Efficiency limits of upconversion

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The existence of one discrete band-gap in single-junction solar cells implies that incident photons with energies below this threshold are not efficiently utilized. For silicon solar cells, these sub-band-gap losses amount to more than 20% of the energy incident from the sun. For other types of solar cells with larger band-gaps, made for example from amorphous silicon or organic materials, these losses are even higher. Upconversion has the potential to reduce these losses by converting two or more photons with energies below the threshold to one photon with sufficient energy.

High efficiency increases due to the application of upconverters to silicon solar cells have been predicted theoretically [1-3], but experimental results show only very little increase in overall system efficiency [4-6]. Therefore the question arises, whether there are any fundamental limitations to the upconversion efficiency that have not been considered in the idealized models, or whether the investigated materials just have the wrong properties. Furthermore, different ways to increase upconversion efficiencies have been suggested, including the use of plasmonic or photonic structures. Here the question is, whether such measures actually shift the fundamental limits, or whether they just help to approach the existing limits, thus compensating shortcomings of the used materials.

In [3], the theoretical limit for the efficiency of a silicon solar cell (band-gap 1.117 eV) with additional upconverter, illuminated by non-concentrated light, is reported to be 40%, compared to a radiative limit efficiency of the solar cell alone of 33.25%. Therefore, the relative increase in efficiency due the upconverter is about 20%.
The presence of an upconverter mainly increases the current of the solar cell at the maximum power point. One can calculate the extra current in a solar cell that could be generated by the upconverted photons, based on the number of photons available in the solar spectrum with energies below the band-gap of silicon. This results in a maximum extra current of 12.5 mA/cm^2 for a silicon solar cell under non-concentrating conditions. This calculation has been based on the assumption of a 50% quantum yield (QY) for the upconversion process. This means that one upconverted photon is produced from exactly two lower energy photons. Furthermore, it requires that one very low energy photon needs to be combined with a higher energy photon (but still with an energy below the band-gap), such that the combined energy is higher than the band-gap threshold and all photons below the band-gap are utilized. This limit for the quantum yield can therefore be understood as being imposed by energy conservation. If only the effect of the current increase is considered, the additional current corresponds to an overall increase in efficiency of about 29% relative (based on the maximum current without upconversion of 43.8 mA/cm^2). One can see that this limit is less restricting than the more advanced analysis based on radiative limits from [1, 3], because it does not consider effects of the emission of non-converted photons, which inevitably have to occur as reciprocal processes of the absorption of photons. Nevertheless, one can estimate from a comparison of the different relative increase values that in the radiative limit case, QY values of around 34% must prevail. One has to note, however, that this is only a rough estimate as additional effects, such like the increase of voltage due to the higher current and photon recycling of emitted photons that are considered in the radiative limit model, have been neglected.

In contrast to these QY values far above 30%, experimentally determined values of the upconversion quantum yield are typically much lower: the highest upconversion efficiencies achieved so far have been reported by Richards and Shalav in [4]. They report an internal quantum yield of the upconverter of 16.7% at a very high irradiance of 2.4 W/cm^2 for the micro-crystalline β-$NaY_{0.8}Er_{0.2}F_4$ upconverter material at one specific excitation wavelength of 1523 nm. For upconversion at shorter wavelengths than those suitable for silicon solar cells, good results have been achieved with organic materials, which show triplet-triplet annihilation. Upconversion internal quantum yields as high as 16% have been achieved here [7].

To find an explanation for the considerably lower experimental QY values, the idealizations of the used models have to be critically reviewed. The model of Refs. [1, 3] is based on an equivalent circuit description of the upconverter/solar cell system. One very critical assumption is that photon selectivity is assumed. There are two different upwards transitions involved in the upconversion, which are stimulated by photons of different energies. Therefore, such an upconverter would show no upconversion at all, when excited with a monochromatic source, unlike most of the upconverter materials that have been investigated experimentally, so far. On the other hand, our analyses using a simplified three-level rate equation model show, that also for monochromatic excitation it should be possible to reach an internal QY close to 50%, if all transitions involved can be adapted such that the sequence of processes necessary for the upconversion is the by far most likely event. This would mean that the rate of transitions from the second to the third level, as well as the emission from the third to the ground level have to be much faster, than the transitions from the ground level to the first excited state. In such a configuration the internal QY might be high, while the external QY would be low, as hardly any photons are being absorbed. Nevertheless, this simple analysis points into the direction that a favourable relation between the different transitions is a necessary condition for high efficiencies.

Photonic and plasmonic structures offer control of at least some of the involved transition rates. In a comprehensive theoretical model describing the impact of a photonic structure onto an upconverting material, we showed that an optimized waveguide structure can increase overall luminescence by a factor of 268 and the overall quantum yield by a factor of 9.3 [8]. The model was based on a realistic upconverter material, the resulting overall upconversion quantum yield was 8%, compared to only 0.86% without the structure [9]. The key to the successful optimization of the structure was to increase the local density of photon states especially at the emission energy of the upconverted photons.

The potential impact of the photonic structures are only partly considered in the published efficiency limit models [1, 3]: first, the photonic structures change the local irradiance taking effect on the upconverter, while the irradiance on the solar cell remains the same. In the models, this should increase the emission from the upconverter onto the solar cell, while the emission from the solar cell remains the same. As this means that the net-balance for the solar cell improves, the overall efficiency should increase beyond the limits determined so far. Furthermore, the photonic structures can change the angular emission characteristic, thus they can help to achieve the minimum emission case, which has been found to have the highest efficiency limit. Third, the modified transition probabilities affect the spectral distribution of the emission. These changes would also be present in the absorption spectra. In the models, however, these spectra are already ideal, so no impact on the ideal efficiency limits is expected from this effect. A quantitative analysis of these effects is still ongoing work. Moreover, more complex systems, e.g. with spectral and geometric concentration, as proposed in [2] needs to be investigated.

References

1. Trupke, T., M.A. Green, and P. Würfel, *Improving solar cell efficiencies by up-conversion of sub-band-gap light.* Journal of Applied Physics, 2002. **92**(7): p. 4117-22.
2. Goldschmidt, J.C., et al. *Advanced upconverter systems with spectral and geometric concentration for high upconversion efficiencies*. in *IEEE Conference on Optoelectronic and Microelectronic Materials and Devices (COMMAD 2008)*. 2008. Sydney, Australia.
3. Johnson, C.M. and G.J. Conibeer, *Limiting efficiency of generalized realistic c-Si solar cells coupled to ideal up-converters.* Journal of Applied Physics, 2012. **112**(10): p. 103108.
4. Richards, B.S. and A. Shalav, *Enhancing the near-infrared spectral response of silicon optoelectronic devices via up-conversion.* IEEE Transactions on Electron Devices, 2007. **54**(10): p. 2679-84.
5. Fischer, S., et al., *Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization.* Journal of Applied Physics, 2010. **108**: p. 044912 1-11.
6. Goldschmidt, J.C., et al., *Experimental analysis of upconversion with both coherent monochromatic irradiation and broad spectrum illumination.* Solar Energy Materials and Solar Cells, 2011. **95**(7): p. 1960-1963.
7. Cheng, Y.Y., et al., *On the efficiency limit of triplet-triplet annihilation for photochemical upconversion.* Physical Chemistry Chemical Physics, 2010. **12**(1).
8. Herter, B., et al., *Increased upconversion quantum yield in photonic structures due to field enhancement and a modification of the local density of states – a simulation based analysis.* to be submitted to Physical Review B, 2013.
9. Fischer, S., et al., *Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization.* Journal of Applied Physics, 2010. **108**(4): p. 044912.