer to their theoretical maximum, for example by tailoring material properties. At the same time, nanostructures have potentially low fabrication costs, moving to structures or materials which can be fabricated using chemically or biologically formed materials. Despite this potential, there are multiple and significant challenges in achieving viable nanostructured solar cells, ranging from the demonstration of the fundamental mechanisms, device-level issues such as transport mechanisms and device structures and materials to implement nanostructured solar cells, and low cost fabrication techniques to implement high performance designs. This paper presents the challenges and approaches for using nanostructured solar cells in devices which can approach the thermodynamic limits for solar energy conversion.

NANOSTRUCTURED SOLAR CELLS

Nanostructured solar cells offer several advantages for solar cells including; (1) the ability to exceed a single junction solar cell efficiency by implementing new concepts; (2) the ability overcome practical limitations in existing devices, such as tailoring the material properties of existing materials or using nanostructures to overcome constraints related to lattice matching and; (3) the potential for low cost solar cell structures using self-assembled nanostructures. The multiple potential uses for nanostructures show why there is large interest in these approaches, since they may be able to improve on current technology, whether in high efficiency or lowest $/Wp. Further, since they offer both higher efficiency and low cost, they offer the potential to circumvent both existing efficiency and cost drivers.

While nanostructured solar cells have significant potential to advance photovoltaics, there are also substantial challenges. The efficiency even of precisely grown devices such as MBE-grown structures is presently lower than devices without the nanostructures. Further, experimentally demonstrated advances in nanostructure solar cells using lower cost approaches often rely on absorption/emission mechanisms which do not necessarily correlate to the ability to make devices. Moreover, nanostructured devices do not achieve large absorption (the easiest solar cell parameter to control), much less the collection, voltage, and FF of existing semiconductor devices.

Given these challenges as well as the large number of options and approaches for nanostructured solar cells, it is important to examine nanostructured approaches which may have a practical contribution in the short to medium term and to identify approaches and key challenges in reaching the potential of nanostructured solar cells. This paper examines the options for nanostructured solar cells and identifies key research areas in nanostructures photovoltaics, focusing on components necessary to allow nanostructured PV to contribute to high efficiency devices

NEW CONCEPTS FOR SOLAR CELLS

An important advantage for nanostructured solar cells is that they can be used to incorporate new physical mechanisms which allow an efficiency greater than that of a one-junction solar cell. While the ultimate thermodynamic efficiency limit is the same for

Table 1: New concept approaches to solar cells.

Assumption in Shockley-Queisser	Approach which circumvents assumption	Examples
Input is solar spectrum	Multiple spectrum solar cells: take the input spectrum and transform to one with same energy but narrower wavelength range	Up/down conversion Thermophotonics
One photon = one electron-hole pair	Multiple absorption path solar cells: any absorption path in which one photon ≠ one-electron hole pair	Impact ionization Two-photon absorption
One quasi-Fermi level separation	Multiple energy level solar cells: Existence of multiple meta-stable light-generated carrier populations within a single device	Intermediate band Quantum well solar cells
Constant temperature = cell temperature = carrier temperature	Multiple temperature solar cells. Any device in which energy is extracted from a difference in carrier or lattice temperatures	Hot carrier solar cells
Steady state (≈ equilibrium)	AC solar cells: Rectification of electromagnetic wave.	Rectenna solar cells

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nanostructured solar cells as for a tandem solar cell, nanostructured approaches have several advantages. The most important of these for increasing solar cell efficiency is the possible increase in efficiency ***for a given number of materials***. For example, the quantum dot intermediate band solar cell (IBSC) [1], two materials give a similar efficiency to a three-junction tandem, while hot-carrier approaches [2] allow the use of one absorber material to yield efficiencies over 50% under concentration.

Numerous suggested approaches for increasing the efficiency above the Shockley-Queisser limit have been proposed, but for ease of analysis all the approaches can be grouped in to several categories, based on which assumption in the theoretical detailed efficiency limit calculations they approach avoids. These categories are shown in Table 1 [3].

Of these approaches, the ones receiving the majority of the attention and focus for experimental implementation and are thermophotonics, multiple absorption path solar cells, and multiple energy level solar cells. For these, theoretical calculations which include realistic physical limits show that they have efficiencies similar to a three junction tandem at a given concentration level. For example, thermophotonics has realistic efficiency limits of 50% [4], intermediate band solar cells have efficiencies of 62.3%, just under the three-junction tandem limit, and multiple exciton generation solar cells also have efficiencies of xx%, assuming an ideal exciton generation for a single threshold energy [5].

In order to reach ultra-high efficiency with these approaches, the most straight forward approach is to use two devices, each receiving half of the solar spectrum. With two solar cells, an efficiency similar to a six junction tandem can be reached. Multiple absorption path (via exciton generation or Auer absorption) or multiple energy level solar cells (via quantum dots or quantum wells) can readily be configured such that two such devices are connected optically in series similar to the way a two junction tandem is connected. Thermophotonic approaches would be more difficult to use in such a configuration, but the goal of thermophotonics relates to increasing the efficiency of existing solar cells rather than reaching the thermodynamic limits. Consequently, the goal of reaching ultra-high efficiency (capable of approaching the thermodynamic limits and efficiency > 50%) in a mid-term time frame is most directly addressed by MAP and MEL approaches.

Multiple Exciton Generation

The most advanced experimental approach to MAP solar cells is multiple exciton generation (similar to Auger or impact ionization). Ideally, such a device would have a threshold voltage of $n\times E_G$ and a quantum efficiency of $n\times 100\%$, where n is the number of electron hole pairs generated per photon. Experimental measurements in colloidal PbS and PbSe quantum dots show process close to this ideal [56][]. These results make exciton generation approaches the only of the new concepts to experimentally demonstrate the physical mechanisms on a scale required for high efficiency.

Despite the experimental results, MAP devices have several challenges. One issue in MAP solar cells, in common with all new concepts approaches, is that the fundamental mechanisms are incompletely understood. For example, demonstrating Auger absorption in materials which have optimum band gaps, and improved understanding of which materials and configurations may demonstrate high Auger absorption are both areas which require additional analysis and experiments. A second issue relates to transport of carriers. Since the metastable energy for the carriers is at the lower energy levels for the quantum dot, either carriers must be excited from this lower energy to the continuum of states (similar to a MEL device), or the band structure must be designed to allow transport from this lower energy level, either via the formation of mini-bands or by designing the band structure such that the lowest energy level is within the thermal energy of the continuum of states.

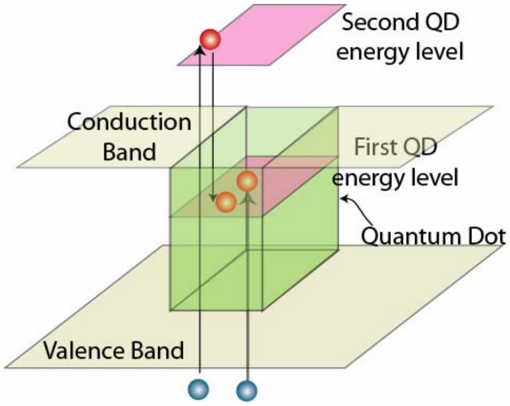

Figure 1: Multiple exciton solar cell.

A final issue relates to how to incorporate MAP devices into a shorter-term path in realization. MEL devices presently are most suited towards high energy portion of the spectrum, since processes involving 3 to 4 electrons require band gaps of approximately 1.0 eV or higher. Such a high energy converter fit well with the optimum region of the solar spectrum and moreover the colloidal approaches are also a low cost technology. However, it meshes poorly with existing high efficiency designs, since the portion of the spectrum which it would convert already has well understood components which are relatively close to their optimum. Consequently, MEG devices are most suited to stand-alone low, cost high efficiency concepts.

Virtual Band Gap Solar Cells

Multiple energy level (MEL) solar cells, in which multiple energy levels or bands are simultaneously radiatively coupled via both generation and recombination, are another approach to exceeding the Shockley-Queisser limit. The multiple quasi-Fermi levels can arise from a band or through localized energy levels, as shown in Figure 2. Further, the band or energy levels may be introduced either by designing a material or defect level which contains multiple bands or by using nanostructures, such as quantum dots, wires or wells. Although materials with inherent multiple band structures offer an elegant and conceptually simper approach, the numerous other requirements for a photovoltaic material, such as the ability to dope it, good mobilities, requirements of the density of states, make such an approach viable primarily for longer term. Similarly, while impurity photovoltaic (IPV) devices could potentially be used if a defect with optimum properties is found, the ability to design or find such a material and defect reduce the utility of IPV solar cells.

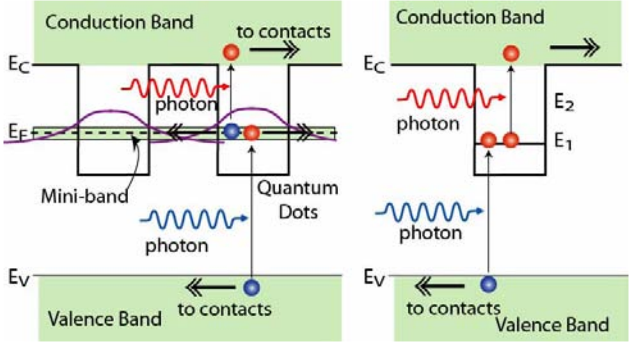

Figure 2: (a) Mini-band approach and (b) localized approach for virtual band gap solar cells.

Approaches which utilize nanostructures to implement the energy levels have an “effective” band gap introduced by the difference between the conduction (or valence) band offsets of other materials. These approaches, here called virtual band gap solar cells, have to-date demonstrated the highest efficiency nanostructures, substantially because the barrier material uses existing solar cell materials and provides a substantial fraction of the total energy conversion.

Key challenges remain in the development of virtual band gap solar cells, including the demonstration of the simultaneous optimum radiative coupling between all the bands [7], the identification of optimum material systems and nanostructure configuration, and issues related to implementation in a device, particularly transport and optical absorption. However, a central advantage of virtual band gap solar cells is that they allow the understanding and technology developed for other types of nanostructured devices to be applied to solar cells. For example, of the six transitions which are necessary, all have been demonstrated ***separately*** in other semiconductor devices. Therefore, despite the fact that simultaneous radiative coupling with individual quasi-Fermi levels has not been demonstrated, this most likely reflects device engineering rather than fundamental physics.

Because of the more established physics and technology surrounding virtual band gap solar cells, they provide the shortest path for realizing a high efficiency nanostructured solar cell. In particular, they have an advantage for low energy photons for solar cells with a large number of band gaps, since the intersubband transitions required at the low energy photon range are well-documented and commercially using in quantum-well infrared photo detectors. Furthermore, efficient conversion of low energy photons faces challenges using pn junction approaches, as demonstrated by the difficulty in thermo-photovoltaics (TPV) for lower temperature sources. By not requiring a low physical band gap, virtual Eg devices can achieve higher efficiency in this energy range.

NANOSTRUCTURES FOR ENHANCING EXISTING SOLAR CELLS

The likely most immediate use of nanostructured materials is their use to realize practical advantages in conventional device structures rather than utilizing new physical mechanisms for efficiency increases. Given the ability of nanostructures to modify material parameters, there are many avenues by which nanostructures can increase solar cell efficiency closer to the theoretical limit for a particular device. Suggested approaches include changing optical/material interactions by approaches such as nano-texturing or plasmon absorption; by using nanostructured material to modify the band gap of an existing materials; or by using nanostructures to modify the strain between two materials or the impact of dislocations. While these offer the greatest short-term potential for using nanostructures, they also have the greatest variety, with the benefits and gains dependent on the specific device configuration in which the nanostructures are included.

LOW COST APPROACHES FOR NANOSTRUCTURES

The ultimate goal in photovoltaics is to achieve a high efficiency technology which can be manufactured at low cost and large scale. Low-cost self-assembled nanostructures may be more efficient in material usage and may have much lower fabrication costs. Existing low cost approaches typically use colloidal formation of quantum dots, which are then inserted or used in a device structure. Since the colloidal nanocrystals are solution based, they are readily incorporated in organic and dye-sensitized approaches, in which case they act as an absorber material with the transport and junction supplied by the remaining device [8]. Recently, an inorganic solar cell using quantum dots was also demonstrated []. Other low-cost approaches focus on the development of new self-assembly techniques,

KEY ISSUES IN NANOSTRUCTURED SOLAR CELLS

Despite the many potential uses and ways to include nanostructures in photovoltaic devices, these solar cells share several issues and challenges. The most basic issue is that the device design rules for nanostructured solar cells do not exist, and thus many choices or design parameters do not have sufficient theoretical or experimental guidance. Figure 3 shows several of the design issues. The design rules for achieving a high efficiency nanostructured solar cell are substantially different than a conventional device. For example, current collection in conventional devices is typically achieved by increasing the diffusion length (or increasing the electric field). In nanostructured photovoltaics, the collection depends on different factors, such as the time taken to remove the carrier from the nanostructure compared to the recombination, and the transport through the device.

Transport is an issue which affects nearly all uses of nanostructures, whether for high efficiency or primarily for low cost. The inherent confining potentials in nanostructures allow tailoring of material properties, but also introduce a barrier to transport of carriers at the low energy levels in the nanostructure. LEDs and lasers avoid this problem since they require carrier injection into, not collection from, the nanostructures. Similarly, photo detectors circumvent this issue by using large electric fields, low confining potentials and intersubband optical absorption. There are two fundamental solutions to the transport problem: (1) use of closely space nanostructured arrays which promote the formation of mini-bands as shown in Figure 2a in which the miniband transports carriers; or (2) excitation of the carriers in the confining potential to the conduction/valence band of the barrier or matrix material (either thermally, via an electric field, or via photon-induced transitions), which then acts to transport carriers. For high efficiency approaches, the closely spaces array must be a quantum dot (QD) array, since only QDs have a zero density of states between the bands. In other nanostructured arrays, carriers quickly thermalize to the lowest energy level, representing a loss. In addition, the closely spaced array should ideally be periodic, since variations in the QD spacing change the absorption edge. However, closely spaced arrays of QDs with long range order are difficult to fabricate.

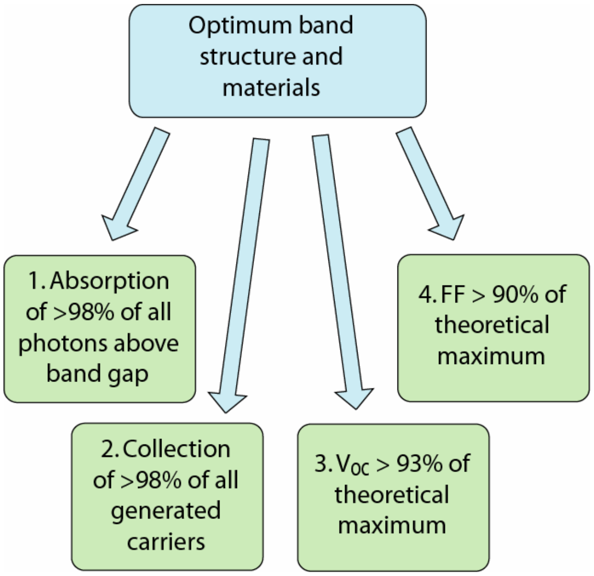

Figure 3: Design issues in nanostructured solar cells.

The other approach to transport in nanostructured materials is to use photons to excite carries to the upper energy band. This process is used in quantum well and quantum dot intra-red photodetectors (QWIP and QDIPs). Once at this energy, carriers must be prevented from being captured back into the nanostructure. Transport in the barrier allows high performance provided that the barrier or matrix material surrounding the nanostructure has good transport properties, that there is a strong electric field, and that carriers are not transported in the nanostructure where recombination rate can be high. To avoid transporting carriers in the nanostructure, the direction of transport of carriers should be perpendicular to the confinement of the nanostructure, which allows QD and QW structures, but not nanorods aligned parallel to the direction of light absorption.

An additional requirement in nanostructured solar cells is the need to include structures which increase absorption. Due to the low volume of nanostructure material and the need to keep devices thin for transport reasons, a necessity of these approaches is features which promote effective absorption. New approaches to increasing the optical absorption include nanostructured features for light trapping and plasmon absorption.

CONCLUSION

While there is substantial research required to realize a fully a nanostructured, low cost solar cell, certain aspects are more immediately applicable to high efficiency solar cells and serve as a route towards a high performance low-cost nanostructured solar cell. Virtual band gap solar cells for conversion of low energy photons have the advantage of being able to use phenomena demonstrated in existing semiconductor devices, coupled with the relatively lower efficiency of on junctions in this energy range. Other approaches with potential in the short term focus on using nanostructured to enhance performance of existing solar cells, such as improved light trapping or reducing the effects of lattice mismatch. In order to have the largest impact, the demonstration of nanostructures using low cost approaches with improved transport properties is essential. A closely-spaced ordered array of quantum dots allows implementation of any of the potential uses of nanostructures. Nanostructures without long range order have a challenge in demonstrating efficient transport.

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