Presented at the 29th European PV Solar Energy Conference and Exhibition, 22-26 September 2014, Amsterdam, The Netherlands

RECORD EFFICIENT UPCONVERTER SOLAR CELL DEVICES

Jan Christoph Goldschmidt[1*], Stefan Fischer[2], Barbara Herter[3], Benjamin Fröhlich[4], Karl W. Krämer[5], Bryce S. Richards[6], Aruna Ivaturi[7], Sean K.W. MacDougall[8], Jose Marques-Hueso[9], Elena Favilla[10], Mauro Tonelli[11]

[1,2,3,4]Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany
[5]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
[6]Institute of Microstructure Technology (IMT) and Light Technology Institute (LTI), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[7,8,9] School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland
[10,11]Dipartimento di Fisica - Universita' di Pisa, Largo B. Pontecorvo, 3, 56127 PISA, Italy
[*]jan.christoph.goldschmidt@ise.fraunhofer.de

ABSTRACT: In this paper, we give a historic overview over the development of upconverter solar cell devices and show how performance has increased in the past few years. We present measurements of upconverter solar cell devices showing a world-record increase in short-circuit current density due to upconversion of 0.5% relative for a bifacial crystalline silicon solar cell. Finally, we discuss concepts to further increase upconversion performance: photonic structures that combine local irradiance enhancement and resonant emission amplification and spectral concentration to enlarge the utilized spectral range.

Keywords: Upconversion, Antireflection Coating, Silicon Solar Cell, Concentrators, Spectral Conversion

1 INTRODUCTION

For silicon solar cells, 20% of the energy incident from the sun is lost, because sub-bandgap photons cannot generate electron-hole pairs in the silicon. For other emerging solar cell technologies with higher bandgaps, such as GaAs or perovskite solar cells, these losses are considerably higher, with 34% and 39%, respecttively being lost. Upconversion – the generation of one high-energy photon out of at least two low-energy photons – can reduce these losses. Despite theoretical limits close to 40% for ideal silicon solar cells with attached up-converters [1, 2] real devices stayed far below those values [3-6]. While the early works performed experiments with monochromatic excitation, upconversion has been increasingly investigated under broad-spectrum illumination to determine its potential for solar energy harvesting and efficiencies have increased considerably [7-10]. In this paper, we give an overview of the historic developments in the field of upconverter solar cell devices. Then, we present our measurement results, which constitute new record performances for upconverter solar cell devices. Finally, we discuss how upconversion performance can be further increased with photonic structures and spectral concentration.

2 HISTORIC DEVELOPMENT

As summarized in [20], the first proof-of-concept upconverter solar cell device was realized by Gibart *et al*. in 1996, who attached an trivalent erbium (Er^{3+}) and trivalent ytterbium (Yb^{3+}) co-doped vitroceramic to a gallium-arsenide (GaAs) solar cell [11]. In 2005, Shalav *et al*. were the first to apply a β-$NaYF_4$: 20% Er^{3+} upconverter to a bifacial silicon solar cell [3]. The upconversion in Er^{3+}, which is beneficial for silicon solar cells, occurs mainly via ground state absorption, energy transfer between two excited ions (donor → acceptor) and subsequent spontaneous emission of a high energy photon. Under excitation at 1523 nm the dominant upconversion emission is at 980 nm. Other relevant processes are multi-photon relaxation and - to a limited extent - excited state absorption.

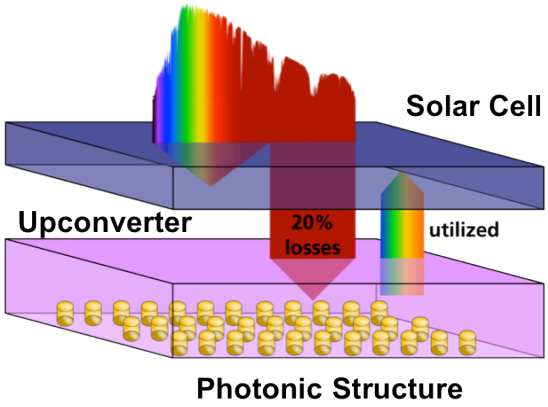

Figure 1 The purpose of upconversion is to harvest photons with sub-bandgap energy and to convert them into photons with sufficient energy for utilization in the solar cell. To avoid any parasitic losses, the upconverter should be placed at the back of the solar cell, which then has to feature a bifacial functionality. Photonic structures can be applied to increase the upconversion performance.

In 2007, Shalav *et al*. reported an external quantum efficiency (EQE) of the combined silicon solar cell upconverter systems of 3.4% under monochromatic excitation with a laser wavelength of 1523 nm and an irradiance of 24000 W/m^2 [12]. Typically, the upconversion quantum yield and therefore the EQE due to upconversion of sub-bandgap photons increase with the irradiance. To facilitate the comparison for values determined at different irradiances, the EQE can be normalized to the irradiance [13]. The values published by Shalav *et al* correspond to a normalized EQE of 0.014 cm^2W^{-1}. In 2010, Fischer *et al*. reported an EQE of 0.34% (1090 W/m^2 at 1523 nm) equivalent to a normalized EQE of 0.03 cm^2W^{-1} [5]. Most of the analyses have been carried out under monochromatic excitation [3, 5, 11, 12, 14-16], while for the application

in photovoltaics broad-band illumination is relevant. The first experiments applying broad-band illumination on upconverter solar cell devices were reported by Goldschmidt *et al*. in 2011. An EQE of 0.81% under broad-band excitation with a photon-flux equivalent to 458 suns was achieved [7]. Since then, the material quality has been improved and the utilized solar cells were customized for the application of upconverters [17]. In Ref. [10], Fischer *et al*. reported an average EQE of 0.69% in the spectral region of 1450 – 1600 nm at 78 suns concentration (equivalent to a normalized EQE of 0.03 cm^2W^{-1}) for β-$NaYF_4$: 25% Er^{3+} embedded in the polymer perfluorocyclobutyl (PFCB) with a powder to polymer concentration of 75.7 w/w%. Using the pure upconverter material β-$NaYF_4$: 25% Er^{3+}, which was filled into a powder cell and attached to the back of an optimized solar cell, an even higher EQE of 1.28% at 77 suns (0.05 cm^2W^{-1}) was achieved [9].

For sun-like illumination, an average EQE value for a certain spectral region is not a very meaningful figure-of-merit. Instead it is more interesting to know, how much additional current can be generated due to upconversion under illumination with the full solar spectrum onto the upconverter solar cell device. In Ref [10] Fischer *et al*. reported an additional short-circuit current density due to upconversion of 13.1 mA/cm^2 for an upconverter silicon solar cell device using a solar concentration of 210 suns. The used upconverter material was β-$NaYF_4$: 25% Er^{3+} embedded in PCFB. The increase in short-circuit current density constitutes a relative increase of the solar cell's short-circuit current density of 0.19%. This is more than a magnitude higher than the value of 0.014% achieved three years earlier [7].

2 DEVICE MEASUREMENTS

Approach

The microcrystalline upconverter materials β-$NaYF_4$: 25% Er^{3+} and Gd_2O_2S: 10% Er^{3+} were embedded in PFCB with 84.9w/w% concentration [6], and mono-crystalline samples of BaY_2F_8: 30% Er^{3+} [18] were attached with an index matching liquid to the rear side of planar bifacial crystalline silicon solar cells that featured broad-band anti-reflection coatings [17]. The created upconverter solar cell devices were characterized using concentrated light of a solar simulator. The incident light was concentrated with a Fresnel lens and the concentration level adjusted by the height of the lens above the device. To facilitate the detection of the upconversion signal, photons with energies above the bandgap were blocked from reaching the solar cell. The measurements were performed with the upconverter material and un-doped references containing no erbium attached to the solar cells. The difference of the two determined short-circuit current densities results in the additional short-circuit current density due to upconversion $\Delta j_{SC,UC}$. A spectral mismatch correction [9] was applied to the results.

Results

As reported in [19], we determined a maximum additional short-circuit current density due to upconversion $\Delta j_{SC,UC}$ of 17.2±3.0 mA/cm^2 at illumination with 94±17 suns for an upconverter solar cell device with an mono-crystalline BaY_2F_8: 30% Er^{3+} upconverter. This translates into a record relative enhancement of 0.55±0.14%, considering the 33.4 mA/cm^2 short-circuit current density of the used silicon solar cell with 17.6% efficiency. A $\Delta j_{SC,UC}$ of 8.1±0.7 mA/cm^2 at 70±6 suns and 5.3±0.5 mA/cm^2 at 67±6 suns were achieved with the micro-crystalline upconverter materials β-$NaYF_4$: 25% Er^{3+} and Gd_2O_2S: 10% Er^{3+}, respectively. These values demonstrate the huge progress that has been made in the last years and constitute a nearly 40 fold increase compared to the only 3 year old best values [7].

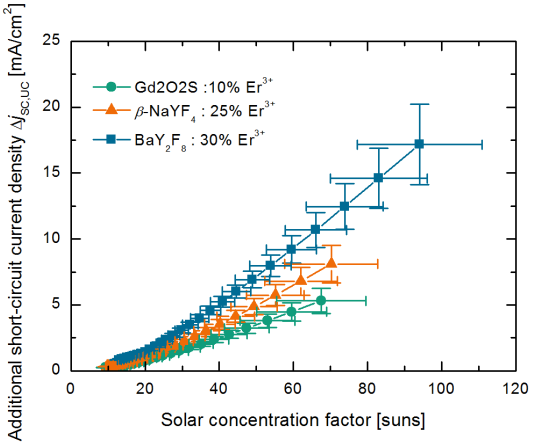

Figure 2: In solar simulator measurements mono-crystalline BaY_2F_8: 30% Er^{3+} showed the highest additional short-circuit current density due to upconversion of sub-bandgap photons $\Delta j_{SC,UC}$. A record value of 17.2±3.0 mA/cm^2 at 94±17 suns was achieved.

3 MEANS TO INCREASE UPCONVERSION PERFORMANCE

Despite the promising progress in the last years, further means to increase upconverter solar cell device performance are necessary, to make upconversion really relevant for photovoltaics. One can distinguish between concepts that enhance the actual process of upconversion and concepts that enlarge the utilized spectral range.

Photonics and external concentration

As we have already summarized in [20], one approach to enhance the upconversion process is to use plasmonic or dielectric photonic structures to a) increase the local irradiance on the upconverter and b) modify the local density of photon states to enhance wanted radiative emission processes and suppress the unwanted [21, 22]. An enhancement of upconversion luminescence by a factor of 3.8 was found in experiments for a single Er^{3+} and Yb^{3+} co-doped upconverter nanoparticle placed at an optimized position in proximity to a gold nanoparticle [23]. Theoretical analyses showed local enhancement factors of the same magnitude, but no significant enhancement averaged over the volume around the metal nanoparticle [24, 25]. The presence of the metal nanoparticle introduces new non-radiative loss processes that may override any positive effects. Dielectric nanostructures, however, are more promising, as they show lower parasitic absorption. In this field, work has concentrated mainly on enhancing the photoluminescence of erbium at a wavelength of 1530 nm (no upconversion). There are less works on the enhancement of

upconversion luminescence. Niu *et al*. reported a 27-fold increase for the emission at around 660 nm under excitation at 980 nm for β-$NaYF_4$: Er^{3+} nanoparticles coated on top of an opal photonic crystal [26]. Johnson *et al*. reported a 6-fold increase for the dominant erbium upconversion emission at 980 nm for β-$NaYF_4$: Er^{3+} nanoparticles embedded into a Bragg stack consisting of 30 bilayers [27].
Furthermore, there are only very few theoretical works investigating the effects of dielectric photonic structures on upconversion that take into account all relevant effects, which are the increased irradiance, the changed local density of photon states, and the internal dynamics of the upconverter [28]. In such a complete analysis [29], investigating the effect of a grating structure, we could show that upconversion luminescence could be increased in average by a factor of 3.0 compared to an unstructured references, while the upconversion quantum yield could be increased by an average factor of 1.5.
Another concept is to use external concentration onto the upconverter to exploit the non-linearity of the upconversion process, which results into higher upconversion quantum yields at higher excitation . Here, it is especially promising to place the concentrator between the solar cell and the upconverter, such that each element can be operated at its optimum concentration level (which usually lower for the silicon solar cell than for the upconverter) [30].

Spectral concentration
The absorption range of the rare-earth ions, where photons can be converted to higher energies, is rather narrow. Typically, Er^{3+}-based upconverter materials feature an absorption range from roughly 1480 nm to 1580 nm. This limited spectral range can be extended by either co-doping of a sensitizer, or by the use of a second luminescent material that absorbs in a wide spectral range and emits in the absorption range of the upconverter [31, 32]. The use of a second luminescent material has the advantage that additional to the larger used spectral range, also the photon flux in the absorption range of the upconverter is enhanced, which then leads to higher upconversion quantum yields. Because a larger spectral region is funnelled into the narrow spectral region where the upconverter is active, this process is also called spectral concentration [31, 32]. Assuming an upconversion quantum yield of 17% (a value that should be attainable with good material at high concentration), about 0.5 mA/cm^2 could be generated by an upconverter material that is active in the spectral range from 1480 to 1580 nm, such as Er^{3+}. Assuming that the photons between the bandgap of silicon and 1480 nm could be shifted to the absorption range of the upconverter with an efficiency of 80% and again assuming 17% quantum yield for the upconversion results into 1.2 mA/cm^2 that could be gained by the spectral concentration and an overall 1.7 mA/cm^2 that could be achieved by upconversion and spectral concentration under 1 sun illumination. This would translate in a roughly 4% relative efficiency gain for a good silicon solar cell. However, for higher bandgap solar cells the potential gains and also the relative impact due to the current enhancements are more substantial. This is also true in the context of silicon based tandem solar cells, where the overall current is lower – usually limited by the silicon solar cell – and therefore significantly higher relative gains could be expected.

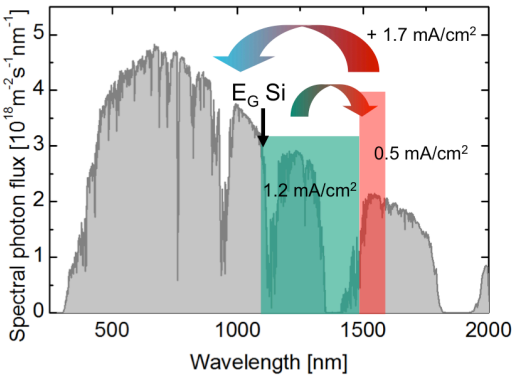

Figure 3: The concept of spectral concentration. Photons in the spectral range between the bandgap of the solar cell and the active region of the upconverter are shifted into the active region of the upconverter by a second luminescent material. For silicon solar cells, 1.2 mA/cm^2 extra could be gained by spectral concentration on top of 0.5 mA/cm^2 from the Er^{3+} upconverter alone assuming 80% quantum efficiency of the downshifting and 17% quantum yield of the upconversion.

4 SUMMARY

The performance of upconverter solar cell devices has increased considerably in the past few years. Recently a new record value of 17.0±3.0 mA/cm^2 additional short-circuit current density due to upconversion of sub-bandgap photons for a sun-like illumination with 94±17 suns was achieved, for an upconverter solar cell device consisting of an bifacial crystalline silicon solar cell and a mono-crystalline BaY_2F_8: 30% Er^{3+} upconverter [19]. This translates into a record relative enhancement of 0.55±0.14%, considering the 33.4 mA/cm^2 short-circuit current density of the used silicon solar cell. These values constitute a nearly 40 fold increase compared to the only 3 year old best values. To further increase the upconversion performance, photonic structures could be applied, for instance. Theoretical analyses show that a grating structure could increase the upconversion quantum yield by a factor of 1.5. Furthermore, spectral concentration, the downshifting of photons with energies between the bandgap of the solar cell and the active region of the upconverter into the active region of the upconverter, could more than triple upconverter performance.

5 ACKNOWLEDGEMENT

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n°[246200] within the Nanospec project and from the German Federal Ministry of Education and Research in the project “InfraVolt – Infrarot-Optische Nanostrukturen für die Photovoltiak” (BMBF, project numbers 03SF0401B), as well as from Fondazione Pisa in the project "Increased solar energy conversion" ACES (183/2011).

6 REFERENCES

[1] C.M. Johnson and G.J. Conibeer, *Limiting efficiency of generalized realistic c-Si solar cells coupled to ideal up-converters,* Journal of Applied Physics, 112(10) (2012)

[2] T. Trupke, *et al.*, *Efficiency enhancement of solar cells by luminescent up-conversion of sunlight,* Solar Energy Materials & Solar Cells, 90(18-19), 3327-38 (2006)

[3] A. Shalav, *et al.*, *Application of $NaYF_4:Er^{3+}$ up-converting phosphors for enhanced near-infrared silicon solar cell response,* Applied Physics Letters, 86(1), 13505 (2005)

[4] B.S. Richards and A. Shalav, *Enhancing the near-infrared spectral response of silicon optoelectronic devices via up-conversion,* IEEE Transactions on Electron Devices, 54(10), 2679-84 (2007)

[5] S. Fischer, *et al.*, *Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization,* Journal of Applied Physics, 108(4), 044912 (2010)

[6] A. Ivaturi, *et al.*, *Optimizing infrared to near infrared upconversion quantum yield of β-$NaYF_4:Er^{3+}$ in fluoropolymer matrix for photovoltaic devices,* Journal of Applied Physics, 114(1), 013505 (2013)

[7] J.C. Goldschmidt, *et al.*, *Experimental analysis of upconversion with both coherent monochromatic irradiation and broad spectrum illumination,* Solar Energy Materials and Solar Cells, 95(7), 1960-3 (2011)

[8] S.K.W. MacDougall, *et al.*, *Ultra-high photoluminescent quantum yield of β-NaYF4: 10% Er^{3+} via broadband excitation of upconversion for photovoltaic devices,* Opt. Express, 20(S6), A879-A887 (2012)

[9] S. Fischer, *et al.*, *Absolute upconversion quantum yield of β-$NaYF_4$ doped with Er^{3+} and external quantum efficiency of upconverter solar cell devices under broad-band excitation considering spectral mismatch corrections,* Solar Energy Materials and Solar Cells, 122(0), 197-207 (2014)

[10] S. Fischer, *et al.*, *Upconverter Silicon Solar Cell Devices for Efficient Utilization of Sub-Band-Gap Photons Under Concentrated Solar Radiation,* IEEE Journal of Photovoltaics, 4(1), 183-189 (2014)

[11] P. Gibart, *et al.*, *Below band-gap IR response of substrate-free GaAs solar cells using two- photon up-conversion,* Japanese Journal of Applied Physics, 35(8), 4401-2 (1996)

[12] A. Shalav, *et al.*, *Luminescent layers for enhanced silicon solar cell performance: up-conversion,* Solar Energy Materials & Solar Cells, 91(9), 829-42 (2007)

[13] F. Auzel, *Upconversion and anti-stokes processes with f and d ions in solids,* Chemical Review, 104, 139-73 (2004)

[14] C. Strümpel, *et al.*, *Modifying the solar spectrum to enhance silicon solar cell efficiency — An overview of available materials,* Solar Energy Materials & Solar Cells, 91, 238-49 (2007)

[15] J.-C. Boyer and F.C.J.M. van Veggel, *Absolute quantum yield measurements of colloidal $NaYF_4$: Er^{3+}, Yb^{3+} upconverting nanoparticles,* Nanoscale, 2(8), 1417-9 (2010)

[16] J. de Wild, *et al.*, *Enhanced near-infrared response of a-Si:H solar cells with β-NaYF4:Yb3+ (18%), Er3+ (2%) upconversion phosphors,* Solar Energy Materials and Solar Cells, 94(12), 2395-2398 (2010)

[17] M. Rüdiger, *et al.*, *Bifacial n-Type Silicon Solar Cells for Upconversion Applications,* Solar Energy Materials and Solar Cells, submitted (2013)

[18] A. Boccolini, *et al.*, *BaY_2F_8 doped with Er^{3+}: An upconverter material for photovoltaic application,* Journal of Applied Physics, 114(6), 064904 1-6 (2013)

[19] S. Fischer, *et al.*, *Record Efficient Upconverter Solar Cell Devices with Optimized Bifacial Silicon Solar Cells and Monocrystalline Ba_2F_8:30% Er^{3+} Upconverter,* submitted to Solar Energy Materials and Solar Cells, (2014)

[20] J.C. Goldschmidt, *et al.*, *Photon management with luminescent materials and photonic structures*, Proceedings of SPIE, 2014, p. 91400G 1-8

[21] J.C. Goldschmidt, *et al.*, *Increasing upconversion by plasmon resonance in metal nanoparticles - a combined simulation analysis,* IEEE Journal of Photovoltaics, 2(2), 134-40 (2012)

[22] J.C. Goldschmidt, *et al.*, *Increasing upconversion by metal and dielectric nanostructures*, Proceedings of SPIE, 2012, p. 825602 1-9

[23] S. Schietinger, *et al.*, *Plasmon-enhanced upconverion in single $NaYF_4:Yb^{3+}/Er^{3+}$ codoped nanocrystals,* Nano Letters, 10(1), 134-8 (2010)

[24] S. Fischer, *et al.*, *Plasmon enhanced upconversion luminescence near gold nanoparticles - simulation and analysis of the interactions,* Optics Express, 20(1), 271-82 (2012)

[25] S. Fischer, *et al.*, *Plasmon enhanced upconversion luminescence near gold nanoparticles - simulation and analysis of the interactions: Errata,* Optics Express, 21(9), 10606-10611 (2013)

[26] W.B. Niu, *et al.*, *3-Dimensional photonic crystal surface enhanced upconversion emission for improved near-infrared photoresponse,* Nanoscale, 6(2), 817-824 (2014)

[27] C.M. Johnson, *et al.*, *Theoretical and experimental evaluation of silicon photonic structures for enhanced erbium up-conversion luminescence,* Solar Energy Materials and Solar Cells, 112, 168-181 (2013)

[28] B. Herter, *et al.*, *Increased upconversion quantum yield in photonic structures due to local field enhancement and modification of the local density of states - a simulation-based analysis,* Optics Express, 21(18), A883-A900 (2013)

[29] Barbara Herter, *et al.*, *Photonic Structures Enhancing Upconversion Luminescence,* in preparation, (2014)

[30] G.E. Arnaoutakis, *et al.*, *Enhanced up-conversion for photovoltaics via concentrating integrated optics,* Optics Express, 22(5), A452-A464 (2014)

[31] C. Strümpel, *et al.*, *Erbium-doped up-converters of silicon solar cells: assessment of the potential*, Proceedings of the 20th European Photovoltaic Solar Energy Conference, 2005, p. 43-6

[32] J.C. Goldschmidt, *et al.*, *Advanced Upconverter Systems with Spectral and Geometric Concentration for high Upconversion Efficiencies*, Proceedings of Optoelectronic and Microelectronic Materials and Devices (COMMAD), 2008, p. 307-11