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Solar Spectrum Conversion for Photovoltaics Using Nanoparticles

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1. Introduction

The possibility to tune chemical and physical properties in nanosized materials has a strong impact on a variety of technologies, including photovoltaics. One of the prominent research areas of nanomaterials for photovoltaics involves spectral conversion. Conventional single-junction semiconductor solar cells only effectively convert photons of energy close to the semiconductor band gap (E_g) as a result of the mismatch between the incident solar spectrum and the spectral absorption properties of the material (Green 1982, Luque and Hegedus 2003). Photons with an energy E_{ph} smaller than the band gap are not absorbed and their energy is not used for carrier generation. Photons with energy E_{ph} larger than the band gap are absorbed, but the excess energy $E_{ph} - E_g$ is lost due to thermalization of the generated electrons. These fundamental spectral losses in a single-junction silicon solar cell can be as large as 50% (Wolf 1971), while the detailed balance limit of conversion efficiency for such a cell was determined to be 31% (Shockley and Queisser 1961). Several routes have been proposed to address spectral losses, and all of these methods or concepts obviously concentrate on a better exploitation of the solar spectrum, e.g., multiple stacked cells (Law et al. 2010), intermediate band gaps (Luque and Marti 1997), multiple exciton generation (Klimov 2006, Klimov et al. 2007), quantum dot concentrators (Chatten et al. 2003a) and down- and up-converters (Trupke et al. 2002a, b), and down-shifters (Richards 2006a, Van Sark 2005). In general they are referred to as Third or Next Generation photovoltaics (PV) (Green 2003, Luque et al. 2005, Martí and Luque 2004). Nanotechnology is essential in realizing most of these concepts (Soga 2006, Tsakalakos 2008), and semiconductor nanocrystals have been recognized as 'building blocks' of nanotechnology for use in next generation solar cells (Kamat 2008). Being the most mature approach, it is not surprising that the current world record conversion efficiency is 43.5% for a GaInP/GaAs/GaInNAs solar cell (Green et al. 2011), although this is reached at a concentration of 418 times.

As single-junction solar cells optimally perform under monochromatic light at wavelength $\lambda_{opt} \sim 1240/E_g$ (with λ_{opt} in nm and E_g in eV), an approach "squeezing" the wide solar spectrum (300-2500 nm) to a single small band spectrum without too many losses would greatly enhance solar cell conversion efficiency. Such a quasi-monochromatic solar cell could in principle reach efficiencies over 80%, which is slightly dependent on band gap (Luque and Martí 2003). For (multi)crystalline silicon ((m)c-Si) solar cells $\lambda_{opt} = 1100$ nm (with $E_g = 1.12$ eV); for amorphous silicon (a-Si:H) the optimum wavelength is $\lambda_{opt} = 700$ nm (with $E_g = 1.77$ eV). However, as these cells only contain a thin absorber layer, the optimum spectrum response occurs at about 550 nm (Schropp and Zeman 1998, Van Sark 2002).

Modification of the spectrum by means of so-called down- and/or upconversion or -shifting is presently being pursued for single junction cells (Richards 2006a), as illustrated in Fig. 1, as a relatively easy and cost-effective means to enhance conversion efficiency. In addition, so-called luminescent solar converters (LSC) employ spectrum modification as well (Goetzberger 2008, Goetzberger and Greubel 1977). Downconverters or -shifters are located on top of solar cells, as they are designed to modify the spectrum such that UV and visible photons are converted leading to a more red-rich spectrum that is converted at higher efficiency by the solar cell. Upconverters modify the spectrum of photons that are not absorbed by the solar cell to effectively shift the IR part of the transmitted spectrum to the NIR or visible part; a back reflector usually is applied as well.
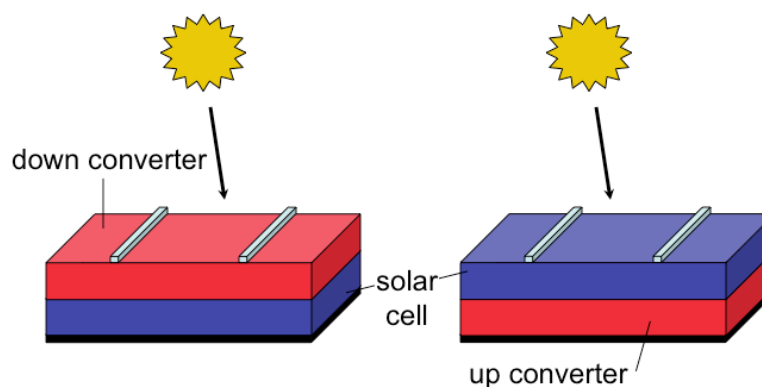

Fig. 1. Schematic drawings of a solar cell with down converter (or down shifter) layer on top (left) and a solar cell on top of an upconverter layer.

In case of downconversion (DC) an incident high-energy photon is converted into two or more lower energy photons which can lead to quantum efficiency of more than 100%, therefore it is also termed 'quantum cutting' (Timmerman et al. 2008, Wegh et al. 1999); for upconversion (UC) two or more low energy photons (sub band gap) are converted into one high-energy photon (Strümpel et al. 2007), see also Fig. 2. Downshifting (DS) is similar to downconversion where an important difference is that only one photon is emitted and that the quantum efficiency of the conversion process is lower than unity (Richards 2006a), although close to unity is preferred to minimize losses. Downshifting is also termed photoluminescence (Strümpel et al. 2007). DC, UC and DS layers only influence solar cell performance optically. As DC and DS both involve one incident photon per conversion, the intensity of converted or shifted emitted photons linearly scales with incident light intensity. UC involves two photons; therefore the intensity of converted light scales quadratically with incident light intensity.
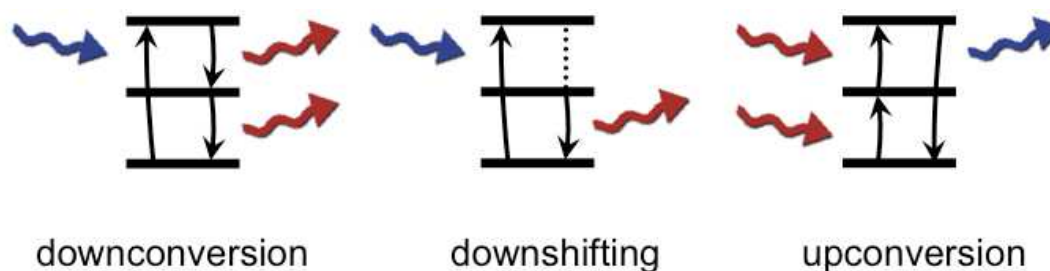
Fig. 2. Energy diagrams showing photon adsorption and subsequent downconversion, downshifting, and upconversion.

In this chapter a review is presented on the use of nanometer sized particles (including quantum dots) in solar spectrum conversion. Modification of the spectrum requires down- and/or upconversion or -shifting of the spectrum, meaning that the energy of photons is modified either to lower (down) or higher (up) energy. Nanostructures such as quantum dots, luminescent dye molecules, and lanthanide-doped glasses are capable of absorbing photons at a certain wavelength and emitting photons at a different (shorter or longer) wavelength. We will discuss down- and upconversion and -shifting by quantum dots, luminescent dyes, and lanthanide compounds, and assess their potential in contributing to ultimately lowering the cost per kWh of solar generated power.

2. Downconversion

2.1 Principles

Downconversion was theoretically suggested first by Dexter in the 1950s (Dexter 1953, 1957), and shown experimentally 20 years later using the lanthanide ion praseodymium Pr^{3+} in an yttrium fluoride YF_3 host (Piper et al. 1974, Sommerdijk et al. 1974). A VUV photon (185 nm) is absorbed in the host, and its energy is transferred into the $^1S_0$ state of the Pr^{3+} ion, from where two photons (408 and 620 nm) are emitted in a two-step process ($^1S_0 \rightarrow {}^3P_J$ at 408 nm followed by $^3P_J \rightarrow {}^3F_2$ at 620 nm). In this way a single absorbed high energy photon results in the emission of two visible photons and a higher-than-unity quantum efficiency is realized. Another frequently used ion is gadolinium Gd^{3+} (Wegh et al. 1997), either single or co-doped (Wegh et al. 1999). These lanthanide ions are characterized by a rich and well-separated energy level structure in the so-called Dieke energy diagrams (Dieke 1968), and have been identified as perfect "photon managers" (Meijerink et al. 2006). The energy levels arise from the interactions between electrons in the inner 4f shell. Trivalent lanthanides have as electronic configuration $[Xe]4fn5s^25p^6$. Inside the filled 5s and 5p shells, there is a partially filled 4f shell where the number of electrons (n) can vary between 0 and 14. The number of possible arrangements for n electrons in 14 available f-orbitals is large (14 over n), which gives rise to a large number of different energy levels that are labelled by so-called term symbols. Transitions between the energy levels give rise to sharp absorption and emission lines. Energy transfer between neighbouring lanthanide ions is also possible and helps converting photons that are absorbed to photons of different energy. Based on their unique and rich energy level structure, lanthanide ions are promising candidates to realize efficient down conversion and recent research in this direction will be discussed below.

Downconversion in solar cells was theoretically shown to lead to a enlarged conversion efficiency of 36.5% (Trupke et al. 2002a) for nonconcentrated sunlight when applied in a single junction solar cell configuration, such as shown in Fig. 1. Note that detailed-balance

calculations for single junction c-Si cells lead to a maximum efficiency of 31% (Shockley and Queisser 1961). These calculations were performed as a function of the band gap and refractive index of the solar cell material, for a 6000K blackbody spectrum. The efficiency limit is reached for a band gap of 1.05 eV, and asymptotically approaches 39.63% for very high refractive indices larger than 10. For c-Si, with refractive index of 3.6, the limit efficiency is 36.5%. Analysis of the energy content of the incident standard Air Mass 1.5 Global (AM1.5G) spectrum (ASTM 2003) and the potential gain DC can have shows that with a DC layer an extra amount of 32% is incident on a silicon solar cell (Richards 2006a), which can be converted at high internal quantum efficiency. Figure 3 illustrates the potential gains for DC and UC.
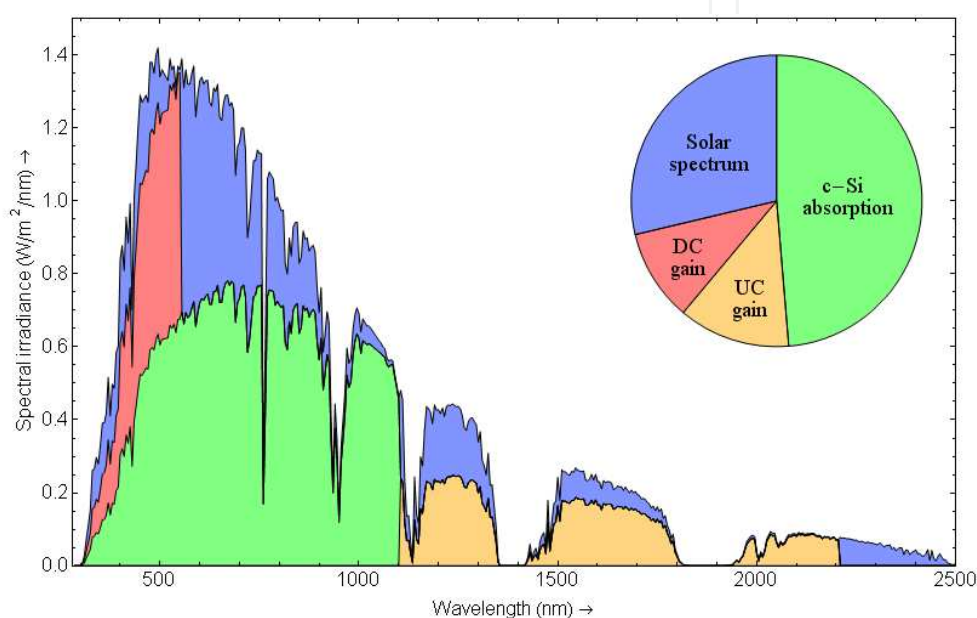

Fig. 3. Potential gain for down- and upconversion for a silicon solar cell. The green part reflects the energy conversion of the absorbed part of the solar spectrum for a c-Si solar cell, the red part reflects the extra energy conversion if every photon with an energy higher than $2E_g$ results in two NIR photons and the beige part reflects the energy gain if every pair of photons with an energy between $0.5E_g$ and E_g is converted to one NIR photon. Note that the figure considers no other losses than spectral mismatch losses (Courtesy of F. Rabouw, Utrecht University).

2.2 State of the art

The most promising systems for downconversion rely on lanthanide ions. The unique and rich energy level structures of these ions allow for efficient spectral conversion, including up- and downconversion processes mediated by resonant energy transfer between neighboring lanthanide ions (Auzel 2004, Wegh et al. 1999). Considering the energy levels of all lanthanides, as shown in the Dieke energy level diagram (Dieke 1968, Peijzel et al. 2005, Wegh et al. 2000) it is immediately evident that the energy level structure of Yb^{3+} is ideally suited to be used in down conversion for use in c-Si solar cells. The Yb^{3+} ion has a single excited state (denoted by the term symbol $^2F_{5/2}$) some 10,000 cm^{-1} above the $^2F_{7/2}$ ground state, corresponding to emission around 1000 nm. The absence of other energy levels allow Yb^{3+} to exclusively 'pick up' energy packages of 10,000 cm^{-1} from other lanthanide ions and

emitting ~1000 nm photons that can be absorbed by c-Si. Efficient downconversion using Yb^{3+} as acceptor requires donor ions with an energy level around 20,000 cm^{-1} and an intermediate level around 10,000 cm^{-1}. From inspection of the Dieke diagram one finds that potential couples are (Er^{3+}, Yb^{3+}), (Nd^{3+}, Yb^{3+}) and (Pr^{3+}, Yb^{3+}) for a resonant two-step energy transfer process. Also, cooperative sensitization is possible where energy transfer occurs from a high excited state of the donor to two neighboring acceptor ions without an intermediate level.

The first report on efficient downconversion for solar cells was based on cooperative energy transfer from Tb^{3+} to two Yb^{3+} ions in $Yb_xY_{1-x}PO_4$:Tb^{3+} (Vergeer et al. 2005), as shown schematically in Fig. 4. The $^5D_4$ state of Tb^{3+} is around 480 nm (21,000 cm^{-1}) and from this state cooperative energy transfer to two Yb^{3+} neighbors occurs, both capable of emitting a 980 nm photon.
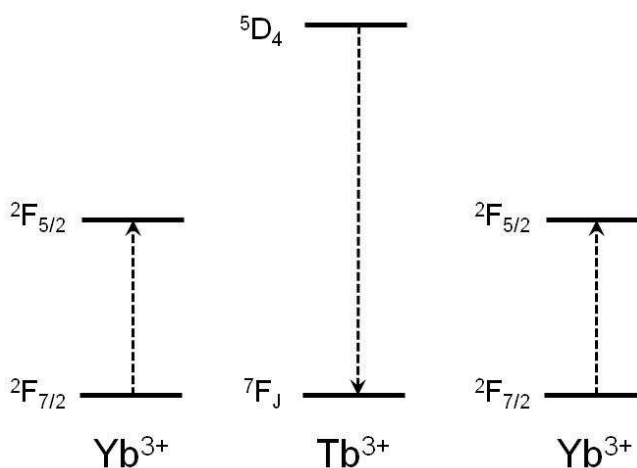

Fig. 4. Cooperative energy transfer from Tb to two Yb ions. From the $^5D_4$ state of one Tb ion two neighbouring Yb ions are excited to the $^2F_{5/2}$ state from where emission of 980 nm photons can occur (after Meijerink et al. 2006, Vergeer et al. 2005).

The same efficient down conversion process was observed in other host lattices: Zhang et al. (Zhang et al. 2007) observed cooperative quantum cutting in (Yb,Gd)Al$_3$(BO$_3$)$_4$:Tb^{3+} and quantum efficiencies up to 196% were reported. Cooperative downconversion for other couples of lanthanides was also claimed. For the couple (Pr, Yb) and (Tm, Yb) co-doped into borogermanate glasses a decrease of the emission from higher energy levels of Pr and Tm was observed (Liu et al. 2008). In case of Pr^{3+} the starting level for the cooperative down conversion is the $^3P_0$ level while for Tm^{3+} the $^1G_4$ is at twice the energy of the $^2F_{5/2}$ level of Yb^{3+}. The efficiency of the downconversion process was estimated from the decrease of the lifetime of the donor state. For the Tm^{3+} emission a decrease from 73 μs (for the sample doped with Tm only) to 45 μs (for a sample co-doped with 20% of Yb) was observed, giving a transfer efficiency of 38%. For the same glass co-doped with Pr and Yb a 65% decrease of the lifetime was observed, implying a 165% quantum yield. Similar results were found for the (Pr, Yb) couple in aluminosilicate glasses (Lakshminarayana et al. 2008). More recent work on the (Pr, Yb) couple confirmed the presence of downconversion, but the mechanism involved was pointed out to be a resonant two-step energy transfer rather than a cooperative energy transfer (Van der Ende et al. 2009a, b). For the (Pr, Yb) couple an intermediate level ($^1G_4$) is available around 10,000 cm^{-1}, which makes a two-step resonant energy transfer process possible. This

first-order process will have a much higher probability than the second-order (cooperative) transfer process. The results demonstrated efficient quantum cutting of one visible photon into two NIR photons in $SrF_2:Pr^{3+}$, Yb^{3+}. Comparison of absorption and excitation spectra provided direct evidence that the downconversion efficiency is close to 200%, in agreement with a two-step energy transfer process that can be expected based on the energy level diagrams of Pr^{3+} and Yb^{3+}. This first order energy transfer process is effective at relatively low Yb^{3+} concentrations (5%), where concentration quenching of the Yb^{3+} emission is limited. Comparison of emission spectra, corrected for the instrumental response, for $SrF_2:Pr^{3+}$ (0.1%) and $SrF_2:Pr^{3+}$ (0.1%), Yb^{3+} (5%) revealed an actual conversion efficiency of 140%.

An important aspect for downconversion is the incorporation in a solar cell. The solar spectrum has to be converted before entering the solar cell. A promising design is incorporation of downconverting material in a thin (10-100 nm) transparent layer on top of the solar cell. After downconversion the isotropically emitted 1000 nm need to be directed towards the solar cell. This can be achieved by a narrow-band reflective coating for 1000 nm NIR on top of the downconversion layer, thereby avoiding absorption in the other parts of the spectrum. The narrow band emission of the Yb^{3+} emission allows for a narrow band reflective coating. To realize a transparent downconversion layer, the downconverting lanthanide ion couples need to be incorporated in nanocrystals with dimensions smaller than ~50 nm to prevent light scattering. Chen et al. reported downconversion in transparent glass ceramics with embedded $Pr^{3+}/Yb^{3+}:\beta$-YF_3 nanocrystals (Chen et al. 2008a). Quantum cutting downconversion was shown in borate glasses using co-doping of Ce^{3+} and Yb^{3+} (Chen et al. 2008b). A UV photon (330 nm) excites a Ce^{3+} ion, and cooperative energy transfer between the Ce^{3+} and Yb^{3+} ion leads to the emission of two NIR photons (976 nm) with a 174% quantum efficiency, based on a 74% energy transfer efficiency calculated from the luminescence decay curves and assuming cooperative energy transfer. Recent work on the (Ce, Yb) couple suggests that the energy transfer mechanism is not cooperative energy transfer, but single step energy transfer via a metal-to-metal charge transfer state. If this is the case, the quantum efficiency is not above 100%. Efficient downconversion for other lanthanide ion couples has been reported, including the (Er, Yb) couple in low phonon hosts (Eilers et al. 2010). Research on new downconversion couples continues. It is not straightforward to establish the efficiency of the conversion to NIR photons and careful studies providing convincing evidence for the energy transfer mechanism and efficiency are required (Van Wijngaarden 2010).

Timmerman et al. (Timmerman et al. 2008) demonstrated so-called space-separated quantum cutting within SiO_2 matrices containing both silicon nanocrystals and Er^{3+}. Energy transfer from photo exited silicon nanocrystals to Er^{3+} had been observed earlier (Fujii et al. 1997), but Timmerman et al. show that upon absorption of a photon by a silicon nanocrystal a fraction of the photon energy is transferred generating an excited state within either an erbium ion or another silicon nanocrystal. As also the original silicon NC relaxes from a highly excited state towards the lowest-energy excited state, the net result is two electron-hole pairs for each photon absorbed. Recent quantum yield measurements as a function of excitation wavelength confirmed the occurrence of carrier multiplication in Si nanocrystals (Timmerman et al. 2011).

3. Downshifting

3.1 Principles
Downshifting (DS) or photoluminescence is a property of many materials, and is similar to downconversion, however, only one photon is emitted and energy is lost due to non-

radiative relaxation, see Fig. 2. Therefore the quantum efficiency is lower than unity. DS can be employed to overcome poor blue response of solar cells (Hovel et al. 1979), due to, e.g., non-effective front surface passivation for silicon solar cells. Shifting the incident spectrum to wavelengths where the internal quantum efficiency of the solar cell is higher than in the blue can effectively enhance the overall conversion efficiency by ~10% (Van Sark et al. 2005). Improvement of front passivation may make down shifters obsolete, or at least less beneficial. Downshifting layers can also be used to circumvent absorption of high-energy photons in heterojunction window layers, e.g., CdS on CdTe cells (Hong and Kawano 2003). A recent review is presented by Klampaftis et al. (2010).

Downshifting was suggested in the 1970s to be used in so-called luminescent solar concentrators (LSCs) that were attached on to a solar cell (Garwin 1960, Goetzberger and Greubel 1977). In these concentrators, organic dye molecules absorb incident light and re-emit this at a red-shifted wavelength. Internal reflection ensures collection of all the re-emitted light in the underlying solar cells. As the spectral sensitivity of silicon is higher in the red than in the blue, an increase in solar cell efficiency was expected. Also, it was suggested to use a number of different organic dye molecules of which the re-emitted light was matched for optimal conversion by different solar cells. This is similar to using a stack of multiple solar cells, each sensitive to a different part of the solar spectrum. The expected high efficiency of ~30% (Smestad et al. 1990, Yablonovitch 1980) in practice was not reached as a result of not being able to meet the stringent requirements to the organic dye molecules, such as high quantum efficiency and stability, and the transparency of collector materials in which the dye molecules were dispersed (Garwin 1960, Goetzberger and Greubel 1977).

Nowadays, new organic dyes can have extremely high luminescence quantum efficiency (LQE) (near unity) and are available in a wide range of colors at better re-absorption properties that may provide necessary UV stability. Quantum dots (QDs) have been proposed for use in luminescent concentrators to replace organic dye molecules: the quantum dot concentrator (Barnham et al. 2000, Chatten et al. 2003a,b, Gallagher et al. 2007). Quantum dots are nanometer-sized semiconductor crystals of which the emission wavelength can be tuned by their size, as a result of quantum confinement (Alivisatos 1996, Gaponenko 1998). Recently, both QDs and new organic dyes have been evaluated for use in LSCs (Van Sark et al. 2008a). QDs have advantages over dyes in that: (i) their absorption spectra are far broader, extending into the UV, (ii), their absorption properties may be tuned simply by the choice of nanocrystal size, and (iii) they are inherently more stable than organic dyes (Bruchez Jr. et al. 1998). Moreover, (iv) there is a further advantage in that the red-shift between absorption and luminescence is quantitatively related to the spread of QD sizes, which may be determined during the growth process, providing an additional strategy for minimizing losses due to re-absorption (Barnham et al. 2000). However, as yet QDs can only provide reasonable LQE: a LQE > 0.8 has been reported for core-shell QDs (Peng et al. 1997). Performance in LSCs has been modeled using thermodynamic as well as ray-trace models (Burgers et al. 2005, Chatten et al. 2003b, 2004a, b, Chatten et al. 2005, Gallagher et al. 2004, Kennedy et al. 2008), and results are similar and also compare well with experimental values (Kennedy et al. 2008, Van Sark et al. 2008a). Calculated efficiencies vary between 2.4% for an LSC with mc-Si cell at certain mirror specifications to 9.1% for an LSC with InGaP cell for improved specifications.

Alternatives for dye molecules used in LSCs are luminescent ions. Traditionally, efficient luminescent materials rely on the efficient luminescence of transition metal ions and lanthanide ions. In case of transition metal ions intraconfigurational $3d^n$ transitions are

responsible for the luminescence, while in case of lanthanide ions both intraconfigurational $4f^n$-$4f^n$ transitions and interconfigurational $4f^n$-$4f^{n-1}5d$ transitions are capable of efficient emission. In most applications efficient emission in the visible is required and emission from lanthanide ions and transition metal ions is responsible for almost all the light from artificial light sources (e.g. fluorescent tubes, displays (flat and cathode ray tube, CRT) and white light emitting diodes (LEDs) (Blasse and Grabmaier 1995). For LSCs to be used in combination with c-Si solar cells efficient emission in the NIR is needed. The optimum wavelength is between 700 and 1000 nm, which is close to the band gap of c-Si and in the spectral region where c-Si solar cells have their optimum conversion efficiency. Two types of schemes can be utilized to achieve efficient conversion of visible light into narrow band NIR emission. A single ion can be used if the ion shows a strong broad band absorption in the visible spectral range followed by relaxation to the lowest excited state from which efficient narrow band or line emission in the NIR occurs. Alternatively, a combination of two ions can be used where one ion (the sensitizer) absorbs the light and subsequently transfers the energy to a second ion (the activator), which emits efficiently in the NIR. Both concepts have been investigated for LSCs by incorporating luminescent lanthanides and transition metal ions in glass matrices. The stability of these systems is not a problem, in contrast to LSCs based on dye molecules, however, the quantum efficiency of luminescent ions in glasses appeared to be much lower than in crystalline compounds, especially in the infrared, thus hampering use for LSCs.

3.2 State of the art

Chung et al. (Chung et al. 2007) reported downshifting phosphor coatings consisting of Y_2O_3:Eu^{3+} or Y_2O_2S:Eu^{3+} dispersed in either polyvinyl alcohol or polymethylmethacrylate on top of mc-Si solar cells: an increase in conversion efficiency was found of a factor of 14 under UV illumination by converting the UV radiation (for which the response of c-Si is low) to 600 nm emission from the Eu^{3+} ion. The used solar cells used were encapsulated in an epoxy that absorbs photons with energy higher that ~3 eV. This protective coating can remain in place and down converters or shifters can easily be added. A 2.9% relative increase in efficiency has been reported for Eu^{3+} containing ethyline-vinyl-acetate layers (EVA) on top of c-Si cells; this is very relevant as EVA nowadays is the standard encapsulating matrix used for c-Si technology.

Svrcek et al. (Svrcek et al. 2004) demonstrated that silicon nanocrystals incorporated into spin-on-glass (SOG) on top of c-Si solar cells are successful as downshifter leading to a potential absolute efficiency enhancement of 1.2%, while they experimentally showed an enhancement of 0.4% (using nanocrystals of 7 nm diameter with a broad emission centered around 700 nm). McIntosh et al. (McIntosh et al. 2009) recently presented results on encapsulated c-Si solar cells, of which the PMMA encapsulant contained down-shifting molecules, i.e., Lumogen dyes. These results indicate a ~1% relative increase in the module efficiency, based on a 40% increase in external quantum efficiency for wavelengths < 400 nm. Mutlugun et al. (Mutlugun et al. 2008) claimed a two-fold increase in efficiency applying a so-called nanocrystal scintillator on top of a c-Si solar cell; it comprises a PMMA layer in which CdSe/ZnS core-shell quantum dots (emission wavelength 548 nm) are embedded. However, the quality of their bare c-Si cells is very poor. Yuan et al. (2011) presented a 14% improved internal quantum efficiency of a silicon oxide layer containing silicon nanocrystals on top of c-Si cells.

Stupca et al. (2007) demonstrated the integration of ultra thin films (2-10 nm) of monodisperse luminescent Si nanoparticles on polycrystalline Si solar cells. 1-nm sized blue emitting and 2.85-nm red emitting particles enhanced the conversion efficiency by 60% in the UV, and 3 to 10% in the visible for the red and blue emitting particles, respectively, similarly to what has been predicted (Van Sark et al. 2005). An 8% relative increase in conversion efficiency was reported (Maruyama and Kitamura 2001) for a CdS/CdTe solar cell, where the coating in which the fluorescent coloring agent was introduced increased the sensitivity in the blue; a maximum increase in efficiency was calculated to be 30-40%. Others showed results that indicate a 6% relative increase in conversion efficiency (Maruyama and Bandai 1999) upon coating a mc-Si solar cell. The employed luminescent species has an absorption band around 400 nm and a broad emission between 450 and 550 nm. As QDs have a much broader absorption it is expected that in potential the deployment of QDs in planar converters could lead to relative efficiency increases of 20-30%. Downshifting employing QDs in a polymer composite has been demonstrated in a light-emitting diode (LED), where a GaN LED was used as an excitation source for QDs emitting at 590 nm (Lee et al. 2000). Besides QDs, other materials have been suggested such as rare earth ions and dendrimers (Serin et al. 2002). A maximum increase of 22.8% was calculated for a thin film coating of $KMgF_3$ doped with Sm on top of a CdS/CdTe solar cell, while experimental results show an increase of 5% (Hong and Kawano 2003).

Recent efforts to surpass the historical 4% efficiency limit of LSCs (Goetzberger 2008, Wittwer et al. 1984, Zastrow 1994), albeit for smaller area size, have been successful. For example, Goldschmidt et al. (2009) showed for a stack of two plates with different dyes, to which four GaInP solar cells were placed at the sides, that the conversion efficiency is 6.7%; the plate was small (4 cm^2), and the concentration ratio was only 0.8. It was argued that the conversion efficiency was limited by the spectral range of the organic dyes used, and that if the same quantum efficiency as was reached for the 450-600 nm range could be realized for the range 650-1050 nm an efficiency of 13.5% could be within reach. They also discuss the benefits of a photonic structure on top of the plate, to reduce the escape cone loss (Goldschmidt et al. 2009). The proposed structure is a so-called rugate filter; this is characterized by a varying refractive index in contrast to standard Bragg reflectors, which suppresses the side loops that could lead to unwanted reflections. The use of these filters would increase the efficiency by ~20%, as was determined for an LSC consisting of one plate and dye. Slooff et al. (2008) presented results on 50x50x5 mm^3 PMMA plates in which both CRS040 and Red305 dyes were dispersed at 0.003 and 0.01 wt%, respectively. The plates were attached to either mc-Si, GaAs or InGaP cells, and a diffuse reflector (97% refection) was used at the rear side of the plate. The highest efficiency measured was 7.1% for 4 GaAs cells connected in parallel (7% if connected in series).

As stated above, quantum dots are potential candidates to replace organic dye molecules in an LSC, for their higher brightness, better stability, and wider absorption spectrum (Barnham et al. 2000, Chatten et al. 2003a, b, Gallagher et al. 2007). In fact, the properties and availability of QDs started renewed interest in LSCs around 2000 (Barnham et al. 2000), with the main focus on modeling, while more recently some experimental results have been presented. Schüler et al. (2007) proposed to make LSCs by coating transparent glass substrates with QD-containing composite films, using a potentially cheap sol-gel method. They reported on the successful fabrication of thin silicon oxide films that contain CdS QDs using a sol-gel dip-coating process, whereby the 1-2 nm sized CdS QDs are formed during

thermal treatment after dip-coating. Depending on the anneal temperature, the colors of the LSC ranged from green for 250 °C to yellow for 350 °C and orange for 450 °C. Reda (2008) also prepared CdS QD concentrators, using sol-gel spin coating, followed by annealing. The annealing temperature was found to affect absorption and emission spectrum: luminescent intensity and Stokes' shift both decreased for 4 weeks outdoor exposure to sunlight, which probably was caused by aggregation and oxidation. It is known that oxidation leads to blue-shifts in emission (Van Sark et al. 2002). Blue-shifts have also been observed by Gallagher et al. (2007) who dispersed CdSe QDs in several types of resins (urethane, PMMA, epoxy), for fabrication of LSC plates.

Bomm et al. (2011) have addressed several problems regarding incorporation of QDs in an organic polymer matrix, viz. phase separation, agglomeration of particles leading to turbid plates, and luminescence quenching due to exciton energy transfer (Koole et al. 2006). They have synthesized QDSCs using CdSe core/multishell QDs (Koole et al. 2008) (QE = 60%) that were dispersed in laurylmethacrylate (LMA), see also Lee et al. (2000) and Walker et al. (2003). UV-polymerization was employed to yield transparent PLMA plates with QDs without any sign of agglomeration. To one side of this plate, a mc-Si solar cell was placed, and aluminum mirrors to all other sides. Compared to the bare cell (5x0.5 cm²) that generated a current density of 40.28 mA/cm² at 1000 W AM1.5G spectrum, the best QDC made generated a current of 77.14 mA/cm², nearly twice as much. The QDC efficiency is 3.5%. In addition, exposure to a 1000 W sulphur lamp for 280 hours continuously showed very good stability: the current density decreased by 4% only, on average. However, re-absorption may still be a problem, as is demonstrated by a small red shift in the emission spectrum for long photon pathways; also absorption by the matrix is occurring. Besides QDs also nanorods (NRs) have been dispersed in PLMA, showing excellent transmittance of 93%; for long rods (aspect ratio of 6) a QE of 70% is observed, which is only slightly smaller than the QE in solution, implying that these rods are stable throughout the polymerization process. In addition, these NRs have also been dispersed in cellulosetriacetate (CTA), and a ~10 μm thin film on a glass substrate was made showing bright orange luminescence (Bomm et al. 2010).

Hyldahl et al. (2009) used commercially available CdSe/ZnS core/shell QDs with QE=57% in LSCs, both liquid (QDs dissolved in toluene, between two 6.2x6.2x0.3 cm glass plates) and solid (QDs dispersed in epoxy), and they obtained an efficiency of 3.98% and 1.97%, respectively. They also used the organic dye Lumogen F Red300, and obtained efficiency of 2.6% in toluene.

4. Upconversion

4.1 Principles

Upconversion was, like DC also suggested in the 1950s, by Bloembergen (1959), and was related to the development of IR detectors: IR photons would be detected through sequential absorption, as would be possible by the arrangement of energy levels of a solid. However, as Auzel (2004) pointed out the essential role of energy transfer was only recognized nearly 20 years later. Several types of upconversion mechanisms exist (Auzel 2004), of which the APTE (addition de photon par transferts d'energie) or, in English, ETU (energy transfer upconversion) mechanism is the most efficient; it involves energy transfer from an excited ion, named sensitizer, to a neighbouring ion, named activator (see Fig. 5).
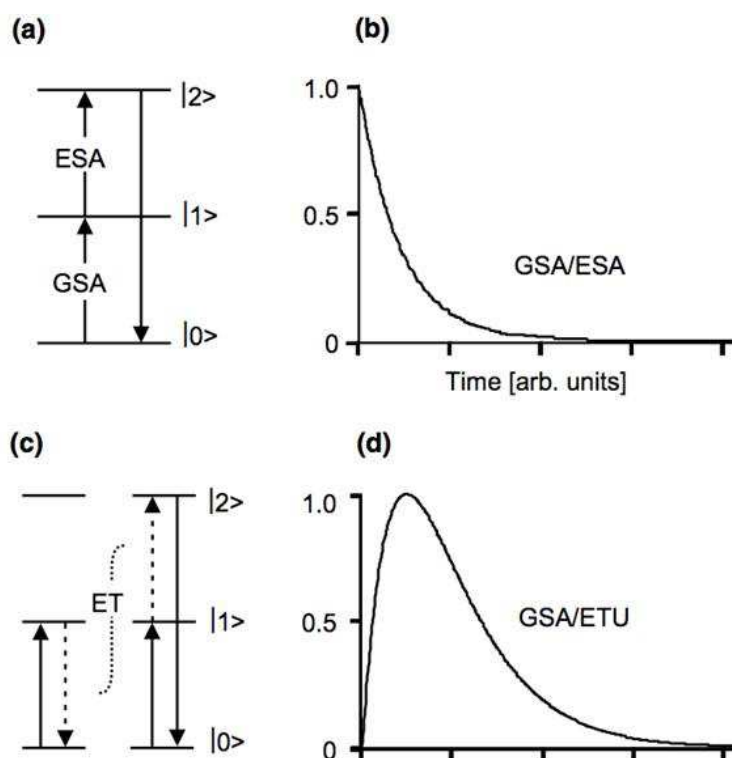
Fig. 5. Schematic representation of two upconversion processes and the characteristic time response of the up converted emission after a short excitation pulse. (a), (b) Ground state absorption (GSA) followed by excited state absorption (ESA). This is a single ion process and takes place during the excitation pulse. (c), (d) Upconversion is achieved by GSA followed energy transfer between ions and the delayed response is characteristic of the energy transfer up conversion (ETU) (from Suyver et al. 2005a).

Others are two-step absorption, being a ground state absorption (GSA) followed by an excited state absorption (ESA), and second harmonics generation (SHG). The latter mechanism requires extremely high intensities, of about 10^{10} times the sun's intensity on a sunny day, to take place (Strümpel et al. 2007). This may explain that research in this field with focus on enhancing solar cell efficiency was started only recently (Shalav et al. 2007). Upconverters usually combine an active ion, of which the energy level scheme is employed for absorption, and a host material, in which the active ion is embedded. The most efficient upconversion has been reported for the lanthanide ion couples (Yb, Er) and (Yb, Tm); the corresponding upconversion schemes are shown in Fig. 6. The first demonstration of such an UC layer on the back of solar cells comprised an ultra thin (3 μm) GaAs cell (band gap 1.43 eV) that was placed on a 100 μm thick vitroceramic containing Yb^{3+} and Er^{3+} (Gibart et al. 1996): it showed 2.5% efficiency upon excitation of 256 kW/m2 monochromatic sub-band-gap (1.391 eV) laser light (1 W on 0.039 cm2 cell area), as well as a clear quadratic dependence on incident light intensity.
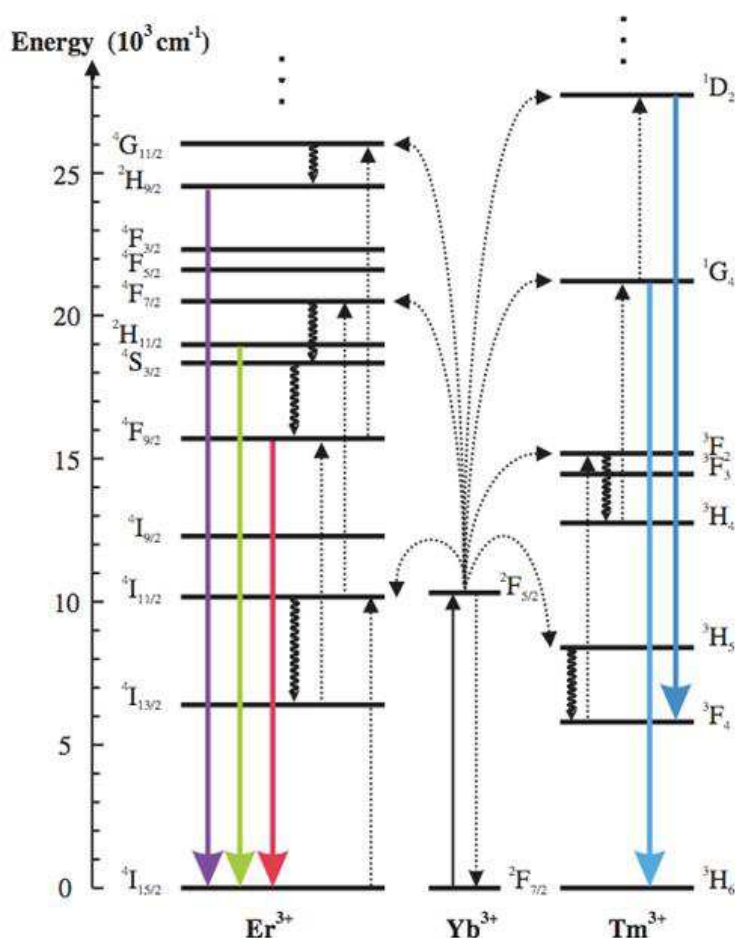
Fig. 6. Up conversion by energy transfer between Yb^{3+} and Er^{3+} (left) and Yb^{3+} and Tm^{3+} (right). Excitation is around 980 nm in the Yb^{3+} ion and by a two-step energy transfer or three-step energy transfer process higher excited states of Er^{3+} or Tm^{3+} are populated giving rise to visible (red, green or blue) emission. Full, dotted, and curly arrows indicate radiative, nonradiative energy transfer, and multiphonon relaxation processes, respectively (from Suyver et al. 2005a).

Upconversion in solar cells was calculated to potentially lead to a maximum conversion efficiency of 47.6 % (Trupke et al. 2002b) for nonconcentrated sunlight using a 6000K blackbody spectrum in detailed-balance calculations. This optimum is reached for a solar cell material of ~2 eV band gap. Applied on the back of silicon solar cells,the efficiency limit would be ~37% (Trupke et al. 2002b). The analysis of the energy content of the incident AM1.5G spectrum presented in Fig. 3 revealed that cells with an UC layer would benefit from an extra amount of 35% light incident in the silicon solar cell (Richards 2006a).

4.2 State of the art
Lanthanides have also been employed in upconverters attached to the back of bifacial silicon solar cells. Trivalent erbium is ideally suited for up conversion of NIR light due to its ladder of nearly equally spaced energy levels that are multiples of the $^4I_{15/2}$ to $^4I_{13/2}$ transition (1540 nm) (see also Fig. 3). Shalav et al. (2005) have demonstrated a 2.5% increase of external quantum efficiency due to up conversion using $NaYF_4$:20% Er^{3+}. By depicting luminescent

emission intensity as a function of incident monochromatic (1523 nm) excitation power in a double-log plot, they showed that at low light intensities a two-step up conversion process ($^4I_{15/2} \rightarrow {}^4I_{13/2} \rightarrow {}^4I_{11/2}$) dominates, while at higher intensities a three-step up conversion process ($^4I_{15/2} \rightarrow {}^4I_{13/2} \rightarrow {}^4I_{11/2} \rightarrow {}^4S_{3/2}$ level) is involved.

Strümpel et al. have identified the materials of possible use in up- (and down-) conversion for solar cells (Strümpel et al. 2007). In addition to the $NaYF_4$:(Er,Yb) phosphor, they suggest the use of $BaCl_2$:(Er^{3+},Dy^{3+}) (Strümpel et al. 2005), as chlorides were thought to be a better compromise between having a low phonon energy and a high excitation spectrum, compared to the $NaYF_4$ (Gamelin and Güdel 2001, Ohwaki and Wang 1994, Shalav et al. 2007). These lower phonon energies lead to lower non-radiative losses. In addition, the emission spectrum of Dysprosium is similar to that of Erbium, but the content of Dy^{3+} should be <0.1%, to avoid quenching (Auzel 2004, Strümpel et al. 2007).

$NaYF_4$ co-doped with (Er^{3+}, Yb^{3+}) is to date the most efficient upconverter (Suyver et al. 2005a, Suyver et al. 2005b), with ~50% of all absorbed NIR photons up converted and emitted in the visible wavelength range. However, the (Yb, Er) couple is not considered beneficial for up conversion in c-Si cells, as silicon also absorbs in the 920-980 nm wavelength range. These phosphors can be useful for solar cells based on higher band gap materials such as the Grätzel-cell (O'Regan and Grätzel 1991), a-Si(Ge):H or CdTe. In that case, the $^2F_{5/2}$ level of Yb^{3+} would serve as an intermediate step for up conversion (Shalav et al. 2007) and IR-radiation between ~700 and 1000 nm that is not absorbed in these wider band gap solar cells can be converted into green (550 nm) light that can be absorbed. Nanocrystals of $NaYF_4$:Er^{3+}, Yb^{3+} also show upconversion. An advantage of using nanocrystals is that transparent solutions or transparent matrices with upconverting nanocrystals can be obtained. An excellent recent review on upconverting nanoparticles summarizes the status of a variety of UC materials that are presently available as nanocrystals, mostly phosphate and fluoride NCs (Haase et al., 2011). A problem with upconversion NCs is the lower upconversion efficiency (Boyer et al., 2010). There is a clear decrease in efficiency with decreasing size in the relevant size regime between 8 and 100 nm. The decrease in efficiency is probably related to surface effects and quenching by coupling with by high energy vibrations in molecules attached to the surface.

When applying an upconverter, it is advantageous to use it with a cell that with a rather high band gap, such as amorphous Si (1.7 eV). A typical external collection efficiency (ECE) graph of a standard single junction p-i-n a Si:H solar cell is shown in Fig. 7. These cells are manufactured on textured SnO_2:F coated glass substrates and routinely have >10% initial efficiency. Typically, the active Si layer in the cell has a thickness of 300 nm and the generated current is 14.0-14.5 mA/cm², depending on the light trapping properties of the textured metal oxide and the back reflector. After light-induced introduction of the stabilized defect density (Staebler-Wronski effect (Schropp and Zeman 1998)), the stabilized efficiency is 8.2-8.5%. From Fig. 7 it can be seen that the maximum ECE is 0.8 at ~550 nm, and the cut-off occurs at 700 nm, with a response tailing towards 800 nm. The response is shown with and without the use of a buffer layer at the front of the cell. The buffer layer causes already an improvement at the short wavelengths, and a down converter or shifter may not be beneficial. The purpose of an upconverter is to tune the energy of the emitted photons to the energy where the spectral response shows a maximum. If the energy of the emitted photons is too close to the absorption limit (the band gap edge), then the absorption coefficient is too low and the up converted light would not be fully used.
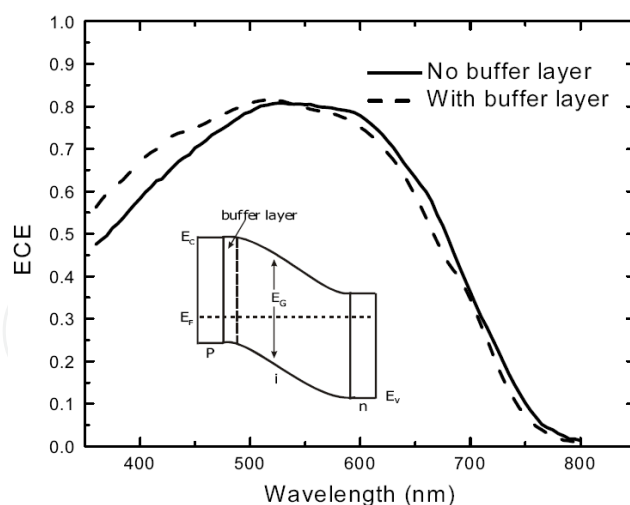
Fig. 7. The spectral response for cells with and without a buffer layer at the p/i interface in the as deposited state obtained at -1 V bias voltage. Inset: the p-i-n- structure showing the position of the buffer layer (from Munyeme et al. 2004).

The photogenerated current could be increased by 40% if the spectral response was sustained at high level up to the band gap cut off at 700 nm and by even more if light with wavelengths $\lambda > 700$ nm could be more fully absorbed. These two effects can be achieved with the upconversion layer, combined with a highly reflecting back contact. While the upconversion layer converts sub-bandgap photons to super-bandgap photons that can thus be absorbed, a non-conductive reflector is a much better alternative than any metallic mirror, thus sending back both the unabsorbed super-bandgap photons as well as the "fresh" super-bandgap photons into the cell. It is estimated that the stabilized efficiency of the 8.2-8.5% cell can be enhanced to ~12 %. Besides a-Si, a material denoted as protocrystalline Si could be used; this is an amorphous material that is characterized by an enhanced medium range structural order and a higher stability against light-induced degradation compared to standard amorphous silicon. The performance stability of protocrystalline silicon is within 10% of the initial performance; its band gap is slightly higher (1.8 eV) than amorphous silicon.

De Wild et al. (2011) have demonstrated upconversion for a-Si cells with $NaYF_4$ co-doped with (Er^{3+}, Yb^{3+}) as upconverter. The upconverter shows absorption of 980 nm (by the Yb^{3+} ion) leading to efficient emission of 653 nm (red) and 520-540 nm (green) light (by the Er^{3+}) after a two-step energy transfer process. The narrow absorption band around 980 nm for Yb^{3+} limits the spectral range of the IR that can be used for up conversion. An external quantum efficiency of 0.02% at 980 nm laser irradiation was obtained. By using a third ion (for example Ti^{3+}) as a sensitizer the full spectral range between 700 and 980 nm can be efficiently absorbed and converted to red and green light by the Yb-Er couple. The resulting light emission in the green and red region is very well absorbed by the cell with very good quantum efficiency for electron-hole generation.

Upconversion systems consisting of lanthanide nanocrystals of $YbPO_4$ and $LuPO_4$ have been demonstrated to be visible by the naked eye in transparent solutions, however at efficiency lower than solid state up conversion phosphors (Suyver et al. 2005a). Other host lattices (Na_XF_4, X=Y,Gd,La) have been used and codoping with Yb^{3+} and Er^{3+}, or Yb^{3+} and Tm^{3+} appeared successful, where Yb^{3+} acts as sensitizer. Nanocrystals of <30 nm in size, to

prevent scattering in solution, have been prepared and they can be easily dissolved in organic solvents forming colloidal solutions, without agglomeration. Further efficiency increase is possible by growing a shell of undoped NaYF$_4$ around the nanocrystal; in addition, surface modification is needed to allow dissolution in water, for use in biological labeling.

Porous silicon layers are investigated for use as up converter layers as host for rare-earth ions, because these ions can easily penetrate the host due to the large surface area and porosity. A simple and low-cost dipping method has been reported (Díaz-Herrera et al. 2009), in which a porous silicon layer is dipped in to a nitrate solution of erbium and ytterbium in ethanol (Er(NO$_3$)$_3$:Yb(NO$_3$)$_3$:C$_2$H$_5$OH), which is followed by a spin-on procedure and a thermal activation process at 900 °C. Excitation of the sample at 980 nm revealed up-conversion processes as visible and NIR photoluminescence is observed; codoping of Yb with Er is essential, doping only with Er shows substantial quenching effects (González-Díaz et al. 2008).

Sensitized triplet-triplet annihilation (TTA) using highly photostable metal-organic chromophores in conjunction with energetically appropriate aromatic hydrocarbons has been shown to be another alternative up conversion system (Singh-Rachford et al. 2008). This mechanism was shown to take place under ambient laboratory conditions, i.e. low light intensity conditions, clearly of importance for outdoor operation. These chromophores (porphyins in this case) can be easily incorporated in a solid polymer so that the materials can be treated as thin film materials (Islangulov et al. 2007). A problem with TTA upconverters is the spectral range. No efficient upconversion of NIR radiation at wavelengths beyond 800 nm has been reported which limits the use to very wide bandgap solar cells (Singh-Rachford et al, 2010).

5. Modeling of spectral conversion

An extension to the models described above was presented in a study by Trupke et al. (2006), in which realistic spectra were used to calculate limiting efficiency values for up conversion systems. Using an AM1.5G spectrum leads to a somewhat higher efficiency of 50.69% for a cell with a band gap of 2.0 eV. For silicon, the limiting efficiency would be 40.2%, or nearly 10% larger than the value of 37% obtained for the 6000K blackbody spectrum (Trupke et al. 2002b). This increase was explained by the fact that absorption in the earths' atmosphere at energies lower than 1.5 eV (as evident in the AM1.5G spectrum) leads to a decrease in light intensity. Badescu and Badescu (2009) have presented an improved model, that according to them it appropriately takes into account the refractive index of solar cell and converter materials. Two configurations are studied: cell and rear converter (C-RC), the usual up converter application, and front converter and cell (FC-C), respectively. They confirm the earlier results of Trupke et al. (2002b) in that the limiting efficiency is larger than that of a cell alone, with higher efficiencies at high concentration. Also, the FC-C combination, i.e., up converter layer on top of the cell, does not improve the efficiency, which is obvious. Further, by studying the variation of refractive indexes of cell and converter separately, as opposed to Trupke et al. (2002b), it was found that the limiting efficiency increases with refractive index of both cell and up converter. In practice, a converter layer may have a lower refractive index (1.5, for a transparent polymer: polymethylmethacrylate (PMMA) (Richards and Shalav 2005)) , than that of a cell (3.4). Using a material with similar refractive index as the cell would improve the efficiency by about 10%.

In a series of papers the groups of Badescu, De Vos and co-workers (Badescu and De Vos 2007, Badescu et al. 2007, De Vos et al. 2009) have re-examined the model for down conversion as proposed by Trupke et al. (2002a), and have added the effects of non-radiative recombination and radiation transfer through interfaces. Analogous to the model for up converters they studied FC-C and C-RC configurations, with down conversion or shifting properties. First, neglecting non-radiative recombination, Badescu et al. (2007) qualitatively confirm the results presented by Trupke and co-workers (2002a). For both configurations, the efficiency of the combined system is larger than that of a single mono-facial cell, albeit that the efficiency is smaller (~26%) due to inclusion of front reflections. Second, including radiative recombination for both converter and cell does only increase the efficiency for high (near unity) radiative recombination efficiency values. Interestingly, they report that in this case the C-RC combination cell-rear converter yields a higher efficiency than the FC-C combination in high-quality solar cells, while for low quality solar cells, this is reversed. More realistic device values and allowing for different refractive indices in cell and converter was studied by (Badescu and De Vos 2007), leading to the conclusion that in reality down converters may not always be beneficial. However, extending the model once more, with the inclusion of anti-reflection coating and light trapping texture, showed a limiting efficiency of 39.9%, as reported by De Vos et al. (2009).

Del Cañizo et al. (2008) presented a Monte Carlo ray-tracing model, in which photon transport phenomena in the converter/solar cell system are coupled to non-linear rate equations that describe luminescence. The model was used to select candidate materials for up- and down-conversion, but was set-up for use with rare-earth ions. Results show that for both converters, the potential gain in short-circuit current is small, and may reach 6-7 mA/cm^2 at intensities as high as 1000 suns, in correspondence with earlier work by Shalav et al. (2007).

Modelling downshifting layers on solar cells was also extended for non-AM1.5G spectra, including varying air mass between 1 and 10, and diffuse and direct spectra (Van Sark 2005). Here, the PC1D model (Basore and Clugston 1996) was used to model quantum dots dispersed in a PMMA layer on top of a multi-crystalline silicon cell (mc-Si) as function of the concentration of quantum dots. Annual performance has been modelled by using modelled spectra from the model SEDES2 (Houshyani Hassanzadeh et al. 2007, Nann and Riordan 1991); these spectra can be considered realistic as actual irradiation data is used as input. It was found that the simulated short current enhancement, which varies between about 7% and 23%, is linearly related with the average photon energy (APE) of the spectra, based on hourly spectra of four typical and other randomly selected days throughout the year, and of monthly spectra. The annual short circuit increase was determined at 12.8% using the annual distribution of APE values and their linear relation (Van Sark 2007), which is to be compared with the 10% increase in case of the AM1.5G spectrum. For mc-Si cells with improved surface passivation and a concomitant improved blue response the relative short current increase has been calculated to be lower (Van Sark 2006).

Modeling large area LSCs has indicated the importance of top-surface losses that occur through the escape cone (Chatten et al. 2007) both through primary emission and through emission of luminescence that has been reabsorbed and might otherwise have been trapped via total internal reflection or by mirrors. As an example, for an idealized (perfectly transparent host, LQE = 1), mirrored (perfect mirrors on one short and two long edges, and the bottom surface), 40×5×0.5 cm LSC doped with CdSe/ZnS core-shell QDs with emission matched to a GaInP cell, 24% of the AM1.5G spectrum is absorbed. The photon concentration ratio, C, which is the ratio of the concentrated flux escaping the right-hand

surface of the LSC to the flux incident on the top surface, is 4.18. However, since the concentrated flux escaping the right-hand surface is a narrow-band matched to the spectral response of the cell it can all be converted and the idealized LSC would produce 8 times the current compared to the cell alone exposed to AM1.5G. However, 78% of the luminescence is lost through the large top-surface area and only 22% may be collected at the right-hand surface. This lead to the use of wavelength-selective cholesteric liquid crystal coatings applied to the top surface in order to reduce the losses (Debije et al. 2006), as these coatings are transparent to incoming light but reflect the emitted light.

Ray-tracing for LSCs uses basic ray-tracing principles, which means that a ray representing light of a certain wavelength travelling in a certain direction, is traced until it leaves the system e.g. by absorption or reflection at the interface (Burgers et al. 2005, Gallagher et al. 2004). The main extension to the standard ray-tracing model is the handling of the absorption and emission by the luminescent species in the LSC. Ray-tracing has been used to perform parameter studies for a 5x5 cm^2 planar LSC to find attainable LSC efficiencies. The concentrator consists of a PMMA plate (refractive index n=1.49, absorption 1.5 m^{-1}) doped with two luminescent dyes, CRS040 from Bayer and Lumogen F Red 305 from BASF, with a FQE of 95% (Slooff et al. 2006). With the ray-tracing model the efficiency of this plate together with a mc-Si solar cell was determined to be 2.45%. Results for attaining efficiencies for other configurations are shown in Table 1 (Van Sark et al. 2008a). Replacing the mc-Si cell by a GaAs cell or an InGaP cell, will increase the efficiency from 3.8% to 6.5% and 9.1%, respectively (based on Voc (FF) values of 0.58 V (0.83), 1.00 V (0.83), and 1.38 V (0.84), for mc-Si, GaAs, InGaP, respectively). Thus, the use of GaAs or InGaP cells will result in higher efficiencies, but these cells are more expensive. A cost calculation must be performed to determine if the combination of the luminescent concentrator with this type of cells is an interesting alternative to mc-Si based solar technology.

mc-Si	GaAs	InGaP	parameters
2.4	4.2	5.9	fixed mirrors, 85% reflectivity, dyes with 95% LQE
2.9	5.1	7.1	97% reflectivity "air-gap mirrors" on sides, and 97% reflectivity Lambertian mirror at bottom
3.4	5.9	8.3	reduce background absorption of polymer matrix from 1.5 m^{-1} to 10^{-3} m^{-1}
3.8	6.5	9.1	increase of refractive index from 1.49 to 1.7

Table 1. Calculated efficiencies (in %) for an LSC for various optimized configurations and parameters (Van Sark et al. 2008a). A Lambertian mirror is one that reflects radiation isotropically.

Currie et al. (2008) projected conversion efficiencies as high as 6.8%, for a tandem LSC based on two single LSCs that consist of thin layer of deposited organic dye molecules onto a glass plate to which a GaAs cell was attached. Using CdTe or Cu(In,Ga)Se2 solar cells conversion efficiencies of 11.9% and 14.5%, respectively, were calculated.

Annual performance has been modeled using an LSC of which the properties and geometry resulted from a cost-per-unit-of-power optimization study by Bende et al. (2008). A square plate of 23.7x23.7x0.1 cm^3 was used and in the ray-trace model attached to four c-Si solar cells (18.59% efficiency) on all sides. Using a Lumogen F Red 305 (BASF) dye it was calculated that 46.5% of all photons in the wavelength range of 370-630 nm were collected, leading to an LSC efficiency of 4.24% (Van Sark et al. 2008b). The annual yield of this LSC

was determined using realistic spectra representative for the Netherlands from Houshyani Hassanzadeh and collaborators (2007) and amounted to 41.3 kWh/m², and this is equivalent to an effective annual efficiency of 3.81%.

6. Discussion and outlook

Two issues remain to be solved before downconverters can be applied in solar cells: the absorption strength needs to be increased as the transitions involved for the trivalent lanthanides are sharp and weak (parity forbidden). A second issue is concentration quenching. High Yb-concentrations are needed for efficient energy transfer as every donor (Tb, Pr or Tm) needs to have two Yb-neighbours for energy transfer. For these high concentrations, energy migration over the Yb-sublattice occurs and trapping of the migrating excitation energy by quenching sites strongly reduces the emission output. At present research is conducted to resolve these issues. The limited absorption can be solved by the inclusion of a sensitizer for the $^3P_0$ level of Pr^{3+}, which is able to absorb efficiently over a broad wavelength range (300-500 nm) and subsequent energy transfer to the $^3P_0$ level of Pr^{3+}. In principle, such sensitization can be realized in an efficient and cost-effective manner by the inclusion of a sensitizer ion. The 4f-5d luminescence of Ce^{3+}, for example, is often used to sensitize the Tb^{3+} luminescence in phosphors for fluorescent tubes. Concentration quenching may be limited by optimization of the synthesis conditions (less quenching sites) while also the synthesis of nanocrystals may be beneficial. In nanocrystals the volume probed by energy migration is limited (due to the small size of the nanocrystal) and for defect-free nanocrystals high quantum yields can be expected, similar to the increase in quantum yield observed for quantum dots vs. bulk semiconductors.

For upconverters based on lanthanides absorption strengths need also to be increased and quenching decreased. In addition, upconversion could be useful for solar cells with band gap higher than that of crystalline silicon; thus, research is directed toward optimum matching of NIR absorption and visible emission with the band gap of the solar cell to which the up converter is attached.

Modelling studies on incorporation of conversion layers on top (down converter or down shifter) or at the bottom (upconverter) of single junction solar cells have shown that the conversion efficiency may increase by about 10% (Glaeser and Rau 2007, Richards 2006b, Strümpel et al. 2007, Trupke et al. 2006, Van Sark 2005, Van Sark et al. 2005). This is still an experimental challenge. Also, stability of converter materials is a critical issue, as their lifetime should be >20 years to comply with present solar module practice.

The usefulness of down- and upconversion and downshifting depends on the incident spectrum and intensity. While solar cells are designed and tested according to the ASTM standard (ASTM 2003), these conditions are rarely met outdoors, as discussed by Makrides and collaborators in Chapter 8 of this book. Spectral conditions for solar cells vary from AM0 (extraterrestrial) via AM1 (equator, summer and winter solstice) to AM10 (sunrise, sunset). The weighted average photon energy (APE) (Minemoto et al. 2007) can be used to parameterize this; the APE (using the range 300-1400 nm) of AM1.5G is 1.674 eV, while the APE of AM0 and AM10 are 1.697 eV and 1.307 eV, respectively. Further, overcast skies cause higher scattering leading to diffuse spectra, which are blue-rich, e.g., the APE of the AM1.5 diffuse spectrum is calculated to be 2.005 eV, indeed much larger than the APE of the AM1.5 direct spectrum of 1.610 eV. As DC and DS effectively red-shift spectra, the more blue an incident spectrum contains (high APE) the more gain can be expected (Van Sark 2005, 2008).

Application of DC layers will therefore be more beneficial for regions with high diffuse irradiation fraction, such as Northwestern Europe, where this fraction can be 50% or higher. Thus, luminescent solar concentrators are expected to be deployed successfully in such regions (Van Sark et al. 2008b). In contrast, solar cells with UC layers will be performing well in countries with high direct irradiation fractions or in early morning and evening due to the high air mass resulting in low APE, albeit that the non-linear response to intensity may be limiting.

The variation of the incident spectra are of particular concern for series-connected multiple junction cells, such as triple a-Si:H (Krishnan et al. 2009) and GaAs-based cells. Current-mismatch due to spectral differences with respect to the AM1.5G standard leads to lowering of the conversion efficiency, as the cell with the lowest current determines the total current. It has been shown that the calculated limiting efficiency of a GaAs-based triple cell is reduced to 32.6% at AM5 while its AM1.5G efficiency was 52.5% (Trupke et al. 2006). A single cell with an UC layer, having an AM1.5G efficiency of 50.7%, does not suffer that much from an increase in air mass: at AM5 the efficiency is lowered to 44.0% (Trupke et al. 2006). This so-called spectral robustness is due to the current matching constraints, which are much more relaxed in the cell/UC layer case.

Successfully optimizing absorption strength and quenching in lanthanides based down converters will bring the theoretical limits within reach. This also holds for up conversion, where, in addition triplet-triplet annihilation and mixed transition metal/lanthanide systems (Suyver et al. 2005a) constitute new material systems.

Future use of DS layers on top of solar cells may be limited as blue response of present cells will advance to higher levels (Van Sark 2006). On the other hand, these improvements might require additional expensive processing, while application of a DS layer is expected to be low-cost, as it only involves coating of a plastic with dispersed luminescent species.

LSC development will focus on material systems that: 1) absorb all photons with wavelength > 950 nm, and emit them red-shifted at ~1000 nm, for use with c-Si solar cells, 2) have as low as possible spectral overlap between absorption and emission spectra to minimize re-absorption losses; 3) have near unity luminescence quantum yield; 4) have low escape cone losses; 5) be stable outdoors for more than 10 years; 6) be easy to manufacture at low cost (Rowan et al. 2008). Much progress has occurred, which is illustrated by the recent efficiency record of 7.1% (Slooff et al. 2008) for organic dyes in PMMA. The present lack of NIR dyes will prohibit further increase of conversion efficiency towards the 30% limit. Here, quantum dots or nanorods may have to be used, as their broad absorption spectrum is very favourable. However, they should be emitting in the NIR at high quantum efficiency, larger than the present ~70-80%, and their Stokes' shift should be larger. The latter would be possible as the size distribution of a batch of QDs influences the Stokes' shift (Barnham et al. 2000). Another strategy could be the use of so-called type II QDs, as their Stokes' shift could be very large (~300 nm), however, but their stability and QE are not good enough yet. Stability could be improved using multishell QDs (Koole et al. 2008), while interfacial alloying can be optimized to obtain type II QDs with desired properties, i.e., a Stokes' shift of ~50-100 nm, without spectral overlap (Chin et al. 2007). An different approach was presented recently that employs resonance-shifting to circumvent reabsorption losses (Giebink et al. 2011). Also, Eu^{3+} has been employed succesfully to address self-absorption loss (Wang et al. 2011). Alternatively, the originally proposed three-plate stack (Goetzberger and Greubel 1977) could be further developed using perhaps a combination of organic dyes

and nanocrystals, or even rare earth ions (Rowan et al. 2008), with optimized dedicated solar cells for each spectral region.

7. Conclusion

The possibility to tune chemical and physical properties in nanosized materials could have a transformational effect on the performance of solar cells and one of the prominent research areas of nanomaterials for photovoltaics involves spectral conversion. In this chapter we reviewed pathways of spectrum modification for application in solar cells by means of down- and upconversion, and downshifting. Nanoparticles, based on semiconductors or lanthanides, embedded in predominantly polymer layers on top or at the back of solar cells are an essential ingredient of spectral conversion mechanisms that may potentially lead to higher solar cell conversion efficiencies.

Increasing the conversion efficiency, while keeping manufacture cost as low as possible is the main R&D target in solar photovoltaic energy for the coming decades. Nanomaterial synthesis and nanotechnology will play a key role in this.

8. Acknowledgements

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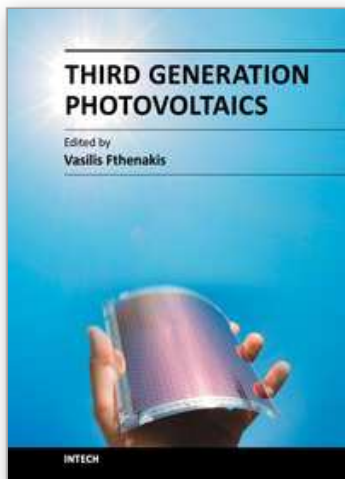
Third Generation Photovoltaics

Edited by Dr. Vasilis Fthenakis

Photovoltaics have started replacing fossil fuels as major energy generation roadmaps, targeting higher efficiencies and/or lower costs are aggressively pursued to bring PV to cost parity with grid electricity. Third generation PV technologies may overcome the fundamental limitations of photon to electron conversion in single-junction devices and, thus, improve both their efficiency and cost. This book presents notable advances in these technologies, namely organic cells and nanostructures, dye-sensitized cells and multijunction III/V cells. The following topics are addressed: Solar spectrum conversion for photovoltaics using nanoparticles; multiscale modeling of heterojunctions in organic PV; technologies and manufacturing of OPV; life cycle assessment of OPV; new materials and architectures for dye-sensitized solar cells; advances of concentrating PV; modeling doped III/V alloys; polymeric films for lowering the cost of PV, and field performance factors. A panel of acclaimed PV professionals contributed these topics, compiling the state of knowledge for advancing this new generation of PV.

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