16
Third Generation Concepts

The term *third generation photovoltaics* refers to all novel approaches that aim to overcome the Shockley-Queisser (SQ) single bandgap limit, preferably at a low cost. The SQ limit — discussed extensively in Chapter 10 — is a thermodynamic approach to estimate the maximum efficiency of a single junction solar cell in dependence of the bandgap of its semiconductor material. For its derivation we assumed that the AM1.5 spectrum is incident on a solar cell. Further, we do not allow the solar cell to increase in temperature but we force it to keep the ambient temperature of 300 K. This means that all energy absorbed by the solar cell can escape the solar cell by either the generated current or by radiative recombination of charge carriers. Under these assumptions the efficiency limit is around 33% in the band gap range from 1.0 eV up to 1.8 eV.

Now we are going to look at some very fundamental limitations of classical single-junction solar cells.

Firstly, in single-junction solar cells only one bandgap material is used. Hence, a large fraction of the energy of the most energetic photons is lost as heat as illustrated in Fig. 10.7. The energy of highly energetic photons could be utilised better if absorbers with a high bandgap would be used or if they would create more than one excited electron in the conduction band.

Secondly, most solar cell concepts are based on an incident irradiance level of 1 sun. However, higher irradiance means more current generation and also higher voltage levels, resulting in a higher overall efficiency.

Thirdly, the photons with energies below the bandgap are not absorbed. Hence, they do not result in charge carrier excitation, as illustrated in Fig. 10.7.

If any of these fundamental limitations could be solved, PV concepts with conversion efficiencies exceeding the Shockley-Queisser limit could be developed. In this chapter, we will discuss several third generation concepts: Multi-junction solar cells, concentrator photovoltaics, spectral up and down conversion, multi-exciton generation, intermediate

band solar cells and hot carrier solar cells. Note, that besides multi-junction and the concentrator approach, none of these concepts have resulted in high efficiency solar cells yet. The other concepts are still in fundamental research phase and it will be a long way to go for them before being implemented in PV modules.

16.1 Multi-junction solar cells

The first limitation discussed in the list above can be attacked by using *multi-junction* solar cells. Depending on the author, these solar cells are seen as part of the second or the third generation, and indeed we already briefly discussed them in Chapter 13 on thin-film solar cells when looking at the III-V technology (Section 13.2) and thin-film silicon technology (Section 13.3). For completeness, we here will summarise this technology.

In multi-junction cells, several cell materials with different bandgaps are combined in order to maximise the amount of the sun light that can be converted into electricity, as we already illustrated in Fig. 10.9. To realise this, two or more cells are stacked onto each other. The top cell has the highest bandgap and will absorb and convert the short wavelength (blue) light. Light with wavelengths longer than the bandgap wavelength can traverse the top cell and be absorbed in the cells below having lower bandgaps. The bottom cell has the lowest bandgap and absorbs the long wavelength (red and near infrared) light. In order to optimise the performance of multi-junction solar cells with two electrical terminals, matching the currents of all the subcells (current matching) is crucial. Multi-junction cells with more terminals do not have this restriction, but their production is more complicated.

In thin-film silicon tandem cells, an a-Si:H top cell is stacked onto a nc-Si:H bottom cell. In order to achieve current matching, the top cell is much thinner than the bottom cell. The cell can be further optimised by using an intermediate reflector between the top and the bottom cell in order to reflect the blue light back into the top cell while letting the red light pass to the bottom cell. The reported record efficiency of a-Si:H/nc-Si:H tandem cells is 12.3% and for a a-Si:H/nc-Si:H/nc-Si:H it is 13.4% [77].

Multi-junction cells containing III-V semiconductors are at present the most efficient solar cells. The current world record efficiency is 46.0% for a four-junction GaInP/GaAs; GaInAsP/GaInAs cell that is used in a concentrator PV-system [65]. Because of the high concentration factor of 508 suns the overall efficiency increases and hence we also tackle the second limitation mentioned in the list above. As a result the SQ limit can be exceeded by more than 10%.

16.2 Spectral conversion

Single-junction solar cells have the limitation that every photon can only generate one collected electron-hole pair at most. This limitation can be tackled by *spectral conversion*. The main idea of spectral conversion to add an additional layer to the solar cell consisting of a material that can alter the incident spectrum. Materials that are investigated for spectral conversion are organic dyes, quantum dots, lanthanide ions, and transition metal ion systems [119].

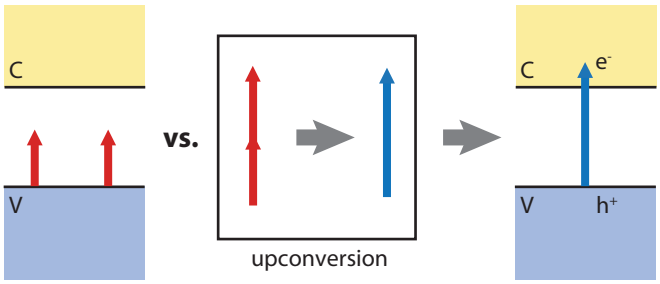

Figure 16.1: Illustrating the principle of spectral up-conversion.

16.2.1 Spectral upconversion

Spectral upconversion works by combining the energies of two absorbed low-energy photons into one higher-energy state, which can then radiate an upconverted photon into the solar cell active layer, as illustrated in Fig. 16.1.

Two distinct material systems have been employed to produce photon upconversion for solar cells: firstly, *triplet-triplet annihilation upconverters*(TTC-UC), which use pairs of organic chromophores with rationally ordered energy levels [120], and secondly, *rare-earth* upconverters, which make use of atomic transitions within lanthanide ions, from elements such as erbium and ytterbium [121].

TTA-UC systems, which are reliant on molecular absorbers, work better at shorter wavelength in between about 500 to 800 nm, while rare-earths work in the region around 1500 nm, where the ions absorb. Hence, the choice of the upconverter technology also depends on the bandgap of the solar cell, to which is is connected. Fot both approaches, enhancement in solar cell efficiency has been demonstrated [122–124].

The upconverting layer should be placed at the back of the solar cell as low-energy photons can pass through the solar cell absorber to this layer and can be converted there to high energy photons that are absorbed by the solar cell in a second pass [119]. In this way, also upconverting layers with low efficiencies might help to increase the photocurrent of the solar cell. Further, placing the upconverting layers at the back prevents them from being irradiated by high-energy photons which might reduce their lifetime. Due to parasitic absorption it is not advised to put these layers at the front of the solar cell.

16.2.2 Spectral downconversion

The idea of *spectral down-conversion* is to split one high-energy photon into multiple lower energy photons [125], as illustrated in Fig. 16.2. A high-energy photon is absorbed at the front of the solar cell and converted into at least two photons with lower energies. If the energy of the initial photon is $E_{\mathrm{ph}} > 2E_g$ and the energies of the resulting two photons are still larger than that of the band gap of the absorber material, both photons can be absorbed and used for exciting charge carriers. As a result, a high energy photon, for example in the blue, can result in two excited electrons. In other words, the maximum theoretical EQE of 100% at the wavelength of the blue photon can be increased to 200%. If the photon had sufficient energy to be split into three photons with sufficient energy, a theoretical EQE of

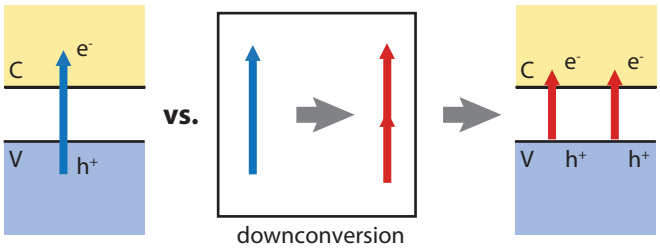

Figure 16.2: Illustrating the principle of spectral down-conversion.

300% could be obtained. In contrast to upconversion, a down-converting layer has to be at the front of the solar cell, as highly energetic photons are always absorbed in the absorber layer. Hence, parasitic absorption might be a problem in this technology.

One possibility that is investigated for realising spectral down-conversion is to use so-called *quantum dots* (QDs). These are small spherical nanoparticles made of semiconductor materials with typical diameters of a few nanometers, as illustrated in Fig. 16.3 (a). These semiconductor particles still behave like a semiconductor material; however, due to so-called *quantum confinement* the bandgap of the semiconductor quantum dots can be larger than that of the same semiconductor in a bulk configuration. The bandgap of the QDs can be tuned by varying their size. The smaller the particles, the larger the bandgap. This enables interesting opportunities for bandgap engineering, such as a multi-junction solar cells based on junctions with different QDs of different sizes in every junction.

If QDs should be used for down-conversion, an ensemble of nanoparticles is embedded in a host material, where the particles are in very close proximity of each other. Figure 16.3 (b) shows the electronic bandgap diagram of two nanoparticles. Now, a high-energy photon is absorbed by one QD and hence one electron is excited into the conduction band of the particle. In difference to a bulk semiconductor, the excess energy of the photon is not necessarily lost as heat, but it can be transferred as a *quantised energy package* to a neighbouring quantum dot. Here a second electron is excited into conduction band of the second quantum dot. As a result, two electron-hole pairs have been created out of one photon. If non-radiative recombination mechanisms like Auger recombination and SRH recombination are sufficiently suppressed, the electron-hole pairs in both quantum dots can radiatively recombine such that each of the two QDs emits one reddish photon. In summary, one incident bluish photon is converted in to two reddish photons, which can be absorbed by a PV material.

Figure 16.4 shows some experimental results by Jurbergs *et al.* on down conversion based on silicon quantum dots in a narrow spectral range [126]. The horizontal axis represents the photon emission wavelength. At around 790 nm a down-conversion efficiency of is 60% achieved. The EQE exceeds 100% in the blue region from 3.1 up to 3.4 eV. The major challenge is have QD layers with a spectral response exceeding 100% at lower photon energies, because the solar spectrum contains far more photons in that spectral range. In practice, only small enhancements in efficiency due to up/down-converters have been reported [127].

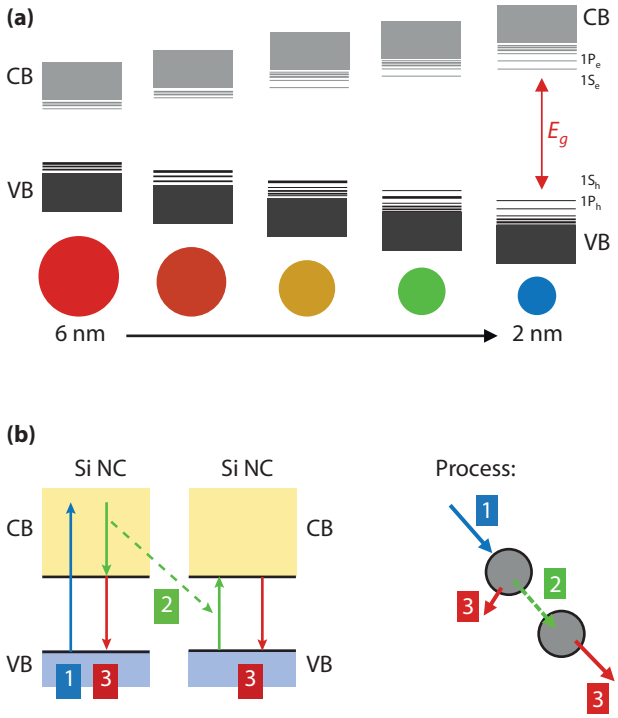

Figure 16.3: Illustrating (a) the effect of the quantum dot (QD) size on the bandgap and (b) spectral down-conversion with QDs.

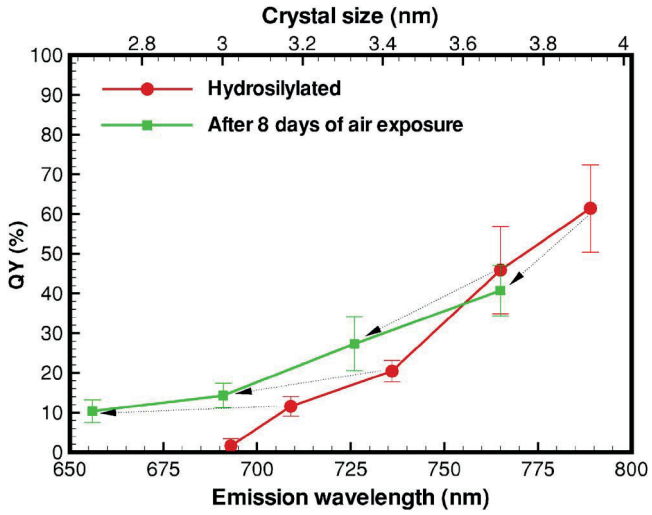

Figure 16.4: Down conversion at Si quantum dots (reprinted with permission from D. Jurbergs, E. Rogojina, L. Mangolini, and U. Kortshagen, Applied Physics Letters, vol. 88, 233116. Copyright (2006), AIP Publishing LLC) [126].

16.3 Multi-exciton generation

Another approach to enhance the charge carrier excitation by a single energetic photon is called *multiple exciton generation* (MEG), where more than one electron-hole pairs is generated from high energy photons. In contrast to spectral downconversion here two or more excitons are generated in the MEG layer, which then are transported to the PV-active layers. It is important to note that they are not converted back to lower-energy photons.

Like down conversion, MEG can be realised with quantum dots, as illustrated in Fig. 16.5. Again, in one particle an electron is excited into the conduction band and the excess energy is transferred to a neighbouring QD, where a second electron is excited in to

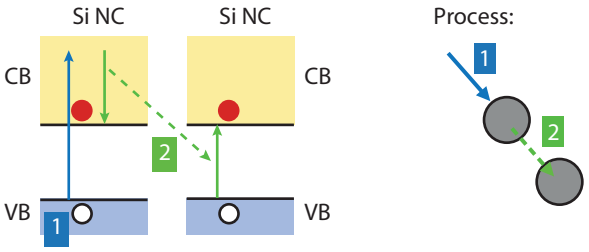

Figure 16.5: Illustrating multi exciton generation with quantum dots (adapted by permission from Macmillan Publishers Ltd: D. Timmerman I. Izeddin, P. Stallinga, I. N. Yassievich, and T. Gregorkiewicz, Nature Photonics, vol. 2, pp. 105-109, copyright (2008)).

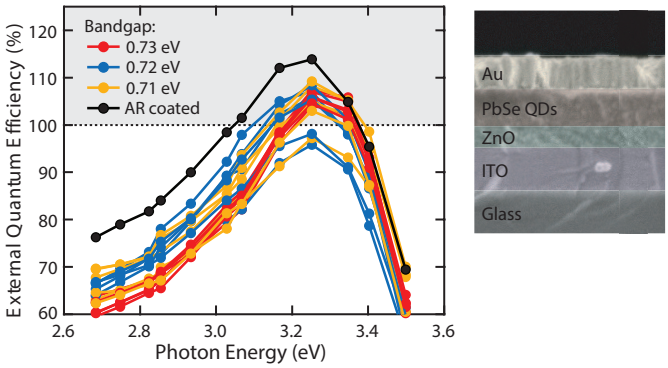

Figure 16.6: Multi-exciton generation using PbSe quantum dots with EQEs exceeding 100% [128]. From O. E. Semonin, J. M. Luther, S. Choi, H.-Y. Chen, J. Gao, A. J. Nozik, and M. C. Beard, Science 334, 1530 (2011). Reprinted with permission from AAAS.

conduction band of the second quantum dot. However, here the charge carriers in the two electron-hole pairs are separated before they can recombine such that one incident photons results in more than one generated electron [129]. Just as for spectral down-conversion, also here quantum efficiencies exceeding 100% are theoretically possible when one incident photon creates statistically more than one charge carriers. Figure 16.6 shows that EQEs exceeding 100% can be achieved as demonstrated by Semonin *et al.* [128]. Here, the absorber layer consists PbSe quantum dots.

Another way of performing downconversion is to utilise *singlet fission*, which for example can be done using tetracene, a polycyclic aromatic hydrocarbon. In fact, singlet fission is the equivalent to MEG in organic materials, where a high-energy singlet excited state fissions into two low-energy triplet states on neighbouring molecules [130, 131].

16.4 Intermediate band solar cells

The concept of *intermediate band solar cells* (IB) tries to tackle the problem photons with energies below the bandgap cannot be utilised for current generation. As shown in Fig. 16.7 (a), in intermediate band cells energy levels are created artificially in the bandgap of the absorber material [132]. As in conventional single-junction solar cells, photons with a sufficient energy can excite an electron from the valence band in to the conduction band. However, in difference to conventional semiconductors photons with energies below the bandgap can excite an electron from the valence band in to the intermediate band. A second low-energy photon is required to excite the electron from the intermediate band into the conduction band. As illustrated in 16.7 (b), therefore the absorption of two photons with energies smaller than the bandgap energy can result in quasi-Fermi level splitting exceeding the energy of each of these photons.

Various studies have been performed on how intermediate band cells can be realised, as for example summarised in Reference [132]. In such solar cells, a layer with the intermediate states is placed in between *p*- and *n*-layers. For example quantum dots can be used

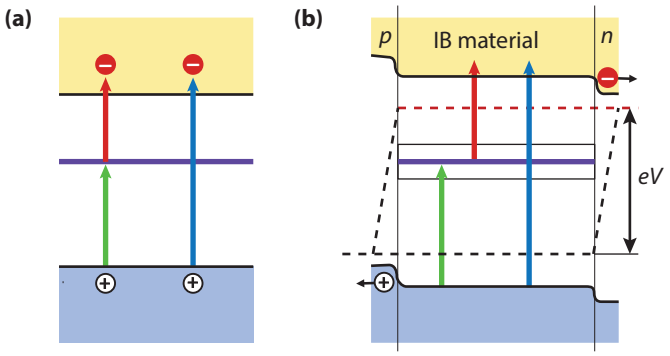

Figure 16.7: Band diagram (a) with the intermediate band depicted and (b) with the quasi-Fermi levels exceeding the energy of the low-energy photons.

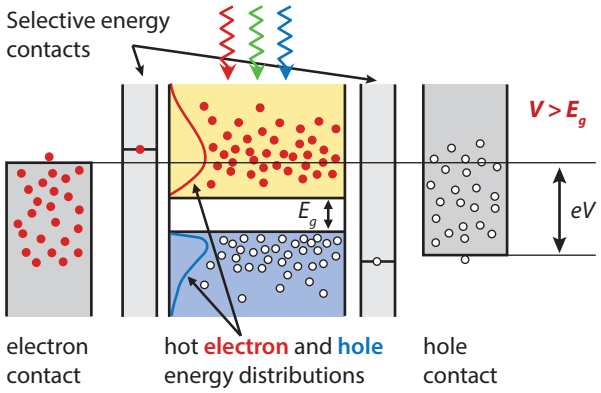

Figure 16.8: Illustrating the working principle of a hot carrier solar cell.

to realise the intermediate states. Further, various bulk materials are studied for realising the intermediate states. One major problem of experimental IB cells is that the voltages are lower than the voltages of reference cells without IB structures.

16.5 Hot carrier solar cells

The idea of *hot carrier solar cells* is to reduce the energy losses due to relaxation and hence thermalisation. As illustrated in Fig. 16.8, this should be achieved by collecting electron-hole pairs of high energy photons just after light excitation and before they have a chance to relax back to the edges of the electronic bands. In the figure, the population of the charge carrier levels reflects the situation just after the excitation by the absorption of a photon. This distribution is not in thermal equilibrium as many electrons are excited into position further up in the conduction band and the holes are excited down to lower levels in the valence band. These charge carriers are called *hot* electrons and holes [26, 133].

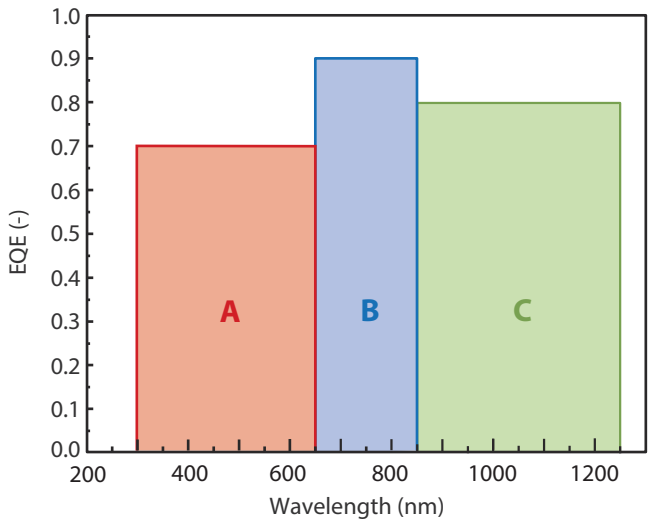

Figure 16.9

It takes only a few picoseconds (10^{-12} s) for the hot charge carriers to relax back to the edges of the electronic bands. The idea of hot carrier cells it to collect the charge carriers as long as they are still *hot*. Hence, an energy larger than the bandgap energy can be utilised per excited charge carrier and the average bandgap utilisation would exceed the bandgap.

The fundamental challenge is to collect the hot carriers before they relax back to the edges of the electronic bands. Such a concept would require *selective contacts*, which only select electrons above a particular energy level in the conduction band and holes below a certain energy level in the valence band, respectively. At the moment the main challenge is to increase the lifetime of the hot charge carriers, such that they have time to move from the absorber material to the selective contacts [134].

16.6 Exercises

16.1 Figure 16.9 shows the EQE of a triple junction cell with junctions A, B and C under short-circuited ($V = 0$ V) condition.

(a) What is the bandgap of the absorber layer of junction A?

(b) What is the bandgap of the absorber layer of junction B?

(c) What is the bandgap of the absorber layer of junction C?

(d) Which of the following statements is true?

i. Junction C acts as the top cell, junction B as the middle cell, and junction A as the bottom cell.

ii. Junction B acts as the top cell, junction C as the middle cell, and junction A as the bottom cell.