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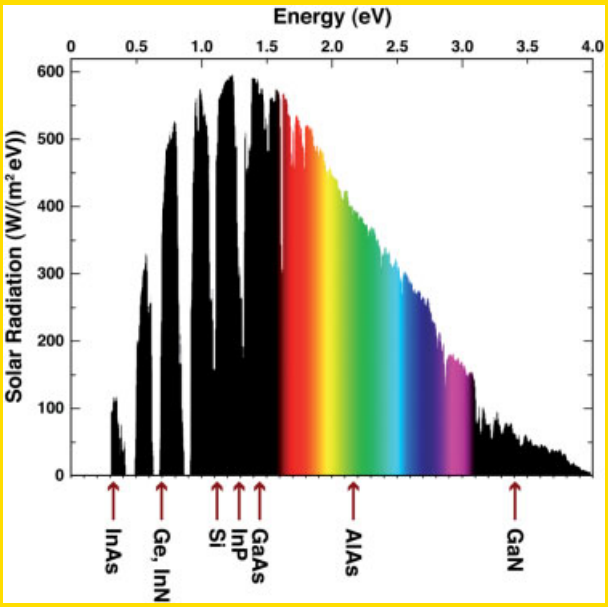
Abstract We review recent progress towards increasing solar cell efficiencies beyond the Shockley-Queisser efficiency limit. Four main approaches are highlighted: multi-junction cells, intermediate-band cells, hot carrier cells and spectrum conversion. Multi-junction cells use multiple solar cells that selectively absorb different regions of the solar spectrum. Intermediate-band cells use one junction with multiple bandgaps to increase efficiencies. Hot-carrier cells convert the excess energy of above-bandgap photons into electrical energy. Spectrum conversion solar cells convert the incoming polychromatic sunlight into a narrower distribution of photons suited to the bandgap of the solar cell.



The AM 1.5 solar spectrum along with the bandgaps of some semiconductors. Third generation photovoltaics strive to maximize the efficiency of converting polychromatic radiation into electricity.

Third generation photovoltaics

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Introduction

Third generation photovoltaics (PVs) strive to drastically reduce the cost of solar energy below the current level of around \$1/Watt to less than \$0.20/Watt [1]. Worldwide power generation of PVs is above 5 GW and the entire industry is growing over 25% per year [2]. A combination of increased energy prices and fears over global warming are pushing up demand for PVs. PVs offer a near limitless supply of carbon neutral energy that could alleviate both problems at the same time [3].

The vast majority of solar cells on the market are single junction silicon devices known collectively as first generation devices. Thermodynamics fundamentally limit their energy conversion efficiency between 31% and 41% depending on the concentration of incoming sunlight [4]. This is known as the Shockley-Queisser efficiency limit. Fig. 1 shows the origin of most of the efficiency losses. In this case, (1) represents photons with energies below the bandgap of the device that are not absorbed ("red losses") and (2) represents photons with energies above the bandgap which lose this excess energy as heat ("blue losses"). As the

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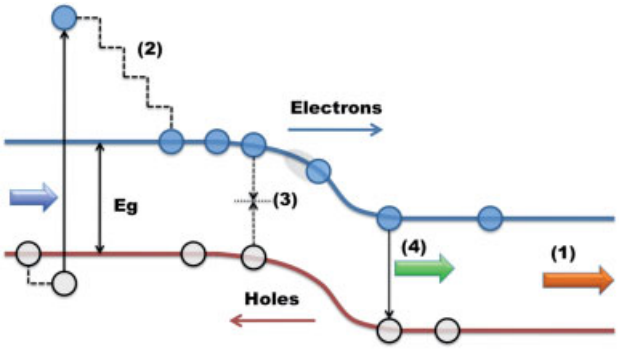

Figure 1 (online color at: www.lpr-journal.org) A diagram showing the primary losses in solar cells adopted from [1]. (1) Incoming photons with energies below the bandgap (labeled as Eg) are not absorbed. (2) Incoming photons with energy in excess of the bandgap are absorbed but the electrons and holes will relax to the conduction band minimum (CBM) / valence band maximum (VBM) by producing phonons (represented by dashed lines). (3) Electrons and holes can recombine with the help of electronic states within the bandgap. These states are typically defects or impurity atoms and the recombination event produces phonons. (4) Electrons and holes can also recombine radiatively and produce a photon with an energy equal to the bandgap. Unlike 1, 2, and 3, this radiated energy is not necessarily lost as these photons can be reabsorbed. However, photons emitted from the front of the cell back towards the incoming sunlight are lost forever and ultimately restrict the maximum efficiency of the cells.

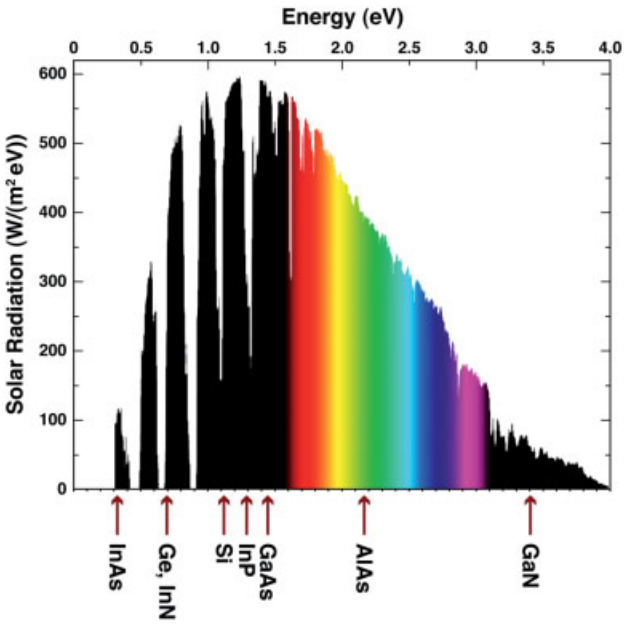

Figure 2 (online color at: www.lpr-journal.org) The AM 1.5 spectrum is the standard used to determine the efficiency of solar cells. The spectrum represents, for a given location and atmospheric conditions on earth, the intensity and spectral distribution of incoming sunlight. Also displayed are the bandgaps of a select number of solar cell materials. For a single junction, the most efficient cells have a bandgap between 1.1 eV and 1.4 eV that includes Si, InP and GaAs. A wide array of bandgaps is available by alloying different semiconductors with each other.

sun is a polychromatic source of light, fixing the bandgap gives a tradeoff between these two losses. Efficiency measurements are usually obtained under AM 1.5 solar conditions that simulate the spectral distribution of sunlight under a given atmospheric condition. Fig. 2 shows the AM 1.5 solar spectrum and a list of bandgaps for some PV materials.

A much smaller but rapidly growing segment of the PV market focuses on thin film designs that are collectively know as second generation devices. Examples are PVs based on amorphous silicon (a-Si), cadmium telluride (CdTe) and Copper Indium (Gallium) Diselenide (CIS, CIGS). These new thin film devices also share the same performance restrictions as conventional Si devices but promise to lower the cost of each device [5]. These lower costs stem from both reduced material usage and high throughput manufacturing. While thin films are cheaper than traditional first generation Si devices, they typically suffer from higher non-radiative recombination losses shown as (3) in Fig. 1. These higher losses are typically due to lower film quality.

Third generation PVs are designed to combine the advantages of both the first and second generation devices. Specifically, this review paper will focus on attempts to improve the efficiency of PVs above the Shockley-Queisser efficiency limit through the following four methods: multi-junction cells, intermediate-band cells, hot carrier cells and spectrum conversion. Some of these concepts are already available in commercial products while some have only scant experimental evidence. They all ultimately share the same promise of reducing the price per watt of PVs to a level where they can form a large portion of the worlds energy supply.

Multi-junction cells

Multi-junction solar cells are the current efficiency leaders and already have commercial uses in powering satellites. It is expected that these cells will eventually become cost effective for terrestrial uses when combined with solar concentrators [6–8]. In 2003, a triple junction InGaP/GaAs/Ge cell was demonstrated with 36% efficiency (AM 1.5 100–500× concentration) [9] and since then maximum efficiency of these cells has been raised above 40% [10].

Multi-junction solar cells are able to achieve such high efficiencies by separating the absorption of the polychromatic solar spectrum into semiconductors with different bandgaps. In that way, high energy photons are absorbed by the high bandgap junction and lower energy photons are absorbed at the lower bandgap. This allows a large portion of the solar spectrum to be absorbed while avoiding thermalization losses from carriers relaxing to the conduction band

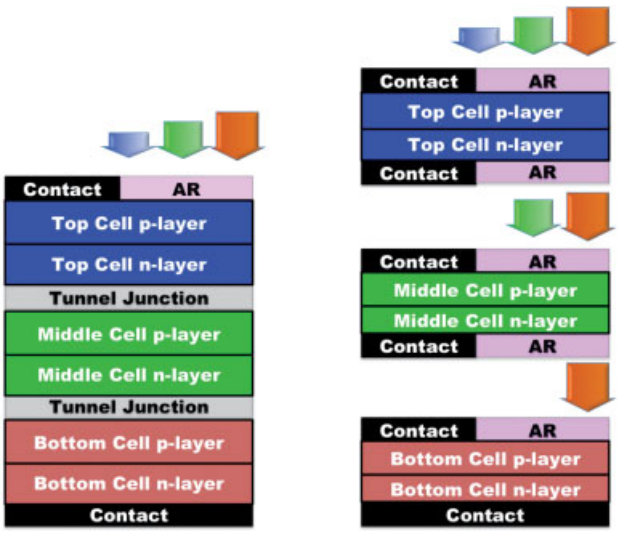

Figure 3 (online color at: www.lpr-journal.org) (Left) A monolithic (two-terminal) multi-junction solar cell is shown. Three different bandgap cells are connected in series to each other with one contact on the front and one contact on the back. 'AR' represents anti-reflection coatings, which are used to increase the amount of sunlight absorbed in the structure. As there are only two contacts in this type of multi-junction cell, the lowest individual current producer limits the total current of the structure. The three cells are connected by tunnel junctions, which are typically very thin regions of highly doped semiconductors. The purpose of the tunnel junctions is to allow holes and electrons to recombine between two adjacent cells while also being optically transparent. (Right) A mechanically stacked (multi-terminal) multi-junction cell features contacts for each individual cell. This structure places no current matching restriction and therefore the arrangement of bandgaps is less important. However, each cell grown requires its own substrate and the fabrication steps making the entire structure much more expensive and complicated to fabricate.

minimum (CBM). In theory, an infinite number of junctions can be stacked for 86% efficiency under maximum solar concentration [11].

The development of these multi-junction solar cells started with double-junction cells of GaAs as the lower cell and an AlGaAs or InGaP as the top cell [12]. There are two distinct approaches to combining the cells: one method is to physically separate them and use multiple contacts while the other integrates the cells monolithically with tunnel junctions joining them in series. Fig. 3 highlights the distinction between the two approaches. For monolithic multi-junction cell designs, it is important to keep the lattice mismatch between each successive layer to a minimum in order to avoid creating misfit dislocations. Dislocations can severely diminish solar cell performance by creating additional regions where carriers can non-radiatively recombine.

For these reasons, InGaP/GaAs/Ge triple-junction cells have proven to be extremely efficient as all three layers are closely lattice matched. However, InGaP/GaAs/Ge structures do not have the optimum arrangement of bandgaps to maximize efficiencies. Monolithic multi-junction cells are restricted as they are connected in series. Therefore, the lowest current-producing subcell will fix the current of the entire cell. In the case of InGaP/GaAs/Ge, the Ge subcell produces excess current that is wasted. Therefore it would be advantageous to have different combinations of bandgaps in the three layers.

With Ge as the bottom cell, the optimum middle and top bandgaps are 1.16 eV and 1.73 eV respectively. This structure could theoretically achieve efficiencies over 60% under 500× concentration [13]. These bandgaps can be achieved by adding additional Indium to the middle and top cells. However, to change the bandgaps of each layer would require moving away from the lattice matched condition. One solution to this problem came from growing metamorphic or lattice mismatched layers on top of the Ge substrate with lower bandgaps, as to reduce the excess current generated in the Ge subcell [10]. Using this approach, an efficiency of 40.7% was reached under a concentration of 240 suns.

Another approach is to remove the bottom Ge subcell and replace it with a wider bandgap semiconductor. This has been achieved by growing a lattice matched GaAs/InGaP on top of a GaAs substrate followed by a graded layer of $In_{1-x}Ga_xP$ and finally a layer of $In_{0.3}Ga_{0.7}As$ [14]. The GaAs substrate is then removed and the entire device is inverted so the bottom layer is $In_{0.3}Ga_{0.7}As$. The first advantage of this technique is the $In_{0.3}Ga_{0.7}As$ layer has a bandgap of 1.0 eV therefore reducing the excess current generated by the bottom layer and increasing the open circuit voltage. The inverted growing technique is beneficial as misfit dislocations are only created in the $In_{0.3}Ga_{0.7}As$ layer while preserving the high quality of the InGaP and GaAs layers. Using this technique an efficiency of 38.9% was achieved at 81 suns concentration.

Wafer bonding is also being considered to alter the bandgaps of the multi-junction cell while avoiding the issue of lattice matching entirely. Wafer bonding is achieved by first implanting a wafer with light elements to create a thin damaged layer. The layer is then contacted to another wafer and heated to enhance the formation of covalent bonds. The interface between the two wafers is incoherent and therefore no misfit dislocations are formed [15]. This technique allows each subcell to have the high carrier lifetimes and mobilities associated with the bulk semiconductors. The concept has been shown to produce high quality heterojunctions and double-junction solar cells [15–18]. This technique also may lead to a quadruple-junction InGaP/GaAs/InGaAsP/InGaAs solar cell that in principle would have a higher efficiency than current InGaP/GaAs/Ge triple-junction cells.

Another approach to improving the efficiencies of multi-junction cells is the incorporation of group III-Nitride semiconductors. It was recently discovered that the bandgap of InGaN spans from 0.65 eV to 3.4 eV making an almost perfect match to the solar spectrum [19, 20]. However, test

cells made using InGaN suffer from relatively low efficiencies [21–24]. The low efficiencies can be attributed to a number of factors including phase separation of the alloy and the difficulty in forming ohmic contacts to p-type material [25]. High Indium content p-type InGaN is difficult to grow due to the formation of native donor defects. The very high electron affinity of InN causes defects to have a strong donor-like nature thereby inverting the surface. The presence of an inverted InN surface makes direct contact to p-type material difficult [26].

Despite this, there are many possible benefits of using III-Nitride multi-junction solar cells. III-Nitrides have already been used extensively in LEDs and have shown to have exceptional electronic properties even with a high density of defects [27]. Additionally, InGaN can be grown directly onto Si substrates allowing for cheaper multi-junction cells compared to current technology grown on Ge [28].

All of the concepts previously discussed regarding multi-junction cells have assumed the cells are arranged on top of one another and hence are optically connected in series. However, it recently has been shown that even higher efficiencies can be achieved by splitting the incoming solar energy into separate bands of a narrower spectral distribution. In doing this, each band of light can be optimally collected with a different solar cell thereby avoiding thermalization losses [29]. Such a design has many advantages over traditional multi-junction cells in that each solar cell does not have to be current matched and hence all the cells can all operate at their optimal efficiency. This also is advantageous in terrestrial applications as fluctuations in the incoming solar spectrum that occur throughout the day can limit the performance of series connected cells. However, the cost of the spectral splitting structure would likely be very high as each cell would be grown on a separate substrate.

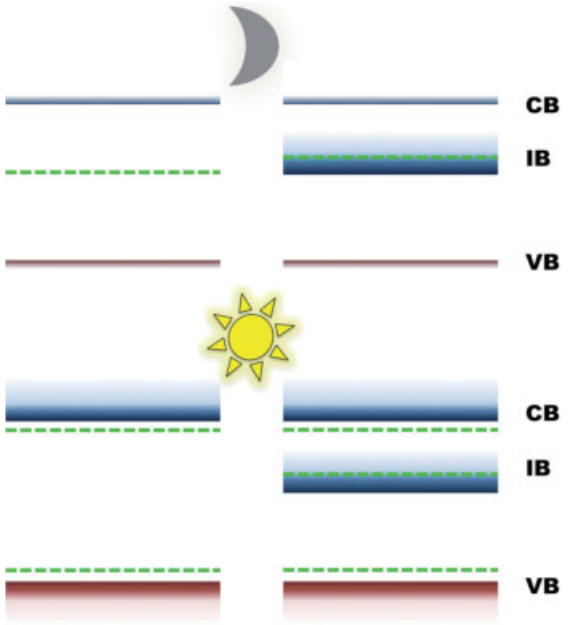

Figure 4 (online color at: www.lpr-journal.org) (Top) Under equilibrium conditions, the Fermi level of a regular semiconductor is fixed by the doping level. In an intermediate band structure, the doping level is arranged such that the Fermi level lies within the intermediate band. (Bottom) Under illumination, a regular semiconductor can be described by two quasi-Fermi levels, which govern the electron and hole distributions. The maximum obtainable open-circuit voltage in this case is the separation between the quasi-Fermi levels. In the intermediate-band case, three quasi-Fermi levels are needed to describe the electron and hole distributions [30]. One level describes the population of holes in the VB, another the population of electrons and holes in the IB and a third describing the electrons in the CB. The maximum open-circuit voltage in this case is approximately the same as for the regular semiconductor. However, the photocurrent obtained in the intermediate band solar cell is higher due to the additional energy level allowing sub-bandgap absorption.

Intermediate-band cells

The concept of using multiple bandgaps to improve efficiencies is not only limited to multi-junction solar cells. Intermediate-band (IB) solar cells are a fascinating new way to improve the overall efficiency of solar cells with only one junction. The basic concept in these cells is that a narrow density of states within the bandgap of a semiconductor can allow sub-bandgap absorption while maintaining the same open-circuit voltage. The key is to have multiple quasi-Fermi levels present with the same system as shown in Fig. 4 [30–32]. Three different absorption processes are available in such a system: Valence Band (VB) → IB, IB → Conduction Band (CB) and VB → CB. These three absorption processes allow the creation of three quasi-Fermi levels corresponding to the population of holes in the VB, electrons/holes in the IB and electrons in the CB.

The first experimental basis for these cells came from introducing impurities into Silicon to extend the sub-bandgap response of these cells and increase efficiencies [33, 34]. However, this approach was expected to achieve modest efficiency improvements at best [30] and the focus switched to using quantum dots [QDs] to form the intermediate band [35, 36].

Fig. 5 illustrates the basic concepts of such a structure. The QDs have a lower bandgap than the barrier regions and as a result of quantum confinement, the QDs form discrete energy levels. Due to the periodic arrangement and close proximity of the QDs, the discrete energy levels overlap and form mini-bands allowing for sub-bandgap absorption.

One important requirement for the operation of IB solar cells is the IB Fermi level must reside within the IB [37, 38]. This allows sufficient numbers of electrons in the IB to be promoted into the CB. It is also beneficial to have no overlap in the absorption coefficients between the three transitions [39]. If this is not the case, high energy photons that should transfer electrons between the VB and CB could be absorbed in a VB → IB transition, losing some of the

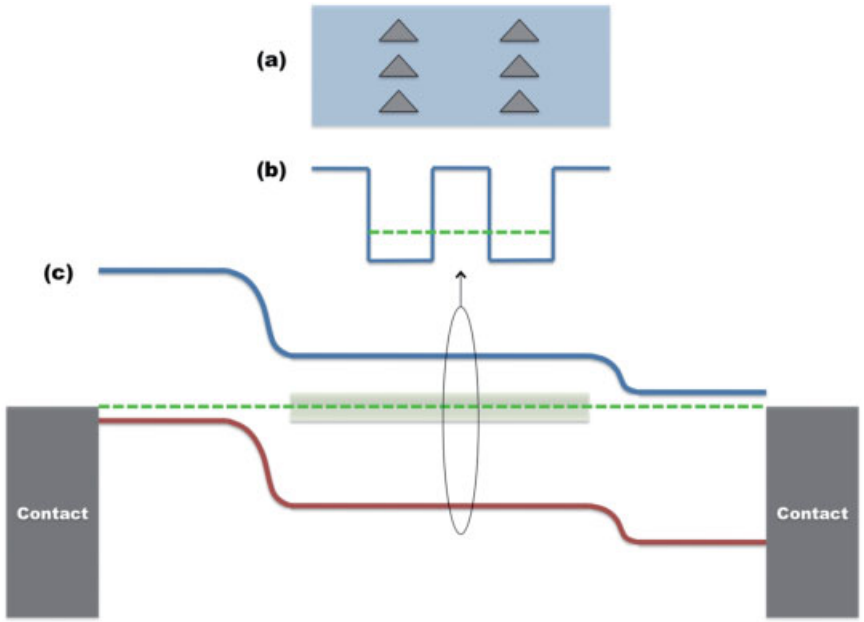

Figure 5 (online color at: www.lpr-journal.org) (a) Periodic arrangements of quantum dots lead to the formation of mini-bands as seen in (b) [35]. The mini-band acts as the IB and allows the promotion of electrons from the quantum dot to the barrier material via photons. (c) The quantum dots are placed in-between a p- and n-type barrier layer. The p- and n-type layers provide the space charge for the solar cell. In this setup, no current is directly collected from the IB; rather, electrons must be promoted from the IB to the CB for collection. Intermediate-band solar cells are not expected to be as sensitive to solar spectral fluctuations compared to traditional multi-junction cells.

energy in a similar way that a traditional single-junction cell experiences blue losses.

Test cells have been fabricated using GaAs layers with imbedded InAs QDs [40, 41] and GaSb QDs [42]. In both cases, sub-bandgap photo-response has been detected indicating the QDs are indeed contributing to the photocurrent of the cells [43]. All experimental cells of this kind shown to date exhibit lower overall efficiencies than cells fabricated with no QDs, due to lower open circuit voltages. However, the experiments do suggest it is possible to have three separate quasi-Fermi levels. The lower open circuit voltage is attributed to non-radiative recombination between the CB and VB suggesting that current growth techniques introduce defects lowering the efficiency of these cells. The presence of the IB itself does not appear to increase non-radiative recombination. This is important if these devices are to increase the efficiency beyond conventional single-junction cells [44, 45].

One of the biggest problems with using QDs as IB solar cells is the QDs are very small and therefore do not absorb much light. Therefore, in order to have enough QDs to significantly improve the photocurrent, it is necessary to have several layers of QDs. Unfortunately, the growth of multiple layers of QDs results in additional structural damage, which degrades performance. In one case, it was shown that the expansion from 10 QD layers to 20 and 50 layers resulted in much lower efficiencies [46]. The lower efficiencies have been attributed to the creation of threading dislocations from the QDs in the intrinsic region [47]. The origin of these dislocations is the lattice mismatch between the QDs and buffer material. However, the addition of strain compensating layers between each QD layer has been shown to improve performance and even increase the short circuit current of QD IB solar cells above test cells with no QD layers [48, 49]. Strain compensation layers are able to reduce the density of dislocations by counterbalancing the compressive strain between InAs and GaAs with tensile strain from InAs and GaP. Unfortunately, even in these cells, the efficiency is lower due to a decreased open circuit voltage.

QDs are not the only method of making IB solar cells. Recently, a new class of materials—known as Highly Mismatched Alloys (HMA)—has been developed at Lawrence Berkeley National Laboratory. Typically the material properties of semiconductor alloys are predicted by a linear interpolation between their endpoints with a bowing parameter to correct for deviations [50]. However, when there are large electronegativity differences between the endpoint semiconductors, this approach is no longer valid and large deviations of properties emerge [51]. These effects have been observed in several III-V and II-VI alloys and can be described by a band anti-crossing model [51–54].

In the band anti-crossing model, localized substitutional impurity states interact with the extended band states of a host semiconductor. When the localized level lies near the CB or VB of the host semiconductor, the extent of the interaction is increased and the CB splits into two sub-bands with the lower band maintaining some of the character of the original impurity states. This leads to a sub-band with a narrow density of states. When the impurity states lie below the CB, a gap in the density of states forms between the two conduction subbands. The lower CB effectively becomes an IB.

This IB has so far been observed in $GaN_xAs_{1-y}P_y$ and $Zn_{1-y}Mn_yTe_xO_{1-x}$ [54, 55]. Fig. 6 shows schematically the band structure of $Zn_{0.88}Mn_{0.12}Te_{0.01}O_{0.99}$ where three distinct optical transitions are available: VB→CB (2.56 eV), VB→IB (1.83 eV) and IB→CB (0.73 eV). Even with this non-optimal bandgap configuration, efficiencies of 45% may be possible. Alloys of $GaN_xAs_{1-y}P_y$ are predicted to

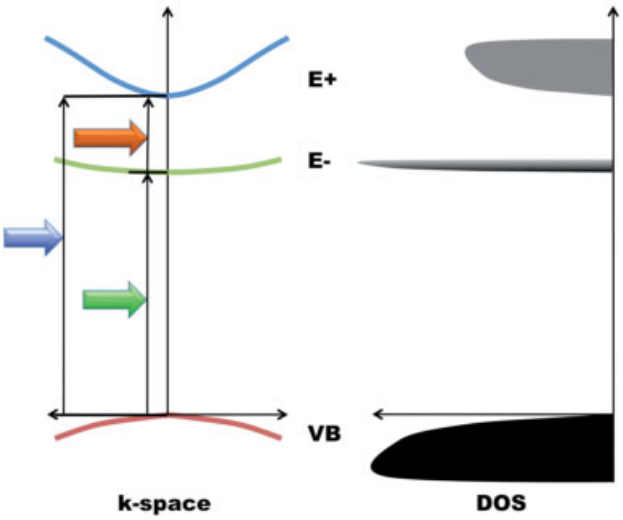

Figure 6 (online color at: www.lpr-journal.org) (Left) Example band structure of a highly-mismatched alloy such as ZnMnTeO [53]. The oxygen in the alloy interacts with the CB of the host material splitting it into E- and E+ bands. At certain compositions, the E- and E+ are separated by a bandgap giving rise to an intermediate band. (Right) The density of states for this alloy shows a narrow distribution of electronic states in the intermediate band. These highly-mismatched alloys potentially could function both as IB solar cells and as the selective energy contacts in hot carrier cells.

have even greater efficiencies of 55–60% [55]. It is also predicted that some AlGaAsN alloys will feature an IB and high quality samples have already been grown using molecular beam expitaxy (MBE) [56].

One advantage of using HMAs over QDs is that the density of states in the IB band is high, indicating that a relatively thin layer of HMA would be sufficient to absorb all the incoming photons with appropriate energies. Another advantage to these alloys is that the Fermi level is believed to already lie within the IB making all three absorption events highly probable with no additional doping. However, given these alloys are a very recent discovery, no working devices using the IB have been created.

In addition to QDs and HMAs, there have been focused efforts in exploring alloys that may feature an IB using computational techniques. Certain alloys such as Ga_3P_4Ti [57, 58] are expected to feature IBs. It is also predicted that $CuGaS_2$ [59] can form an IB if transition metal impurities are added in which the impurity levels are located in the bandgap. If enough of the impurities are added, the wavefunctions associated with the impurities will delocalize and form an IB [45].

Another approach to improving the sub-bandgap photon collection in solar cells is by introducing quantum wells (QWs) of a lower bandgap. The concept was originally proposed 1990 [60] and since then experimental efficiency gains have been achieved [61]. The idea is similar to that of QDs where the QWs can absorb lower energy photons creating electron-hole pairs (EHPs) contributing to the photocurrent.

To employ this technique, a P-I-N structure is created with QWs imbedded in the intrinsic region. In this structure, an electric field exists across the intrinsic region allowing the EHPs to hop out of the QW. Some of the first QW solar cells where made of AlGaAs with GaAs QWs imbedded [62]. Since then, the focus has switched to GaAs/InGaAs structures. However, InGaAs is not lattice matched to GaAs so it was found that growing GaAsP layers allowed for strain compensation and an improvement in photocurrent while maintaining a low density of dislocations [63, 64]. Further improvements were made by introducing Bragg reflectors (alternating layers of high and low indexes of refraction) at the back of the solar cell to increase the probability of absorbing below gap photons [65]. These improvements have resulted in efficiencies above 26% under 200× concentration [61].

While experimental efficiency gains have been found, it is still unclear whether these QW solar cells can improve efficiencies beyond the Shockley-Queisser single junction limit. Thermodynamic treatments of these devices by Luque, Marti and Cuadra [66] have shown that QW solar cells cannot improve upon this limit unless the EHPs in the QW absorb low energy photons to escape out of the wells. In this way the QW devices are just a form of IB solar cells. The probability of such an absorption event is considered very unlikely and therefore this would practically limit these cells to below the Shockley-Queisser limit. However, Mazzer and others have shown electrons can leave the QW without photon absorption and credit this to hot carrier transport [61]. Anderson provides a good review of the controversy [67].

Regardless of whether these devices can achieve efficiencies surpassing the Shockley-Queisser limit, there is little doubt that they can have practical benefits. One of the main benefits is these devices allow for bandgap engineering in multi-junction solar cells while maintaining lattice matching conditions. Triple junction cells made of InGaP/GaAs/Ge could be improved by adding QWs to the GaAs layer creating a more efficient arrangement of bandgaps [7].

Hot carrier cells

The concept of using multiple energy levels to increase the efficiency of solar cells has shown real improvements over standard solar cells. However, it is not absolutely necessary to introduce multiple energy levels to increase efficiencies beyond the Shockley-Queisser single junction limit. In 1982 it was recognized that it could be possible to increase solar cell efficiencies for a single junction by utilizing hot carriers [68].

The concept of hot carriers is shown in Fig. 7. In all solar cells, an incoming photon with energy in excess of the bandgap produces an EHP where the total energy is greater than the bandgap. The electrons and holes will

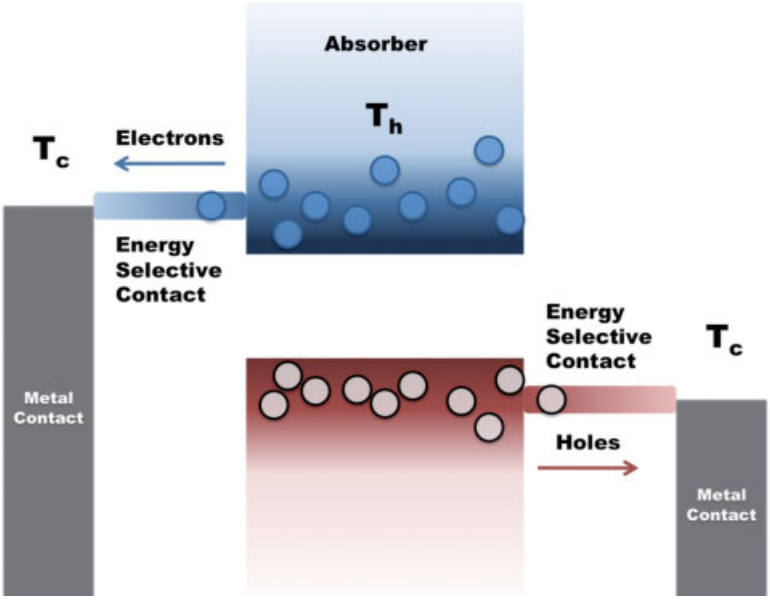

Figure 7 (online color at: www.lpr-journal.org) A schematic showing the operating principle behind hot carrier cells [78]. The photogenerated carriers in the absorber region do not thermalize with the lattice and a carrier temperature much higher than 300 K can describe their distribution. Electrons are extracted out of the CB by an energy selective contact (ESC). This contact has a narrow distribution of states that only allow electrons over a narrow range of energies to leave the system. As carriers are extracted, the electrons in the CB interact with one another and the incident photons to maintain their Fermi distribution and overall temperature T_h. Through the narrow-band ESC, electrons in the absorber cool iso-entropically to the lattice temperature (T_c) in the metal contact, thereby allowing conversion efficiencies closer to the Carnot efficiency ($1 - T_c/T_h$). The same idea applies to holes leaving through their ESC.

first interact with other electrons and holes through carrier-carrier interactions to form carrier populations that can be described by a Boltzmann distribution. At this point, the temperature defining the carrier distribution is above the lattice temperature and hence the carriers are referred to as hot carriers. Typically the additional energy associated with the elevated temperature is contained by the electron due to its lower effective mass [69]. In a typical solar cell, the hot electrons will give off their excess energy to the lattice by producing optical phonons [70]. These optical phonons then interact with other phonons and the energy in excess of the bandgap is lost. In most bulk semiconductors, all of this happens in less than 0.5 picoseconds [71].

It is also possible for the electrons to be separated and collected by contacts before thermalization occurs. However, this is not observed in typical solar cells due to the very fast thermalization times. There are many instances where the thermalization times are much larger than 0.5 picoseconds as was first proposed for semiconductor/electrolyte interfaces [72].

While it at first seems somewhat obvious that preventing carriers from thermalizing would decrease the energy lost, it is not as clear how hot carriers increase efficiencies. There are actually two different possibilities for increasing solar cell efficiencies: hot-carrier extraction and multiple exciton generation (MEG). Both concepts take advantage of slowed carrier cooling phenomena but in different ways.

Theoretical treatments of the hot carrier extraction [68, 73] have shown that efficiencies exceeding 80% are possible under fully concentrated sunlight. However, it is not easy to separate hot electrons and holes to different contacts. The entire concept behind maintaining hot carrier populations is a minimization of electron-phonon interactions. In the presence of a metal contact, it would be very easy for the hot carriers to cool to the lattice temperature through the large number of available electronic states.

Therefore, in order for hot carriers to create an efficiency increases over traditional cells it is necessary to extract the carriers through an energy selective contact (ESC) as seen in Fig. 7. These contacts would only allow carriers at a certain energy to leave the absorbing material. Once the carriers enter the contact, the carriers will cool to the lattice temperature in the metal contact. In thermodynamics this is referred to as an iso-entropic process where a maximal efficiency called the Carnot efficiency is achieved. The energy that would normally be lost to entropy is instead available for additional work.

The other possibility for increasing efficiency is through MEG [74, 75]. In this case, the excess energy of the hot electrons is used to create additional excitons, i.e, bound electron-hole pairs. The hot electron must have the energy of at least two times the bandgap to create one additional EHP, as shown in Fig. 8. This process is explained as impact ionization, which is the opposite of the Auger process, wherein the energy of one photogenerated electron is transferred to another electron. This process is not only limited to electrons with energy of twice the bandgap, but it can also be extended to any higher energies. Under 1 sun AM1.5 spectrum the theoretical efficiency of a MEG-enhanced cell is over 44%, while under maximum sunlight concentration, the efficiency can approach that of hot carrier cells [1, 76]. MEG does occur in bulk semiconductors [77]. However, the probability of this event is so low in the bulk that it does not contribute much to the efficiency of the cells [78].

As mentioned before, there are cases where hot carrier lifetimes exceed the bulk lifetimes of less than a picosecond. This phenomenon is expected to occur in many quantum systems [79]. First, multiple-quantum wells were studied and found to have hot carrier lifetimes much larger than bulk values although only at high illumination levels [80–83]. Hot carrier lifetimes in the hundreds of picoseconds have been observed in multiple-quantum well structures. This increase has been attributed to the hot-

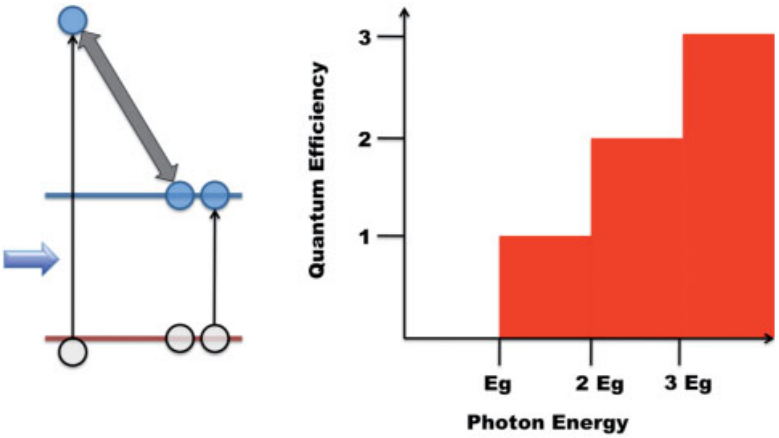

Figure 8 (online color at: www.lpr-journal.org) (Left) The absorption of a photon with an energy over 2 times the bandgap can lead to multiple excitons generation (MEG) [77]. This process is explained as impact ionization and is the opposite of Auger recombination. (Right) MEG is not limited to photons only twice the bandgap. Theoretically, any number of excitons can be formed from one incoming photon provided the energy of the photon is greater than the summation of all the excitons. This can lead to a step like function where the internal quantum efficiency jumps at integer multiples of the bandgap.

phonon bottleneck effect in quantum wells [84, 85]. Hot electrons cool through interactions with optical phonons and at high enough illumination levels a non-equilibrium level of optical phonons are created. Due to the confined nature of the QW, these optical phonons cannot equilibrate with the lattice fast enough thereby slowing the further cooling of hot electrons.

These effects in QWs are not typically observed without high photo-carrier densities, which are not easily achievable through sunlight illumination. For this reason, the QWs are not good candidates for MEG-enhanced solar cells [7]. Therefore, attention has shifted to QDs where increased hot carrier lifetimes are expected to exist under all illuminations. This effect is simply referred to as the phonon bottleneck effect where the 'hot' term no longer applies. In the case of a QD, the electrons are confined in all three dimensions leading to the formation of discrete energy levels. If the spacing between energy levels is greater than the optical phonon energy, hot electrons cannot thermalize without multiple-phonon processes, which are less likely than single-phonon processes. Therefore it is expected that hot carrier lifetimes will increase substantially in QDs.

There is experimental evidence of slowed cooling in QDs [86, 87] where hot electrons exhibited lifetimes from a few picoseconds all the way up to nanoseconds [88]. The hot carrier cooling was found to be greatly affected by the presence of nearby holes. In the case of an exciton in the core of a QD, no reduction in the cooling rate was observed. However, in some QDs it was found that the photogenerated holes are captured by surface states thereby physically separating the electron and hole and increasing the hot carrier lifetimes.

The presence of a hole near the hot electron in a QD greatly increases the thermalization rate. This effect is described as an Auger-like mechanism that effectively breaks the phonon bottleneck [89]. This Auger-like mechanism can be on the order of femtoseconds [90]. Experimentally it has been shown that by changing the nature of QD surface states by adding surface caps, the hot carrier lifetime can increase by orders of magnitude [91, 92].

As a result of the slowed cooling in QDs, it has been shown that MEG processes can be extremely efficient thereby offering great potential to increase solar cell efficiencies [93]. PbSe and PbS QDs have been shown to have quantum yields (EHPs per photon) above 300% [94] and even above 700% [95]. The effect has been observed in numerous other QDs including InAs [96] and Si [97].

Recently it was also shown that not only does MEG occur in QDs but it is possible to extract the excess carriers from the QDs. In one case an electrical bias was used to extract the carriers from PbSe QDs [98] and in another a polymer solar cell tandem device was used to extract carriers [99]. Still, there has been no demonstration of a performance increase in solar cells taking advantage of MEG in QDs.

While experimental evidence for using QDs to generate MEG exists, directly extracting hot carriers through a selective energy contact has not been demonstrated. In fact it is not even known how to prove electrons are being extracted mono-energetically although there is some evidence suggesting it can be done.

The structure of a selective energy contact is shown in Fig. 7. The principal requirement for such a contact is a narrow density of states with a large bandgap between the next available states. However, a narrow density of states also yields extremely low electron mobilities and therefore there must be some compromise between the narrowness of the density of states and maintaining high enough conductivities.

Originally it was proposed that a wide bandgap semiconductor with an impurity band would satisfy this requirement [73]. It is believed that a periodic distribution of defects in a wide bandgap semiconductor could allow for resonant tunneling over a narrow energy range thereby satisfying the requirements of a selective energy contact [100].

Another possibility is the use of a periodic arrangement of QDs which could form minibands of discrete energies [101]. To achieve this, Si QDs have been made imbedded in a SiO_2 matrix. I-V measurements through these QDs have shown negative differential resistance at room temperature indicating electrons have a peaked transmission through the QDs at a particular energy. While this does not prove that the QD superlattice is a proper selective energy contact, it is a good indication that the concept is possible.

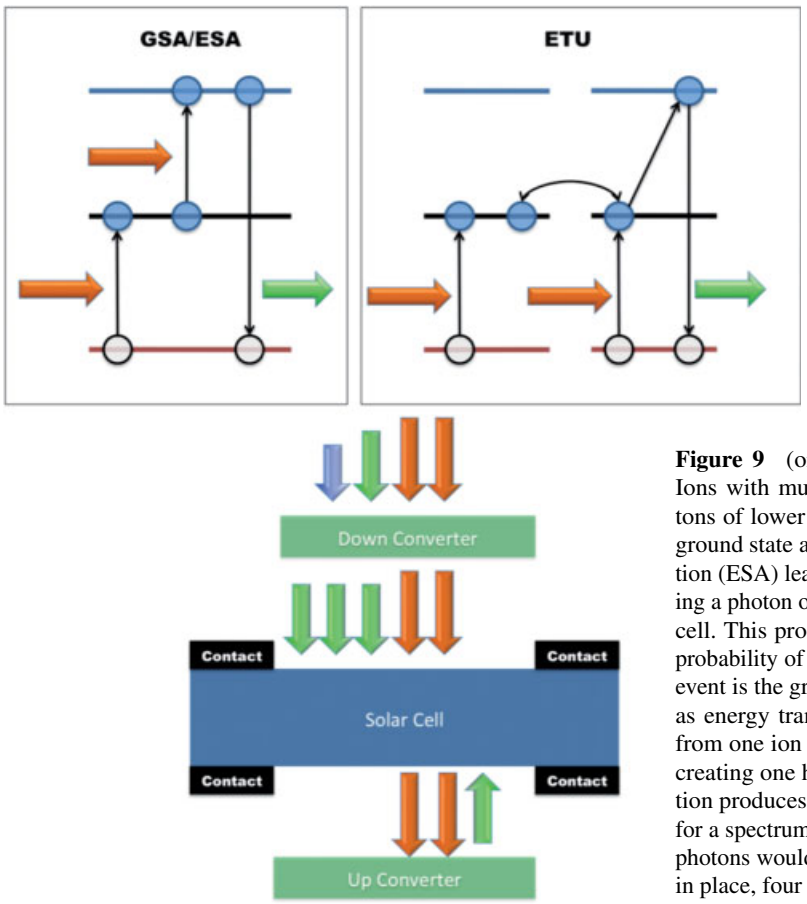

Figure 9 (online color at: www.lpr-journal.org) (Top Left) Ions with multiple discrete energy levels can up-convert photons of lower energy to higher energies [105]. In the first case, ground state absorption (GSA) followed by excited state absorption (ESA) leads to an electron hole recombination event producing a photon of higher energy which can then be passed to a solar cell. This process is relatively unlikely, though, due to the low probability of excited state absorption. (Top Right) A more likely event is the ground state absorption of two adjacent ions, known as energy transfer up-conversion (ETU). The excited electron from one ion can transfer to the excited electron in another ion creating one higher energy electron, which through recombination produces a high energy photon. (Bottom) Sample structure for a spectrum conversion solar cell. Without converters only two photons would be absorbed by the solar cell. With the converters in place, four photons are absorbed.

The HMAs being studied for intermediate-band solar cells could function as energy selective contacts as well [54, 55]. The narrow intermediate band in these alloys can be engineered to different energies therefore offering some flexibility for the bandgap between the IB and CB. The spacing between the mono-energetic band and the next highest band is a crucial point as it is not known how the higher energy bands would affect the hot electron distribution in the absorber material.

Furthermore, InN has shown hot carrier lifetimes much longer than other bulk materials [102]. This effect has been attributed to a large mass difference between the cation and anion in InN which leads to a gap in phonon band structure [103]. This gap makes the decay of optical phonons into acoustic phonons more difficult thereby creating a hot-phonon bottleneck similar to that in quantum well structures.

One issue that will need to be addressed before hot carrier solar cells are produced is the geometry of the cell. Even with the improved hot carrier lifetimes in quantum systems, the distance the hot carriers can travel before cooling is likely to be very short. Therefore it may be necessary to design the cell in such a way that all the EHPs are generated very close to the energy selective contacts to ensure the carriers do not cool before being collected. Therefore, very short absorber regions or convoluted surfaces areas may be required to minimize the distance the hot electrons travel [1].

Spectrum conversion

The final approach, considered by this review paper, to achieve higher solar cell efficiencies is to convert the sun's polychromatic spectrum to a spectrum more suitable for the solar cell. In this way, sub-bandgap photons can be raised above the bandgap in a process called up-conversion (UC) or above-bandgap photons can reduced to multiple lower energy photons in a process called down-conversion (DC). Using one or both of these processes can increase the current collected in a solar cell. One of the unique advantages of this concept is since only the incoming solar spectrum is modified, it is compatible with many existing solar technologies [104].

A schematic representation of the two UC processes most frequently discussed for solar cells is shown in Fig. 9. In the first case two lower energy photons are converted to a higher energy photon through two subsequent absorption events. This process is called ground state absorption/excited state absorption (GSA/ESA). In the other case, the absorption events happen between separate ions where one ion non-radiatively transfers its energy

to its neighbor. This process is called energy transfer upconversion (ETU) [105]. An in-depth analysis of the concept and applicable materials has been previously reported with the conclusion that ETU mechanisms show the most promise [106].

The UC process has been experimentally demonstrated using a substrate free GaAs solar cell on top of a vitroceramic doped with Yb^{3+} and Er^{3+} [107]. A substrate free solar cell is necessary for UC, otherwise the substrate or contacts on the back of the cell would simply absorb all the incoming below bandgap radiation. Unfortunately, the efficiency improvements obtained were low as the emission of above gap photons from this device scaled quadratically with respect to incoming below gap photons.

Attempts have since been made to improve the efficiency of these devices. Richards has demonstrated a bifacial silicon solar cell with a back coating of Erbium doped Sodium Yttrium Fluoride that has sensitivity in the 1480–1580 nm range [108]. While relatively high external quantum efficiencies could be feasible for this design, only about 2% of the solar spectrum is in this range.

In a similar vein, it has been proposed that the efficiency of solar cells can be improved by adding a layer in front of the cell that down-converts one high energy photon into two above-bandgap photons [109]. However, in order for this design to show large increases in efficiency, it is necessary to obtain external quantum efficiencies above 100% (at least one outgoing photon for each incoming photon). Some doped phosphors have shown internal quantum efficiencies close to 200% [110]. However, the addition of a material on the front of solar cells would likely change the index of refraction thereby increasing reflection losses. Given this, it will likely be difficult for these types of devices to show efficiency gains [111, 112].

Conclusion

Many different concepts are being attempted to surpass the Shockley-Queisser limit. Multi-junction solar cells already have produced efficiencies over 40% and are commercially produced. The major hold-up for increasing production of these cells is their prohibitive costs. However, new technologies combined with concentration technology may overcome this issue. Intermediate-band solar cells and hot carrier cells promise similar efficiency improvements and even lower costs than multi-junction cells. However, no cells have to this date exhibited efficiencies surpassing the Shockley-Queisser efficiency limit. Finally, spectrum conversion technologies offer a simple method of improving efficiencies that is compatible with existing solar cell technologies.

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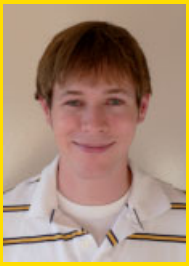

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