Third-generation photovoltaics

Third-generation approaches to photovoltaics (PVs) aim to achieve high-efficiency devices but still use thin-film, second-generation deposition methods. The concept is to do this with only a small increase in areal costs and hence reduce the cost per Watt peak[1] (this metric is the most widely used in the PV industry). Also, in common with Si-based, second-generation, thin-film technologies, these will use materials that are both nontoxic and not limited in abundance. Thus, these third-generation technologies will be compatible with large-scale implementation of PVs. The approach differs from first-generation fabrication of high-quality, low-defect, single-crystal PV devices that have high efficiencies approaching the limiting efficiencies for single-bandgap devices but use energy- and time-intensive techniques.

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Third-generation approaches to PVs aim to decrease costs to well below the $1/W level of second-generation PVs to $0.50/W, potentially to $0.20/W or better, by significantly increasing efficiencies but maintaining the economic and environmental cost advantages of thin-film deposition techniques (Fig. 1 shows the three PV generations)[1]. Increasing efficiency strongly leverages lower costs because the smaller area required for a given power also reduces balance-of-systems costs, such that efficiency values well above 30% could dramatically decrease these costs per Watt. To achieve such efficiency improvements, devices aim to circumvent the Shockley-Queisser limit for single-bandgap devices that limits efficiencies to either 31% or 41%, depending on concentration ratio (Fig. 1). This requires multiple energy threshold devices. There are several approaches to achieve such multiple energy threshold devices[1,2].

The two most important power-loss mechanisms in single-bandgap cells are the inability to absorb photons with energy less than the bandgap (1 in Fig. 2) and thermalization of photon energies exceeding the bandgap (2 in Fig. 2). These two mechanisms alone amount to the loss of about half of the incident solar energy in solar cell conversion to electricity. Multiple threshold approaches can in principle utilize this otherwise lost energy. Such approaches do not in
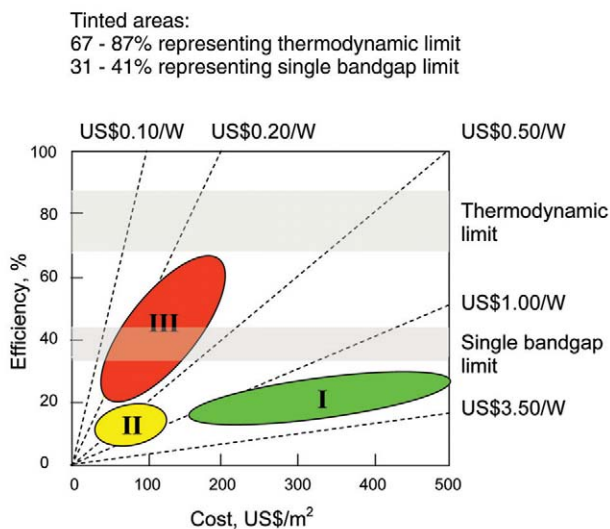
Fig. 1 Efficiency and cost projections for first- (I), second- (II), and third-generation (III) PV technologies (wafer-based, thin films, and advanced thin films, respectively).
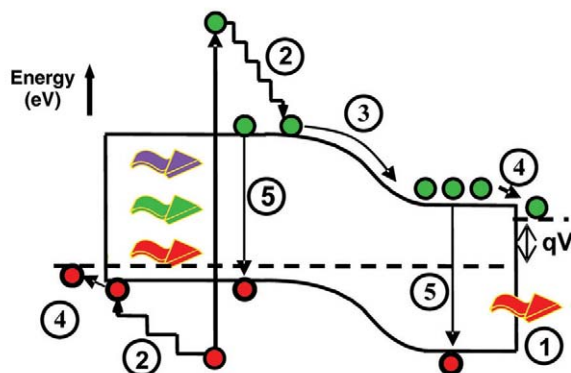

Fig. 2 Loss processes in a standard solar cell: (1) nonabsorption of below-bandgap photons; (2) lattice thermalization loss; (3) and (4) junction and contact voltage losses; (5) recombination loss (radiative recombination is unavoidable).

fact disprove the validity of the Schockley-Queisser limit, rather they avoid it by the exploitation of more than one energy level – in some form – for which the limit does not apply. The limit that does apply is the thermodynamic one, shown in Fig. 1, of 67% or 86.8% (again depending on concentration).

Three families of approaches have been proposed for applying multiple energy levels[2]: (a) increasing the number of energy levels; (b) multiple carrier pair generation per high energy photon *or* single carrier pair generation with multiple low energy photons; and (c) capturing carriers before thermalization. Of these, tandem cells, an implementation of strategy (a), are the only ones that have, as yet, been realized with efficiencies exceeding the Shockley-Queisser limit.

In order to decide which of the many possible approaches are equivalent and which offer genuine fundamental advantages, the approach of detailed particle balance is used to calculate the maximum

possible, or limiting efficiency of a given device. This was first applied to PVs by Shockley and Queisser[3], and is used by many authors to model solar cells. According to this analysis, the number of electrons flowing from an ideal solar cell through an external circuit is equal to the difference between the number of photons absorbed over the energy range E_l to E_h and the number of photons the device emits over the same energy range. The formulation is not detailed here but uses the Planck equation for the spectrum of light received from the sun and a modified Planck equation for the light emitted by the cell, the latter exponentially enhanced by the forward bias of the cell, just as for a light-emitting diode[1,4–6]. The approach is an ideal limiting efficiency one that assumes zero contact resistance and junction losses, infinite mobility, and 100% luminescent efficiency.

The approach predicts ideal current density versus voltage, or *J–V*, characteristics. This way of describing the generation process is more fundamental and is equivalent to the more usual ideal diode equation description, but is easier to understand as it is just the balance of particles into and out of the cell[1]. It gives limiting efficiencies of 31.0% and 40.8% for unconcentrated and maximally concentrated light, respectively, for an optimized bandgap of 1.3 eV and 1.1 eV, respectively (see section on tandem cells below), as first calculated by Shockley and Queisser[3]. For Si and GaAs bandgaps of 1.12 eV and 1.45 eV, respectively, the limiting efficiencies are both ~29% for unconcentrated light. Thus, the record efficiencies in each case of 24.7%[7] and 25.1%[8] at one-sun illumination indicate devices approaching the radiative limit.

Another advantage of the particle balance approach is that it can compare different types of solar cell. The high and low energy limits (E_h and E_l) can be modified to allow for the particular absorption range of the specific energy threshold. The detail of this can determine whether the device neatly splits the spectrum into separate segments, as in a tandem solar cell, or has overlapping energy thresholds competing for photons, as in an intermediate energy level device. The detail of the way the terms are added describes whether the device has the same current through each element – series connection – and is sensitive to the particular spectrum (as in a tandem cell), or whether the device has different currents through the elements – parallel connection – as in some of the other devices described below. (Such parallel connections would also require appropriate voltage matching. This is approached differently in the various devices described.)

Multiple energy level approaches

The concept of using multiple energy levels to absorb different sections of the solar spectrum can be applied in many different device structures. The ideal limiting efficiencies for these are often identical for a given number of energy levels. Hence their differences are manifest in the degree to which each overcomes nonidealities. This includes any inability of a particular cell design to select photon absorption at its optimum energy level in the cell, the presence of

parasitic processes (usually associated with defects), and the ease of manufacture and the abundance of appropriate materials.

Tandem or multicolor cells

The tandem or multicolor cell is conceptually the easiest configuration to understand. It belongs to strategy (a) of increasing the number of energy levels. Solar cells consisting of *p-n* junctions in different semiconductor materials of increasing bandgap are placed on top of each other, such that the highest bandgap intercepts the sunlight first (Fig. 3).

The elegance of the approach – first suggested by Jackson[9] in 1955 – is that both spectrum splitting and photon selectivity are automatically achieved by the stacking arrangement. This complementarity makes the approach difficult, if not impossible, to beat for an ideal device. To achieve the highest efficiency from the overall tandem device, the power from each cell in the stack must be optimized. This is done by choosing appropriate bandgaps, thicknesses, junction depths, and doping characteristics, such that the incident solar spectrum is split between the cells most effectively. The next requirement is to extract electrical power from the device most effectively. Two configurations are used: either a 'mechanically stacked' cell, in which each cell in the stack is treated as a separate device with two terminals for each; or an 'in-series' cell with each cell in the stack connected in series, such that the overall cell has just two terminals on the front and back of the whole stack. For a fixed solar spectrum and an optimal design, these two configurations give the same efficiency. But for a real, variable spectrum, the mechanically stacked design gives greater flexibility because of the ability to optimize the *I-V* curve of each cell externally and then connect them in an external circuit. The reduced flexibility of just optimizing the *I-V* curve for the whole stack, because the same current must flow through each cell, makes the in-series design more sensitive to spectral variations. Furthermore, they become increasingly spectrally sensitive as the number of bandgaps increases. For space-based cells this is not a great problem because of the constant spectrum, but for cells designed for terrestrial use, it is significant because of the variability of the terrestrial solar spectrum. This is particularly the case at the beginning and end of the day when the spectrum is significantly red-shifted by the thickness of the atmosphere. Nonetheless, the much greater ease of fabrication of in-series devices makes them the design of choice for most current devices.

The particle balance limiting efficiency depends on the number of subcells in the device. For 1, 2, 3, 4, and ∞ subcells, the efficiency η is 31.0%, 42.5%, 48.6%, 52.5%, and 68.2% for unconcentrated light, and 40.8%, 55.5%, 63.2%, 67.9%, and 86.8% for maximally concentrated light. Hence, the efficiency increases with the number of subcells in both cases, but the efficiency gain decreases with each subsequent subcell[1,4,10].

III-V tandems

The highest quality, and hence highest efficiency, tandem devices are made using single-crystal III-V materials. These are grown monolithically by epitaxial processes such as metal organic vapor phase epitaxy (MOVPE). Epitaxial techniques are very expensive but give very high quality crystalline material. Epitaxial growth requires control of the lattice parameter at a constant value; and bandgap control is also required for a tandem cell. It is the flexibility of the III-V group of compounds that lends it to the growth of such cells, usually lattice matched on a Ge substrate. This requires most devices to be based on the AlAs/GaAs system, which has a lattice parameter close enough to that of Ge at 5.66 Å to avoid dislocations. Nonetheless, the twin requirements of lattice parameter and bandgap control mean that
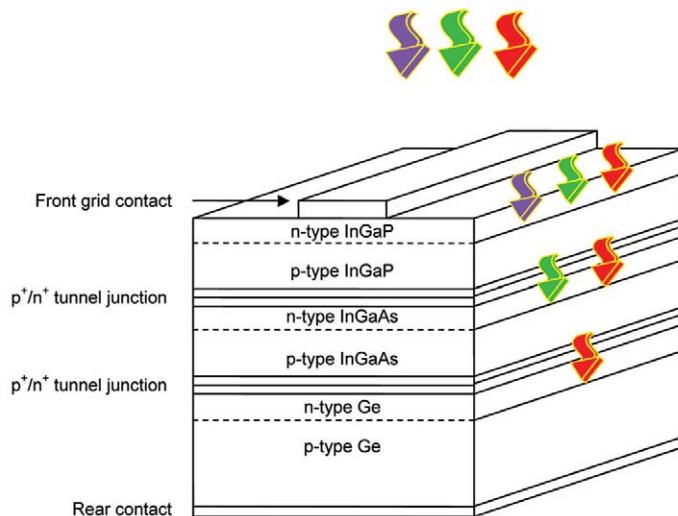

Fig. 3 A simplified schematic of a three-bandgap tandem solar cell. The bandgap of each cell decreases from the front to the back, giving both spectrum splitting and photon selectivity.

ternary (or even quaternary) compounds are required for a three cell stack (e.g. GaInP/GaAs/GaInAs cells[11,12]).

Other researchers are investigating the InN/GaN/AlN system. These three compounds have a nearly constant lattice parameter at ~3.2 Å and a bandgap range easily covering that of interest[13,14]. Another approach, which is proving to be very successful, is to avoid the requirement for strict lattice matching by growing a partially strained stack of cells approximately lattice matched to Ge. Such 'metamorphic' cells do have higher defect concentrations, but this is offset by the increased flexibility in bandgap design – the current world record efficiency for any PV device is held by just such a GaInP/GaInAs/Ge metamorphic device at 40.7% under 240 suns[15], the first device to exceed 40%. These efficiency values are significant fractions of the limiting efficiencies, indicating very high radiative efficiencies.

The next stage is to move onto four- or even five-bandgap cells. These not only have potentially higher efficiencies but also have higher voltage and lower current than three-bandgap cells. This means that series resistance losses are lower, an important consideration for concentrator cells[16].

Concentrator systems

The expense of the growth techniques and of the compounds used means that such devices are usually designed for use in optical concentrator systems operating at a few hundred suns. This means that only a small area of the very efficient but also very expensive cell material is required at the optical focus of a relatively cheap concentrator. Potentially, this can bring the cost per Watt of electricity generated down to low levels[16]. Concentration also gives the higher limiting efficiencies mentioned above because the sun effectively fills all of the sky as far as the cell is concerned. This in turn means that photons emitted by the cell must be emitted towards the sun. Hence, the solid angle over which the cell must accept light is the same as that over which it emits photons, giving the least possible loss. Furthermore, tandems are well suited to concentrator systems because as the number of cells in the stack increases, the voltage-to-current ratio increases, thus decreasing resistive losses in the high current densities of concentrator cells[15]. However, concentrators require direct sunlight and hence do not work with an overcast sky, unlike flat-plate cell modules. They also make the overall system more complex and less modular. Hence, they tend to be more appropriate for large-scale systems located in inland areas where cloud cover is low. Nonetheless, another important advantage for tandem devices is that concentrator systems work best if optimized for operation in the middle of the day when sunlight is strongest. Over this period, the spectrum is least variable and hence spectral sensitivity is less significant.

Thin-film tandems

An alternative approach to reducing the cost per Watt is to use material that is not of as high a quality as epitaxial III-V materials and hence has a higher defect density and lower efficiency, but which can be produced by much cheaper, low-energy intensity deposition methods and uses elements and compounds that are not scarce or toxic. Such devices do not need concentration to reduce the cost per Watt. This thin-film approach thus tackles the twin requirements of third-generation devices, namely low cost per Watt and the use of nontoxic and abundant materials.

a-Si tandems

Amorphous silicon (a-Si)* cells are used for single-junction cells, but tend to give efficiencies of only about 4–5% because of high defect concentrations associated with the lack of crystallinity[17]. These efficiencies can be boosted in tandem cells with a-Si as a top cell with one or two lower cells of an alloy with Ge (a-Si:Ge), which lowers the bandgap. These cells are in-series devices that are grown by thin-film processes such as chemical vapor deposition (CVD) or other vacuum deposition techniques. The lack of a need for crystallization and the vapor-phase deposition mean that much less energy is required for the process, and the use of raw materials tends to be low for the thin layers deposited – a few hundred nanometers. Such two- or three-bandgap stacks can give efficiencies as high as 13% in the laboratory[18], but it is difficult to transfer these to production where efficiencies are around 10%. They also have the same problem of spectral sensitivity shared by all in-series tandems.

Si nanostructure tandems

Another approach is to retain both the advantages of crystalline material and thin-film deposition but to avoid the high costs of epitaxial III-Vs by use of thin-film crystalline Si, which is crystallized by a post-growth solid phase crystallization anneal[19]. Such single-junction cells are now in production at efficiencies just under 10%[20]. To boost the efficiencies of these cells in a tandem and retain the other advantages of third-generation approaches, research is underway on engineering wider bandgaps for Si-based materials using quantum confinement in nanostructures.

This bandgap engineering can be done using either quantum wells (QWs) or quantum dots (QDs) of Si sandwiched between layers of a dielectric based on Si compounds such as SiO_2, Si_3N_4, or SiC[21]. For sufficiently close spacing of QWs or QDs, a true miniband is formed creating an effectively larger bandgap. For QDs of 2 nm (QWs of 1 nm), an effective bandgap of 1.7 eV results – ideal for a tandem cell element on top of Si. These layers are grown by thin-film sputtering or CVD processes followed by a high-temperature anneal to crystallize the Si QWs/QDs. The matrix remains amorphous, thus avoiding some of the problems of lattice mismatch. Much work remains on passivation of defects, formation of junctions, and connection to a Si cell, but the

*Or, strictly, the alloy of a-Si with hydrogen. The hydrogen bonds to the dangling bonds in the amorphous structure and significantly passivates defects. At 1.8–1.9 eV, the bandgap of the alloy is substantially greater than that of Si at 1.1 eV.
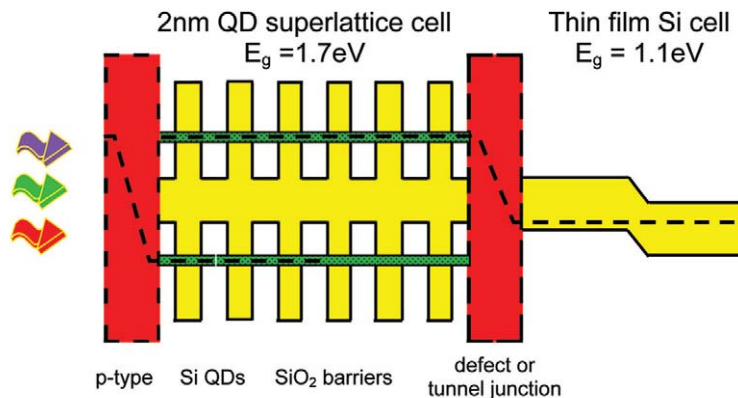
Fig. 4 Si nanostructure/Si tandem cell: the nanostructure cell consists of Si QWs or QDs in an amorphous dielectric matrix connected by a defect tunnel junction to a thin-film Si cell.

approach has great potential, although again, as an in-series tandem, it suffers from the problem of spectral sensitivity. The conceptual design of a complete device is shown in Fig. 4.

Intermediate-level cells: impurity PV and intermediate band solar cells

The approach with these devices is to introduce one or more energy levels within the bandgap such that they absorb photons in parallel with the normal operation of a single-bandgap cell. As such, it is also an implementation of strategy (a). This semi-parallel operation offers the potential to be much less spectrally sensitive but to still give high efficiencies.

Such a device has the same limiting efficiency as a three-level tandem – 63% under maximum concentration, 48% under one sun – because it has the same number of energy thresholds. However, this calculation does not take into account spectral sensitivity and assumes ideal properties such as ideal photon selection, a potential problem with intermediate level devices. Strictly to ensure complete photon selectivity, it is necessary to modify the absorption and emission ranges of the device such that the photon energy ranges do not overlap. This implies limited width conduction and valence bands

that would be very difficult to arrange in practice. Hence, without this rather artificial modification, there is a problem with photon selection – although the device nonetheless collects photons that would otherwise not be absorbed. However, note that the current now only has to be equal across the two lower energy levels while the main current across the bandgap is independent. This reduces the spectral sensitivity and compensates to some extent for the reduced photon selectivity.

These additional sub-bandgap absorbers can either exist as discrete energy levels in an impurity PV (IPV) cell, or as a continuous band of levels nonetheless isolated from the conduction and valence bands – the intermediate band solar cell (IBSC) shown in Fig. 5[22,23].

Both devices can absorb two below-bandgap photons to create one electron-hole pair at the bandgap energy, but the IBSC has the advantage that the delocalization of carriers in its continuous band means that these photons do not necessarily have to be absorbed by the same electron. This gives a much longer lifetime to the intermediate level, allowing much more time for absorption of the second photon. To maximize this advantage, the intermediate band should be half-filled with electrons – i.e. it should have a Fermi level at half the band energy, as illustrated in Fig. 5 – such that absorption
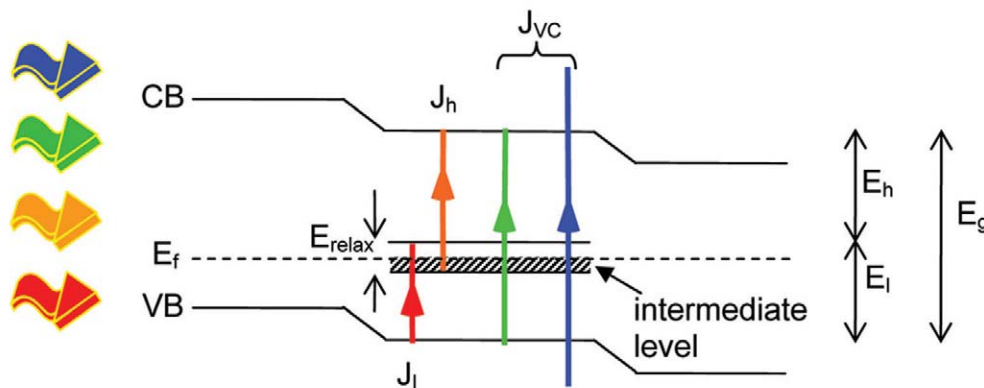

Fig. 5 The intermediate band solar cell. Below-bandgap photons are absorbed by the two transitions to and from the intermediate level contributing to photocurrent, in parallel to normal operation of the cell.

of an electron from the valence band or emission of an electron to the conduction band are equally likely.

The IPV cell is made by incorporation of deep-level defects in a cell – the optimum is at one third of the bandgap energy. An example that has been suggested is B in SiC[24] and another suggested and tried experimentally is In in Si[25]. Such defects also increase the probability of radiative and also nonradiative recombination, as both are enhanced for narrower energy gaps. This can be offset somewhat by arranging for defect incorporation only to occur deep in the cell away from the junction. This allows normal absorption of short wavelength light and separation of minority carriers with little enhanced recombination. But it also allows absorption of long wavelength light below the bandgap deep in the cell. In practice, however, these conflicting requirements make the cell too much of a compromise and no advantage has yet been shown[25,26].

Formation of an intermediate band for an IBSC has been suggested in some III-V, II-VI, and chalcopyrite systems, usually alloyed with a transition metal[27,28]. One specific example is Cr-doped ZnS[29]. They have also been attempted experimentally using the confined energy levels of a GaInAs/GaAs QD superlattice[30]. These devices have demonstrated several of the indicators of true IBSC operation, although they have not yet achieved an efficiency advantage. Nonetheless this seems likely in the near future, particularly if they are operated under concentration.

Multiple carrier excitation

Carriers generated from high-energy photons (at least twice the bandgap energy) absorbed in a semiconductor can undergo impact ionization events resulting in two or more carriers close to the bandgap energy. This approach is an implementation of strategy (b). But impact ionization has a vanishingly small probability in bulk material. Recently, it has been discovered that this process can be much more efficient in QDs[31,32] (Fig. 6). The exact mechanisms involved are not yet entirely clear, but they are related to the reduced requirement for conservation of crystal momentum in the small spatial volume of a QD. There is a

great deal of experimental evidence showing production of up to seven electron-hole pairs for the absorption of a high energy photon – i.e. a quantum efficiency (QE) of seven – with high luminescence efficiencies. The ratio of the photon energy to the bandgap energy (E_{hv}/E_g) must be $\geq$ QE. This phenomenon was first seen in PbSe QDs but has now been seen in quite a wide range of QDs fabricated from II-VIs and other materials, including Si, which is significant for possible future large-scale implementation. However, as yet the phenomenon has only been observed with absorption spectroscopy measurements.

The formulation for the limiting efficiency of such a device is given elsewhere[32]. The efficiency is calculated in a similar way to a single-bandgap cell but with the current enhanced by an energy-dependent quantum yield term, QY(E). The value of this depends on the particular model used to simulate the data. It is always equal to one, up to a threshold energy above the effective bandgap energy, E_0. QY then increases to two, indicating the production of two electron-hole pairs above this energy. This threshold energy varies with material and is usually equal to $\sim 3E_0$, but is sometimes as low as $2E_0$, yielding efficiency limits of 36% and 42%, respectively, at one sun[33].

A device based on this approach requires a means of allowing the multiple electron-hole pairs to be separated, transported, and collected in a bulk structure. This is the subject of ongoing research[32].

Modulation of the spectrum: up/down conversion

One of the practical problems with both the intermediate-level and multiple-carrier generation designs is that they require good optical properties (close to the radiative limit), as well as good electrical properties, to reduce nonradiative recombination and allow carrier transport – compounding the difficulty of making a good device. Separation of these functions into separate elements of a combined device would thus make a device much easier to optimize.

All the devices discussed above use the incident solar spectrum, albeit concentrated in some cases. The principle limitation on PV efficiencies arises from the polychromatic nature of this spectrum.

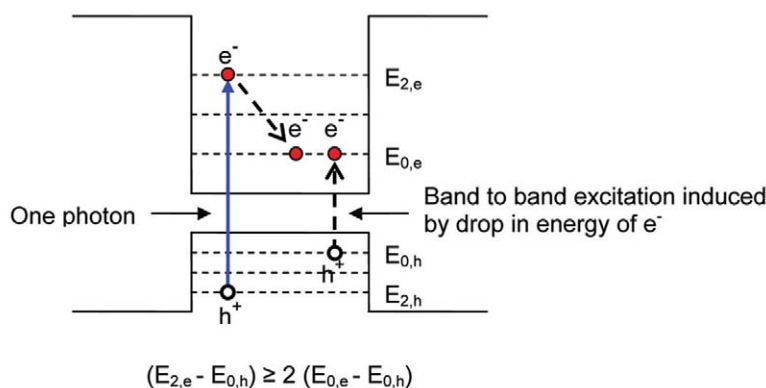$$(E_{2,e} - E_{0,h}) \geq 2 (E_{0,e} - E_{0,h})$$

Fig. 6 Multiple-carrier generation in QDs: a high-energy photon is absorbed at a high energy level in the QD, which then decays into two or more electron-hole pairs at the first confined energy level. Energy is conserved but momentum conservation is relaxed.

Thus, potentially, modification of the incident spectrum could allow a single-junction standard PV cell to operate at a higher efficiency. The problem is then to create a device that either absorbs a photon of at least twice the bandgap energy and emits two photons incident on the cell (a down-converter or DC), or absorbs at least two below-bandgap photons and emits one above-bandgap photon (an up-converter or UC). Schematics of these two devices are shown in Fig. 7, both of which are implementations of strategy (b).

The DC is placed in front of a standard cell and can boost current by converting ultraviolet (UV) photons to a larger number of visible photons. However, the DC does require that more visible photons are emitted than high-energy photons absorbed, i.e. its QE must be greater than unity[†]. High-DC QEs (although still less than one) are exhibited by some luminescent phosphors and by porous Si or Si nanocrystals[34]. It may also be that the multiple-exciton generation in QDs discussed above can be adapted for use as a DC. However, as exceeding unity is a difficult, although not impossible, requirement, research is mostly focused on UCs. Put underneath a fairly standard single-junction cell[‡], a UC can boost current using below-bandgap photons that are not normally absorbed. As the UC does not interrupt the incidence of photons on the front surface, even a very low efficiency UC gives a small current boost and hence an efficiency increase.

A DC material absorbs short wavelength photons over a narrow energy range, as shown in Fig. 7. Carriers generated in this material decay radiatively via a midgap level to give two photons at or just above the bandgap of the cell. Specific differences in the assumptions compared with those for the IBSC (mainly that the lower level must be half the upper level) give the limit for a DC of 36.7% under one sun[35].

[†]The threshold QE in order to achieve a net gain in current is actually greater than unity, as some emitted light will go back to the sun. Nonetheless, this fraction can be kept to below 10% by careful optical matching of refractive indexes.

[‡]This requires a bifacial cell in which grid contacts on the front *and* back allow the cell to be operated with light incident on either face. In fact, bifacial Si cells are quite routinely made and have the added advantage that below-bandgap light is transmitted.

The limiting efficiency for a UC is the same as for the IBSC. The difference between the two is that the UC is electrically separate from the cell, although still optically coupled. The limiting efficiency is given as 48% under one sun[36], the same as the IBSC. This is higher than that for a DC because the solar spectrum has a long high-energy tail. Hence, for any given cell bandgap, there will be more photons to be up-converted at half the bandgap than down-converted at twice the bandgap. The bandgap of a Si cell is close to the optimum bandgap for a DC but is rather lower than that for a UC at about 2 eV.

Experimental progress has been made using UCs in rare earth elements, specifically Er. Er is doped in a matrix that provides a specific separation of the atoms, absorption of 1500 nm photons to the first Er energy level of two adjacent atoms can then boost one electron to a higher energy level, resulting in emission of a 980 nm photon, above the bandgap of Si. A very small but measurable increase in current has been detected using a UC based on this principle[37]. This has a reasonable quantum efficiency of about 4%, but the very narrow bandwidth for absorption makes the device impractical, with little prospect for improvement based on the rare earths, although the general approach is very promising and other UC systems may well fare better.

Hot carrier cells

The final option for increasing efficiencies – strategy (c) – is to allow absorption of a wide range of photon energies but then to collect the photogenerated carriers before they have a chance to thermalize. A hot-carrier solar cell is just such a device that offers the possibility of very high efficiencies (the limiting efficiency is 65% for unconcentrated illumination) but with a structure that could be conceptually simple compared with other very high efficiency PV devices – such as multijunction monolithic tandem cells. For this reason, the approach lends itself to thin-film deposition techniques with their attendant low material and energy usage costs and the ability to use abundant, nontoxic elements.
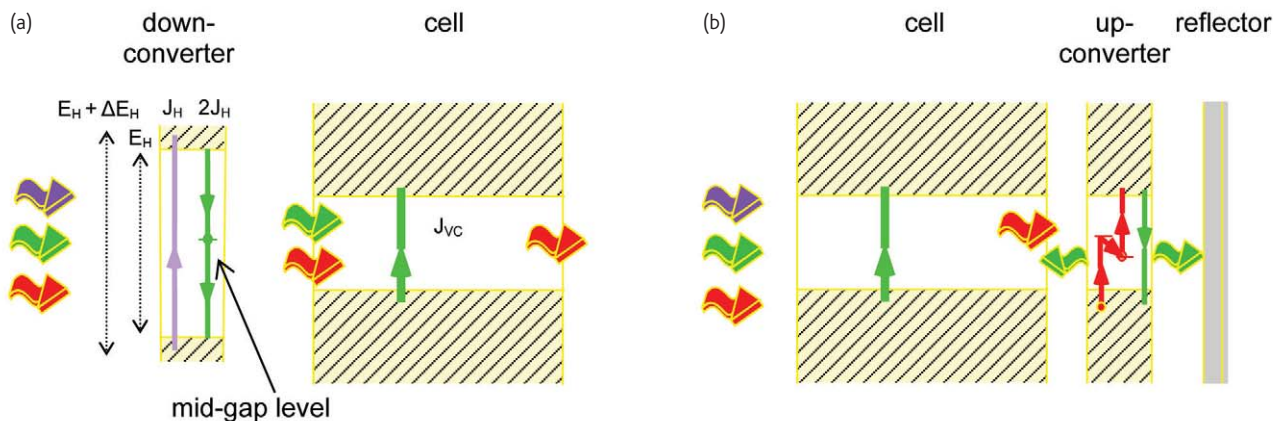

Fig. 7 (a) Down-converter in front of a single-junction cell. (b) Up-converter behind a single-junction cell.
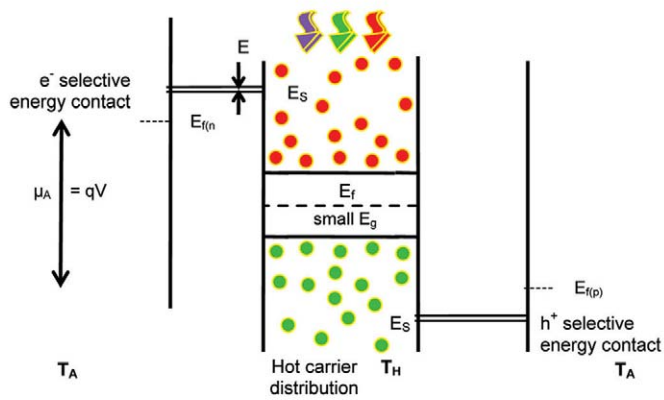
Fig. 8 Band diagram of the hot carrier cell that requires slowed carrier cooling in the absorption and collection of carriers through selective energy contacts.

The concept underlying hot carrier solar cells is to slow the rate of photoexcited carrier cooling, which is caused by phonon interaction in the lattice, to allow time for carriers to be collected while they are still at elevated energies ('hot'). This allows higher voltages to be achieved by the cell[1,38,39]. It thus tackles the major PV loss mechanism of thermalization of carriers (2 in Fig. 2). In addition to an absorber material that slows the rate of carrier relaxation, a hot carrier cell must allow extraction of carriers from the device through contacts that accept only a very narrow range of energies (selective energy contacts), as shown in Fig. 8.

Initial experimental progress has been made on selective energy contacts using double-barrier resonant tunneling structures, with a single layer of Si QDs providing the resonant level[40]. The problem of slowing carrier cooling is very difficult. It has been observed at very high illumination intensities via a phonon bottleneck effect in which carrier energy decay mechanisms are restricted. Compounds with large mass difference between their anions and cations have a gap in their allowed phonon modes that can slow down these decay mechanisms and enhance the bottleneck effect[41]. Examples are GaN and InN, with some experimental evidence for slowed cooling in the latter[42]. Theoretical work on replicating this effect by modifying the phononic band structures of QD nanostructure superlattices[43] will soon be attempted experimentally. Nonetheless, the hot carrier cell, while promising, is still a long way from demonstration.

Other approaches

A few other approaches have been suggested for increasing PV efficiency, including quantum antennas, thermophotonics or thermophotovoltaics (TPVs), and circulators. These are not part of the main discussion of multiple energy level third-generation PVs, but brief descriptions are given below.

The idea of a quantum antenna is to use the wave nature of light rather than its particle nature[44]. In-coming light waves oscillate

electrons in an antenna tuned to the wavelength of light – hence the devices have to be of the order of a few hundred nanometers. The broadband incoherent nature of the solar spectrum also requires a wide range of antenna sizes to match all the wavelengths and the need to arrange two directions of polarization. In addition to these practical problems, it has also been shown that the approach can only achieve 48% even under ideal conditions[45].

Thermal approaches include TPV[46], in which a narrow bandgap cell is illuminated by black- or gray-body radiation from a hot source but at a lower temperature than the sun. Efficiencies can be boosted by use of a selective emitter that only allows light just above its bandgap to be incident on the cell, the rest being reflected back to reheat the primary emitter. Thermophotonics[1,47] is a variation in which the thermal source heats a luminescent diode similar to the TPV cell, this then illuminates the cell with a spectrum strongly peaked just above their common bandgap. These approaches would normally use waste heat from an industrial process or similar and hence not be PV, but they can be coupled to an emitter heated by solar thermal energy. In practice, the large number of different elements, with their multiplying inefficiencies, and the need to thermally insulate some elements from others make the approaches very difficult to optimize.

In Fig. 2, one of the loss mechanisms is from radiative recombination (loss 5). In most devices this is assumed to be a minimum loss that cannot be reduced for a cell at the radiative limit, i.e. no nonradiative recombination. This is necessary as a reciprocal device that can absorb solar wavelengths must also be able to emit those same wavelengths[48]. However, it is possible that a *non*reciprocal device could re-use some of this emitted radiation and boost efficiencies beyond the radiative limit. Such a device is known as a multiport circulator, where incoming light incident on port 1 is emitted at port 2 and incident light on port 2 is emitted at port 3[1,49]. In principle, such a circulator can be used to redirect light emitted from a solar cell onto a second cell, light from this cell can then go through a second circulator to a third cell, etc. It has been shown that such an approach can boost efficiencies to 93%, the Landsberg limit, for an infinite number of circulators illuminating tandem cells with an infinite number of bandgaps[1,5]. The obvious practical difficulties of this are offset to some extent by the fact that most of the efficiency gain is obtained with the first circulator and, as we have seen, a tandem cell has most of its increase in efficiency for the first few layers. The nonreciprocal rotation of the polarization of light by a magnetic field can be and is used to fabricate such esoteric-sounding circulator devices for microwave and laser optics[50]. However, the complexity of the components and the very small efficiency gains make such an approach applied to PVs only appropriate for theoretical considerations.

Conclusions and future directions

The combined methodology of using multiple energy thresholds *and* low cost processes with abundant nontoxic materials in third-

generation devices offers significant leverage in the pursuit of significantly lower cost per Watt PVs. Many of these devices use the unique flexibility of QW and QD nanostructures to optimize absorption, carrier generation, and separation. The technique of detailed balance for calculating limiting efficiencies illustrates the similarity in several third-generation concepts, despite their different approaches, as it depends on the number of energy levels involved. In practice, however, the actual efficiencies and ease of optimization depend on the different physical approaches. Efficiency, spectral robustness, and cost/ease of manufacture are important for a robust technology that can supply very significant increases in PV implementation. No device matches all these goals yet.

Tandem PV devices are the best developed so far and further improvement, whether by increased concentrator system efficiency or by reduced cost and increased efficiency of thin-film designs, can leverage much lower overall costs per Watt. However, these devices tend to suffer from poor spectral robustness. Work on intermediate level devices and up/down conversion is at a much earlier stage, but promises increased efficiencies and greater spectral robustness, potentially with thin-film-type materials. The more advanced concepts of multiple-carrier generation and hot carrier cells are further away still and still have serious theoretical questions to answer. Nonetheless,

implementation of such techniques could dramatically decrease cost per Watt with spectral robustness as they are compatible with conceptually relatively simple thin-film devices.

The even more esoteric approaches of circulators, quantum antennas, and thermophotonics/TPVs are probably impractical even if they can be shown to work theoretically. Combinations of two or more approaches are also a possibility, e.g. the combination of both a UC and a DC on the same cell[6], or the use of a UC with a tandem cell. Alternatively, either an intermediate-level or a multiple-carrier generation device could be used as a DC rather than for producing excess carriers directly. The use of detailed balance analysis helps to show the equivalencies and complementarities between these approaches. Also, no doubt, other approaches not yet conceived will be possible as understanding of the topic continues to improve. mt

Acknowledgments

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