IMPROVED PHOTON UPCONVERSION IN AMORPHOUS SILICON SOLAR CELLS

J. de Wild[1], A. Meijerink[2], J.K. Rath[1], W.G.J.H.M. van Sark[3], R.E.I. Schropp[1]
[1] Utrecht University, Faculty of Science, Debye Institute for Nanomaterials Science, Nanophotonics, P.O. Box 80000, 3508 TA Utrecht, The Netherlands
[2] Utrecht University, Faculty of Science, Debye Institute for Nanomaterials Science, Condensed Matter and Interfaces, P.O. Box 80000, 3508 TA Utrecht, The Netherlands
[3] Utrecht University, Copernicus Institute, Science, Technology and Society, Heidelberglaan 2 3584 CS Utrecht, The Netherlands

ABSTRACT: In this paper we applied two different upconverter materials (Gd_2O_2S: Er^{3+}, Yb^{3+} and β-$NaYF_4$: Er^{3+} 2%, Yb^{3+} 18%) on solar cells and investigated the response of the upconverter for two types of solar cells, flat solar cells and solar cells made on textured glass. The flat solar cells are made in such a way that the intensity of 980 nm light reaching the upconverter layer is still 84% of the incident intensity. Due to the non-linear nature of upconverters, the EQE for sub band gap light is expected to be superior for flat solar cells in comparison to that of standard solar cells made on textured glass. Due to the low response of the upconverter in β-$NaYF_4$ the differences between the flat and textured solar cells could not be detected. However, for the upconverter in Gd_2O_2S it is shown that the flat solar cells indeed perform better, up to the point where saturation sets in.

1 INTRODUCTION

High efficiency solar cells require absorption of photons of the full solar spectrum followed by effective generation and collection of charge carriers. The high band gap of amorphous silicon of ~1.8 eV implies that the material is transparent for sub band gap, near infrared (NIR) light, constituting a high photon loss. Upconversion (UC) may enhance the response of solar cells in the infrared. UC is a luminescence process whereby 2 or more low energy photons are converted to 1 higher energy photon. When a layer containing UC species is attached at the rear of a solar cell the sub band gap photons are absorbed and higher energy photons are emitted; these can subsequently be directed to the solar cell using an optical reflector behind the cell, where they are absorbed in the active layer.

An increasing research effort is undertaken on crystalline silicon solar cells as well as thin film silicon solar cells using upconverters based on lanthanide ions [1-5]. Recently [4,5], we have demonstrated the first proof-of-principle of the upconversion effect for thin film amorphous silicon solar cells. In this paper experiments are performed to investigate the response of different solar cell designs on the non-linear optical properties of the upconverter.

2 THEORY

2.1 Lanthanides Upconverter

Upconversion of lanthanide ions is extensively investigated since the 1960's and an overview is given by Auzel [6]. Lanthanides are most commonly found in the ionized trivalent state and the rich energy level structure over a wide spectral range results in the application of lanthanide luminescence from the UV to the infrared. The energy levels arise from interactions between 4f electrons in the partly filled inner $4f^n$ shell, where n is the number of 4f electrons. Because the 4f electrons are shielded by the outer $5d^1$ and $6s^2$ shells the energy level structure and optical properties are barely influenced by the surrounding host lattice.

The upconverter material used is crucial for obtaining any significant increase in solar energy conversion efficiency. We applied two different upconverter materials to the solar cells. The first one is β-$NaYF_4$: Yb^{3+} (18%), Er^{3+} (2%), which is known as a very efficient upconverter [7,8]. Another upconverter is commercially produced and is Gd_2O_2S: Yb^{3+}, Er^{3+}. Both upconverter materials absorb around 980 nm and emit in the visible spectrum (400-700 nm). These absorption and emission wavelengths are very suitable for use with a-Si:H single junction solar cells, as the band gap is between the wavelengths for absorption and emission and the spectral response is very high in that range of emission.

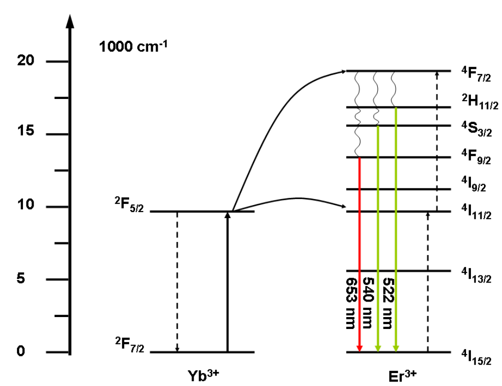

Figure 1: Upconversion in the (Yb^{3+}, Er^{3+}) couple. The dashed lines represent non-radiative energy decay, the full lines the radiative decay and the curly lines indicate multiphonon relaxation processes. A two-step energy transfer leads to excitation to the $^4F_{7/2}$ state of the Er^{3+} ion. After relaxation from this state emission is observed from the $^2H_{11/2}$, the $^4S_{3/2}$ level (green), and the $^4F_{9/2}$ level (red).

2.2 Upconverter Light Intensity Dependence

Different mechanisms are responsible for the UC luminescence. The dominant UC mechanism in upconverter materials doped with a sensitizer is energy transfer upconversion (ETU). Excitation in the $^2F^{7/2} \rightarrow ^2F_{5/2}$ transition of Yb^{3+} leads to emission peaks around 540 and 653 nm which are assigned to the Er^{3+}

$^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. The Yb^{3+} ion has only one excited state and is an ideal sensitizer for Er^{3+} because of the relatively high oscillator strength of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition and the fact that Er^{3+} has a state with similar energy ($^4I_{11/2}$) which is populated by energy transfer from Yb^{3+}. Population of the first excited state of Er^{3+} ($^4I_{11/2}$) is therefore directly proportional to the incoming light intensity. When upconversion is the main mechanism, energy transfer from the first excited state to a higher excited state follows. This process is illustrated in figure 1. Therefore, a higher order dependence of the incoming light is expected:

$$N_n \propto N_{n-1} N_s \propto (N_s)^n \propto P_{in}^n \qquad (1)$$

where n is the number of photons needed to the upconverted state. N_n is the n^{th} excited state in the Er^{3+} ion and N_s the excited state of the sensitizer ion Yb^{3+}. When a higher energy level saturates, other processes i.e. non-radiative relaxation to lower energy states occurs and deviations from the expected power law dependence (i.e. 2, 3) are observed.

The upconverted emission is thus proportional to the population of the higher excited state N_n. For solar cells the photocurrent generation I is due to this emission and the external quantum efficiency thus is:

$$EQE \propto \frac{I(A)}{P_{in}} \propto \frac{P_{in}^n}{P_{in}} = P^{n-1} \qquad (2)$$

where P_{in} is the incoming light intensity and I the photogenerated current in the solar cell. The quantum efficiency is thus dependent on the light intensity and therefore we want as much light as possible reaching the upconverter layer.

3 EXPERIMENTAL

3.1 Solar cell designs

To investigate the influence of the light intensity on the solar cell response, two new solar cells designs are proposed: solar cells deposited on textured substrates and on flat substrates, see figure 2. Ideally the solar cells with upconverter layer at the back do not scatter the sub band gap light and are highly transparent for sub band gap light to hold a high power density of the transmitted light. We adapted the solar cells in such a way that an interference maximum occurs in the solar cells at a wavelength of 980 nm. The i-layer thicknesses for which this happens are 230 and 500 nm, leading to a transparency for 980-nm light of over 93%. As front contact a TCO layer of 1 µm ZnO:Al (from a 0.5% Al_2O_3/ZnO target) was sputtered on glass and textured glass substrate was used. As back contact a 1 µm ZnO:Al layer (also 0.5% doped) was sputtered on both solar cells. The upconverter layer is attached to the solar cell by dissolving it in a PMMA solution and drop cast it over the ZnO:Al back contact of the solar cells. The layer thickness of this layer is approximately 300 µm. As back reflector white paint was used. Solar cells with texture increase the absorption but decrease the efficiency of the upconverter due to light scattering and thus they are less transparent also for 980 nm light. Changing the i-layer thickness doesn't increase the transparency of the solar cells; transmittance values of 40 up to 55% are measured for 980 nm light. For flat solar cells, however, a transmittance up to 84% was measured. Table I summarizes the electrical parameters of the types of solar cells (flat, textured), each for two different thicknesses of the i-layer. The increase in V_{oc} is attributed to decreasing defect density for flat cells as compared to textured cells. It is also seen that thinner layers lead to higher V_{oc} both for flat and textured substrates.. The decrease in I_{sc} is attributed to lower absorption when layers are thinner and when texture is absent.

Tabel I Electrical parameters of the solar cells

Solar Cell	V_{oc} (V)	I_{sc} (mA/cm^2)	FF
Textured 500 nm	0.83	13.8	0.69
Textured 230 nm	0.84	11.7	0.65
Flat 500 nm	0.86	10.8	0.67
Flat 230 nm	0.88	9.3	0.67

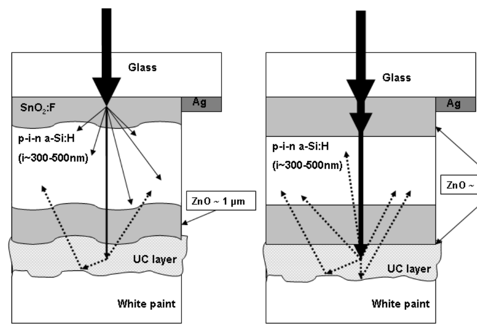

Figure 2: Schematic overview of the two solar cell designs used in these experiments. In flat solar cells the incoming light is not scattered and much higher light density reaches the upconverter layer by placing the interference maximum for the relevant wavelength at the upconverter. The increase in light intensity should lead to a nearly quadratic increase in upconverter response.

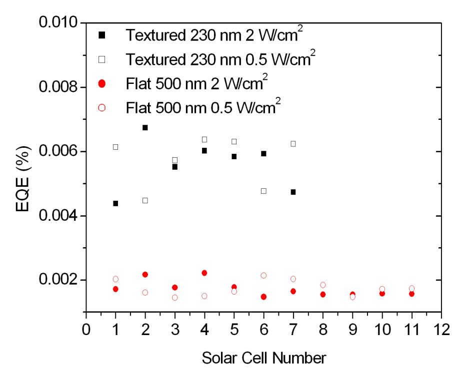

Figure 3: The EQE for different solar cells without upconverter and without diffuse back reflector. No considerable dependence on light intensity is observed.

3.2 Sub band gap response

Previous experiments [4,5] have shown that in reference cells without an upconverter for low light intensities a response of the photocurrent due to sub band gap light is present that is a significant fraction of the total response observed in solar cells with an upconverter. To correct for this we first measured the sub band gap response at different light intensities. The solar cells were illuminated in a black box with a small diode laser. The maximum intensity of the laser was 3 W/cm^2. The light intensity was varied with neutral density filters. First the response of the solar cells without UC and diffuse back reflector (DBR) was determined for the different solar cells with light intensities at 2 W/cm^2 and 0.5 W/cm^2. Figure 3 shows some EQE's for different solar cells at two different power intensities. From Figure 3 it was concluded that the response is independent of the power intensity (which was expected) and therefore the upconverter response can be corrected by a single EQE value for the sub band gap response. Measuring the response without DBR represents a small underestimation; however it made it possible to measure the response of the solar cells before attaching the upconverter layer. Measuring the response with DBR results in an overestimation when compared to solar cells with upconverter layer attached before the DBR, because this layer also absorbs some light itself.

Figure 4 gives the average values of the measured EQE of all solar cells shown in Table I for 980 nm light. From figure 4 it can be seen that the response of the solar cells is highly dependent on the structure and i-layer thickness. In general, the response is higher for solar cells on textured glass, but also shows a larger variation. This might be attributed to the irregular structure of the textured surface that increases the path length of the light, as can be seen in figure 2. Another addition to the increased sub band gap response is that Si deposited on textured surfaces has generally an increased defect density. This results in lower V_{oc} values with increasing thickness and texturization as can be seen in table I. For flat solar cells exactly the opposite is observed. A thicker i-layer results in lower response due to the low hole mobility limiting the collection efficiency, as the the defect density is not increasing with the thickness of the layer.

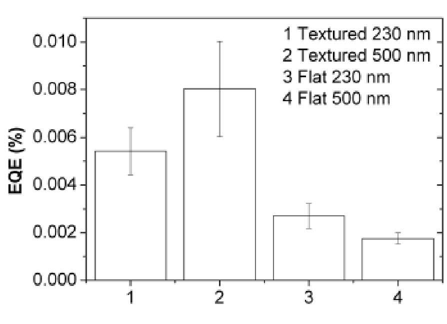

Figure 4: Average EQE values for the different solar cells. The EQE is power density independent, however different values are obtained for different solar cells. Flat solar cells have a more constant value than solar cells on textured substrate.

4 RESULTS

4.1 Upconverter materials

Two different upconverter materials are studied in this paper. A commercial upconverter Gd_2O_2S and β-$NaYF_4$ synthesized at the chemistry department, doped with Yb^{3+} and Er^{3+}. Figure 5 shows the absorption spectra of the phosphors which are determined from reflectance measurements with an integrating sphere**.** The broad absorption peak around 1000 nm is typical for Yb^{3+}, as Er^{3+} has an energy state at that level but a much smaller absorption band of approximate 40 nm with. The upconverters are excited with a small diode laser with a maximum intensity of 3 W/cm^2 and the light is focused with lenses on the upconverter materials. Figure 6 shows the normalized emission from the Er^{3+} $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions around 540 and 650 nm after excitation of 980 nm.

Light intensity dependent measurements are done to show the non-linear behavior of the upconverter materials. Figure 7 shows the plot for the green emission around 520/540 nm for both upconverters. As can be seen, the emission from the commercial upconverter saturates at low intensities, while the β-$NaYF_4$ upconverter reveals a strong quadratic dependence under same light intensities. When saturation occurs either higher order emissions i.e. 3 photons are stronger or non-radiative relaxation occur. However for solar cells performance we are interested mainly in the green emission, because the EQE of the solar cells are the highest for green emission. Although the emission from the β-$NaYF_4$ is several orders of magnitude lower, saturation effects are not present until 20 W/cm^2 and a power conversion from 980 nm light to green 540/520 nm light of 5% are measured [9-11]. Thus the emission from this material will exceed the emission from the commercial upconverter.

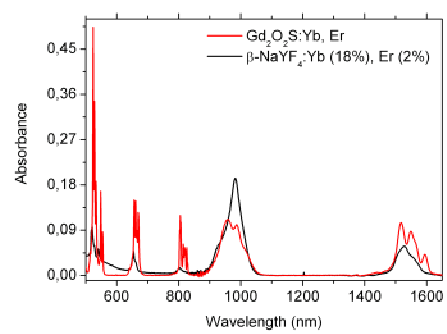

Figure 5: Absorption spectra of the different upconverters. The broad absorption peak around 980 nm is contributed to the Yb^{3+}. All other absorption peaks are Er^{3+} levels.

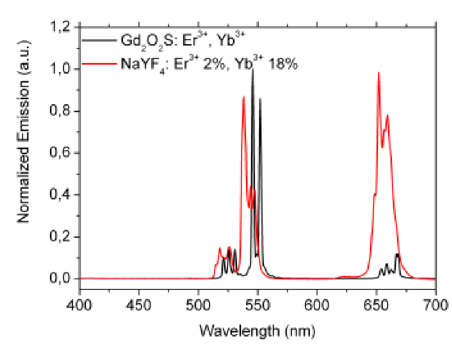

Figure 6: Emission spectra of the different upconverters, after excitation of 980 nm light. The emission peaks are attributed to the $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (520, 540, 650 nm) transitions of Er^{3+}.

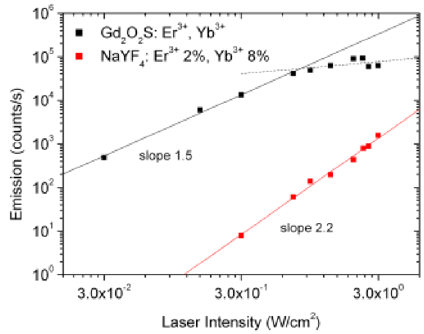

Figure 7: Intensity dependent emission plot for the green emission lines at 520 and 540 nm. Lower deviations from a slope of 2 are observed when the upconverter material saturates. The dashed line is a guide to the eye, reavealing almost constant emission.

4.2 Solar Cells: β-$NaYF_4$ Upconverter

For all different solar cell structures with upconverter layer light intensity dependent measurements were performed. The solar cells were illuminated with the diode laser with a wavelength of 980 nm and a maximum power intensity of 3 W/cm^2 in a close box. All current generation is solely due to upconverted emission from the upconverter layer and the sub band gap response. Figure 8 shows the current measured when illuminated with the diode laser. The response of the textured solar cells is better than that of the flat solar cells. However, these measurements are not corrected for the sub band gap response of the intrinsic layer. When one calculates the EQE one sees that the EQE is of the same order as that of the sub band gap response. Figure 9 illustrates the EQE of the device when corrected for the sub band gap response. The flat solar cells are slightly better, however the thick textured solar cell has the best response. This might also be due to good absorption and carrier collection of the textured solar cells, since the sub band gap response was also the highest. Maximum EQE of 0.01% was measured at 3 W/cm^2.

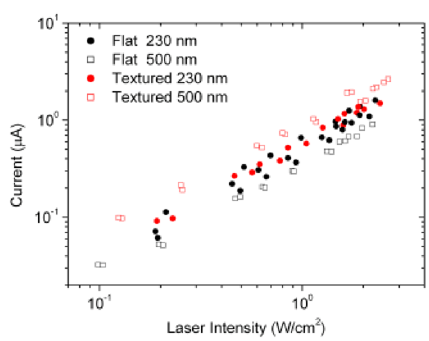

Figure 8: Total current generation in the solar cells due to upconverter and sub band gap response.

4.3 Solar Cells: Gd_2O_2S upconverter

When applying the Gd_2O_2S upconverter on the different solar cells different results are obtained. Figure 10 shows the current, which is at least 1 order of magnitude higher than that for the solar cells with β-$NaYF_4$ upconverter attached. Here it is clear that the response is indeed better for the flat solar cells. At high intensities one can see that saturation occur, which was already visible in figure 7. The current is increasing linearly with the laser intensity when the intensity is higher than 0.6W/cm^2.

Figure 11 shows the calculated EQE corrected for the sub band gap response. However, for this upconverter this is only small part of the response and not much change occur with the substraction. From figure 11 it is clear that the EQE is constant from light intensities of 0.6 W/cm^2 and higher consistent with the linear increase of the current. The maximum quantum efficiency of the upconverter material can be determined. When one considers that all upconverter light is reflected back into the solar cell and not reabsorbed by the UC material and PMMA host and all absorbed photons contribute to the current the quantum efficiency is the measured EQE of the solar cell. However approximately 5% of the emitted light is absorbed in the PMMA layer, 10% reabsorbed by the Er^{3+} $^2H_{11/2}$ and $^4S_{3/2}$ energy levels and from the light that is reflected back into the solar cell approximately 70% contributes to the current generation. This leads to a maximum quantum efficiency of 0.2% for this upconverter material. Thus although the performance is much better than β-$NaYF_4$ under low excitation densities, the EQE shall never be higher than 0.2% at higher intensities for this wavelength with this upconverter due to saturation.

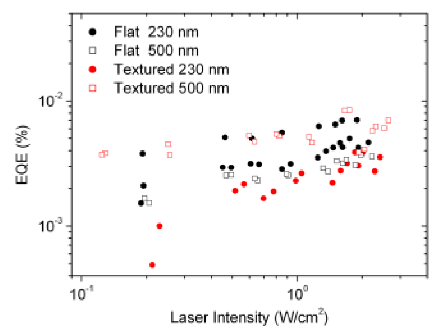

Figure 9: The EQE of the upconverter. The values are corrected for the sub band gap response. The thin flat solar cells and the thick textured solar cells perform the best.

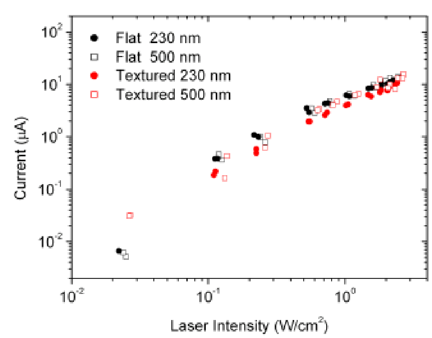

Figure 10: Total short circuit current generation in the solar cells. From approximately 0.6 W/cm^2 the current becomes linearly dependent on the light intensity.

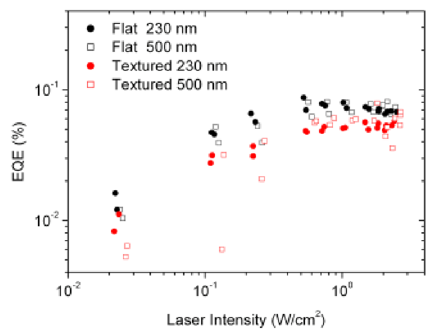

Figure 11: The EQE of the solar cells due to the upconverter. It is clear that flat solar cells have a higher response and that the upconverter efficiency is saturated.

5 DISCUSSION

We adapted the solar cells to increase the response of the solar cells in the near infrared. We studied two sets of solar cells: solar cells on flat TCO and solar cells on atextured TCO layer. We also had two upconverter materials: β-$NaYF_4$ and Gd_2O_2S. Higher response is indeed observed for flat solar cells with the Gd_2O_2S upconverter attached at the back. The fact that no quadratic dependence was observed is attributed to saturation of this upconverter. However, also other aspects play an important role. First of all, it was already visible that the response of textured solar cells was better than that of flat solar cells. Textured surfaces scatter the light, and since this light of mainly 540 nm wavelength is scattered into the solar cells the collection efficiency is also higher for these solar cells.

6 ACKNOWLEDGEMENTS

We gratefully acknowledge Agentschap NL for partial financial support within the framework of the EOS-NEO Programme and Karine van der Werf and Caspar van Bommel for sample preparation.

7 REFERENCES

[1] A. Shalav, B.S. Richards, T. Trupke, K.W. Krämer, H.U. Güdel, Appl. Phys. Lett. 86, 013505 (2005)
[2] T. Trupke, M.A. Green, P. Würfel, J. Appl. Phys. 92 (2002) 4117
[3] W.G.J.H.M. van Sark, A. Meijerink, R.E.I. Schropp, Nanoparticles for solar spectrum conversion, in: L. Tsakalakos (Ed.), Nanotechnology for Photovoltaics, Taylor and Francis, Boca Raton, FL, USA, 2010, pp. 351–390 Chapter 10.
[4] J. de Wild. A. Meijerink, J.K. Rath, W.G.J.H.M. van Sark, R.E.I. Schropp, Towards upconversion for amorphous silicon solar cells, SEMSC (2010), In press
[5] J. de Wild, A. Meijerink, J.K. Rath, W.G.J.H.M. van Sark, R.E.I. Schropp, Enhanced near-infraredresponseofa-Si:Hsolarcellswith b-NaYF4:Yb3+ (18%), Er3+ (2%) upconversionphosphors, SEMSC (2010) . In press
[6] F. Auzel, Chem. Rev. (Washington, D.C.) 104, 139(2004)
[7] N. Menyuk, K. Dwight, J.W. Pierce, Appl. Phys. Lett. 21 (1972) 159
[8] T. Kano, H. Yamamoto, Y. Otomo, J. Electrochem. Soc. 119 (1972) 1561
[9] M.P. Hehlen, M. L. F. Philips, N. J. cockroft and H.U. Güdel, *Encyclopedia pf Materials: Science of Technology* (Pergamon, New York, 2001), Vol. 10 p. 9458
[10] J.F. Suyver, J. Grimm, K.W. Krämer, H.U. Güdel, J. Lumin. 114 (2005) 53.
[11] Page, Ralph H, Schaffers, K. I. Schaffers, P. A. Waise, J. B. Tassano, S. A. Payne, W. F. Krupke, W. K. Bischel J. of the Optical Society of America B: Optical Physics, Volume 15, Issue 3, March 1998, pp.996-1008