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Enhanced near-infrared response of a-Si:H solar cells with β-$NaYF_4$:Yb^{3+} (18%), Er^{3+} (2%) upconversion phosphors

J. de Wild *, J.K. Rath, A. Meijerink, W.G.J.H.M. van Sark, R.E.I. Schropp

Utrecht University, Faculty of Science, Debye Institute for Nanomaterials Science, PO Box 80000, 3508 TA Utrecht, The Netherlands

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ABSTRACT

A near-infrared to visible upconversion phosphor (β-$NaYF_4$:Yb^{3+} (18%), Er^{3+} (2%)) has been applied at the back of a thin film hydrogenated amorphous silicon (a-Si:H) solar cell in combination with a white back reflector to investigate its response to sub-bandgap infrared irradiation. Current–voltage measurements were performed on the solar cells. A maximum current enhancement of 6.2 μA was measured on illumination with a 980 nm diode laser at 28 mW. This corresponds to an external quantum efficiency (EQE) of 0.03% of the solar cell. A small part, 0.01%, was due to the direct absorption of sub-bandgap radiation but the larger part originates from upconversion. These experiments constitute a proof-of-principle for the utilization of photon upconversion in thin film solar cells. A close match between the non-linear behavior of the upconversion material and the EQE was found by varying the intensity of the laser light.

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1. Introduction

Highly efficient solar cells require the absorption of photons over the broadest possible range of the solar spectrum followed by an effective generation and collection of charge carriers. Thin film a-Si:H cells have a high absorption in the visible range, but the wide bandgap of amorphous silicon ($E_g \sim 1.8$ eV) implies that the material is almost transparent for near-infrared (NIR) radiation, constituting a significant efficiency loss known as transmission losses. Upconversion (UC) may enhance the response of solar cells in the infrared region [1–4]. UC is a luminescence process whereby two or more low energy photons are converted to one higher energy photon. When a layer containing an UC phosphor is attached to the rear of a solar cell, sub-bandgap photons that are transmitted by the solar cell can be absorbed by the UC layer and converted into higher energy photons. These photons are emitted isotropically, and with the help of an optical white diffusive reflector behind the cell all emitted photons are directed to the cell, which can be subsequently absorbed in the active layer.

The most efficient UC materials rely on lanthanide ions. UC by lanthanide ions has been investigated extensively since the discovery in the 1960s by Auzel [5]. Lanthanides are most commonly found in the trivalent state and the rich energy level structure over a wide spectral range explains the widespread application of lanthanide luminescence [6]. The energy levels arise from interactions among 4f electrons in the partly filled inner $4f^n$ shell, where n is the number of 4f electrons. Since the 4f electrons are shielded by the outer $5s^2$ and $5p^6$ shells the energy level structure and optical properties are insensitive to the surrounding host lattice. Recently the use of UC was demonstrated to enhance the efficiency for crystalline Si (c-Si) solar cells [1,2]. The bandgap of c-Si is relatively narrow (1.1 eV) and the part of the solar spectrum that cannot be absorbed is limited (wavelengths larger than 1100 nm). Nevertheless, upconversion of photons in this spectral range and subsequent carrier generation in the solar cell enhance the solar cell efficiency. Upconversion of ~1500 nm photons in the UC material $NaYF_4$:Er^{3+} on the back of c-Si solar cells was reported with an external quantum efficiency (EQE) of 2.5% for excitation with a focussed 5.1 mW laser at 1523 nm [1].

In this work we focus on UC for wider bandgap solar cells, specifically a-Si:H solar cells. The transmission losses are much higher in these solar cells compared to c-Si cells and the potential gain from UC is therefore higher. The upconversion phosphor β-$NaYF_4$: Er^{3+} (2%), Yb^{3+} (18%) is very suitable for upconversion in wide bandgap solar cells (E_g up to ~2 eV) as to date it is among the most efficient upconversion materials, converting NIR radiation of around 980 nm to green (525, 550 nm) and red (650 nm) emissions. The collection efficiency of a-Si:H cells is high for these wavelengths, making this phosphor a suitable candidate for upconversion in this type of solar cells. Note that for another host material, PbF_2, very high upconversion efficiencies have been reported due to a lower active phonon energy than that for $NaYF_4$ [7,8].

* Corresponding author.
E-mail address: J.deWild@uu.nl (J. de Wild).

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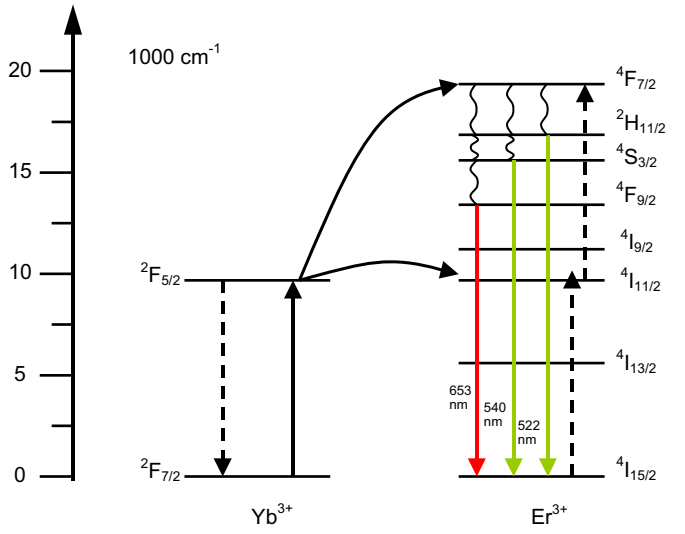

Fig. 1. Upconversion in the (Yb^{3+}, Er^{3+}) couple. The dashed lines represent non-radiative energy transfer, the full lines radiative and the curly lines multi-phonon relaxation processes. A two-step energy transfer leads to excitation of the $^4F_{7/2}$ state of the Er^{3+} ion. After relaxation from this state emission is observed from the $^2H_{11/2}$ and $^4S_{3/2}$ levels (green) and the $^4F_{9/2}$ level (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

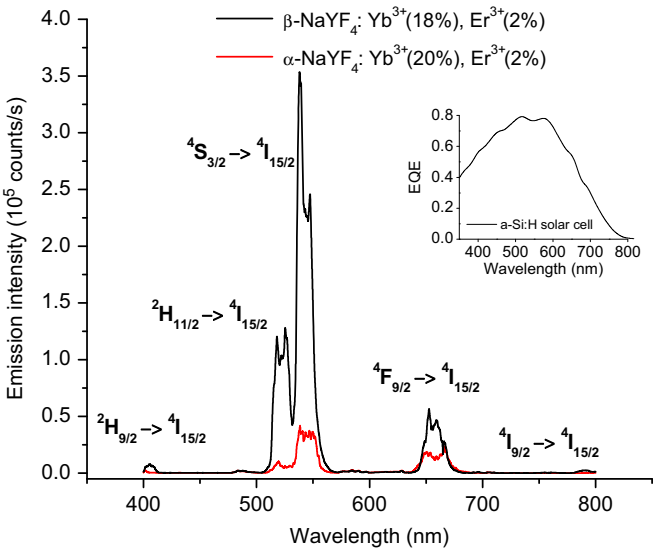

Fig. 2. Emission spectra of the different phases of the $NaYF_4$: Er^{3+}, Yb^{3+} upconverter under identical excitation density. A clear difference in the emission intensity of the cubic α- and hexagonal β-phases is shown. In the inset the spectral response of the a-Si:H solar cell is shown. The highest response of the solar cell is in the green part (500–550 nm), where the upconversion emission is also the most significant.

The main UC mechanism in β-$NaYF_4$: Er^{3+} (2%), Yb^{3+} (18%) is energy transfer upconversion (ETU). Excitation in the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition of Yb^{3+} is followed by a two-step energy transfer process to neighbouring Er^{3+} ions (see Fig. 1), which brings Er^{3+} to the $^4F_{7/2}$ level. Fast relaxation to the $^2H_{11/2}/^4S_{3/2}$ level is followed by green emission ($^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$) and further relaxation to the $^4F_{9/2}$ level yields red emission ($^4F_{9/2}\rightarrow{}^4I_{15/2}$). 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+}. The chance that Er^{3+} is excited by the 980 nm laser light is rather small since the concentration is 9 times smaller and the lifetime of the excited state of Yb^{3+} is also larger than Er^{3+}. Direct Er^{3+} excitation and thereby excited state upconversion is very unlikely. Since two photons are required to obtain upconverted light the emitted power increases quadratically with excitation power. It is generally accepted that $NaYF_4$:Yb, Er is a very efficient UC material. The maximum UC efficiency, defined as ratio of power out to power in, P_{out}/P_{in}, for 520–580 nm light, has been reported to be 5.5%, which was reached at an intensity of 20 W/cm^2 [9,10]. Based on power dependent emission spectra it was also concluded that for high excitation powers 50% of all NIR photons absorbed by the material are converted to visible photons, i.e. blue (405 nm), green (540 nm) and red (650 nm) emission [11].

2. Material and methods

The β-$NaYF_4$:Er^{3+} (2%), Yb^{3+} (18%) phosphors were synthesized by mixing NaF, YF_3, YbF_3 and ErF_3 powders and heating the mixture in a nitrogen atmosphere for 3 h at 750 °C. X-ray diffraction (XRD) measurements showed that predominantly β-$NaYF_4$ was formed. At higher temperatures the less efficient α-phase was formed (see Fig. 2). The UC powder mixture was applied to the rear of the solar cells by first dissolving it in a solution of polymethylmethacrylate (PMMA) in chloroform after which it was spin coated, resulting in an upconverter layer thickness of 200–300 μm. As a back reflector white paint was used.

Standard p–i–n amorphous silicon solar cells were made by 13.56 MHz plasma enhanced chemical vapor deposition (PECVD) with an area of 0.16 cm^2 and an intrinsic layer thickness of 500 nm. As a back contact 1 μm sputtered aluminium doped zinc oxide from a $ZnO:Al_2O_3$ 0.5% target was used. Frontside illumination with AM1.5 light yields an efficiency of 8% and backside illumination (through the *n*-layer) an efficiency of 5%. The external quantum efficiency (EQE) conveniently peaks at around 530 nm and was 0.77, as shown in the inset of Fig. 2.

To demonstrate the enhancement of solar cell performance due to UC, current–voltage (*I–V*) measurements were performed. The solar cells were illuminated with a NIR diode laser and with a maximum power of 28 mW. The laser emits light at 981 and 986 nm wavelengths, which are suitable for absorption by Yb^{3+} [12]. The laser beam was not focussed and the area was 1 mm^2, which results in a power density of 3 W/cm^2. Note that this power is far below the power for which the highest upconversion efficiencies have been obtained [9,10]. The solar cells were mounted in a box in which no light from outside can penetrate, so that the response of the solar cell is only due to the diode laser. It is well known for a-Si:H that sub-bandgap absorption arises due to a continuous density of localized states. As a result, a part of the NIR radiation is absorbed by the cell, before it reaches the backside of the cell where it can be upconverted. To distinguish the response to upconverted light from the primary response due to absorption of sub-bandgap radiation, the response to NIR radiation of the solar cell without the upconverter but with otherwise the same cell structure as reference was measured as well.

3. Experimental results

Fig. 3 shows the *I–V* curves of two cells, one with and one without upconverter (denoted as reference). The reference cell shows a short-circuit current of 2.1 μA. There is a clear three-fold

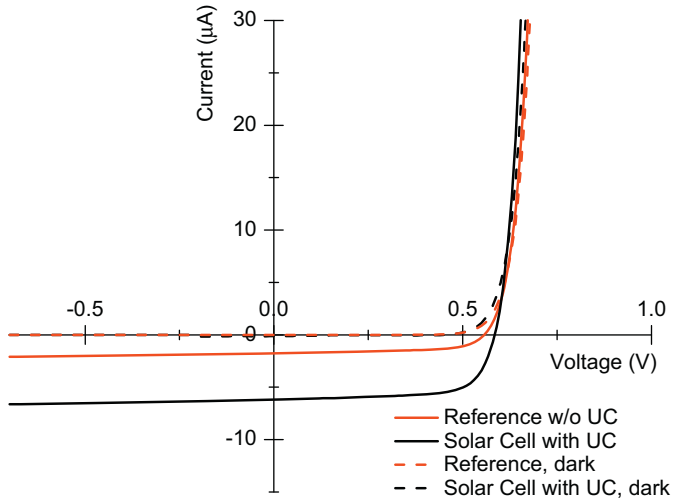

Fig. 3. *I–V* curves of a-Si:H solar cells with and without UC attached at the back. The reference cell has only the white back reflector. In dark the solar cells have the same *I–V* curve; however when illuminated with the NIR diode laser (~980 nm), current is generated in both solar cells. The current in the cell with the UC phosphor is a factor of three larger.

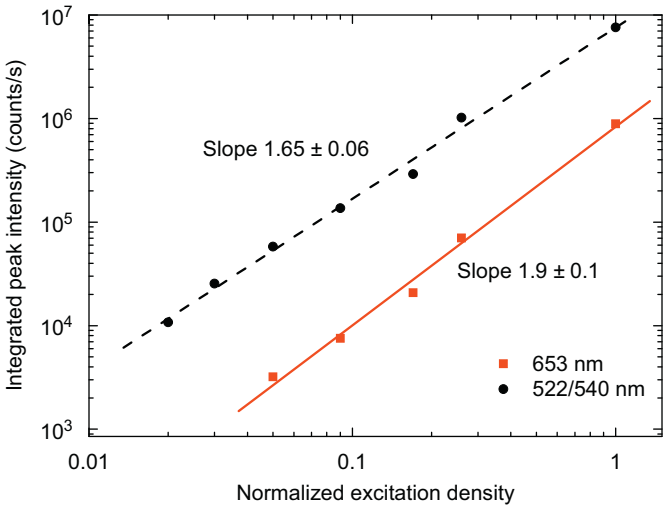

Fig. 4. Power dependence of the UC emission intensity in β-$NaYF_4$. The slope in a double logarithmic plot gives the dependence of the emitted light on the excitation power density. The slope of the 525/550 nm emission is 1.65 ± 0.06 (dashed line) and of the 650 nm emission is 1.9 ± 0.1 (solid line), revealing a quadratic dependence of the emitted power on the excitation density.

improvement due to UC, leading to a short-circuit current of 6.2 μA. The EQE is calculated as

$$EQE = \frac{I_{sc}}{P_{in} q/hv} \quad (1)$$

where I_{sc} is the short circuit current, q the electron charge and hv the energy of the photon. A maximum value of 0.03% was calculated for 980 nm photon energy. This EQE is dependent on the UC efficiency, the carrier photogeneration efficiency and the collection efficiency of the device. The UC efficiency is strongly dependent on the excitation power (W/cm^2). Unfortunately, we cannot compare the obtained EQE with that reported for $NaYF_4:Er^{3+}$ and c-Si solar cells using a 1523 nm laser [1] since different upconversion routes are undertaken.

As the intensity of solar illumination in the NIR in practice is much lower than that of a laser, it is important to study the dependence of the emission as a function of excitation density. Therefore, intensity dependent measurements have been done on UC material and solar cells. The intensity was varied with neutral density filters. The slope of a log–log curve is used to find the power dependence of UC. Fig. 4 shows the dependence for the red (653 nm) and green (522 and 540 nm) emissions, and the slopes are 1.9 ± 0.1 and 1.65 ± 0.06, respectively. This is consistent with a two-photon absorption process. The deviation from the expected slope of 2 is commonly observed and marks the transition to a slope of 1 in the high power regime [13]. The red emission is at least 10 times less intense than the green one. For the higher excitation densities the relative intensity of the red emission increases since feeding through a three-photon process starts to contribute at higher powers. This also explains the difference in slope for the two emissions.

The external quantum efficiency (EQE) of solar cells due to non-linear processes like UC is strongly dependent on the illumination intensity. From Eq. (1) it follows that EQE is proportional to $I_{sc}/P_{in,}$ while the current I_{sc} itself is proportional to $P_{out} \propto P_{in}^{n}$. A power dependence of the external quantum efficiency on the illumination intensity is then expected according to

$$EQE \propto \frac{P_{out}}{P_{in}} = P_{in}^{n-1} \quad (2)$$

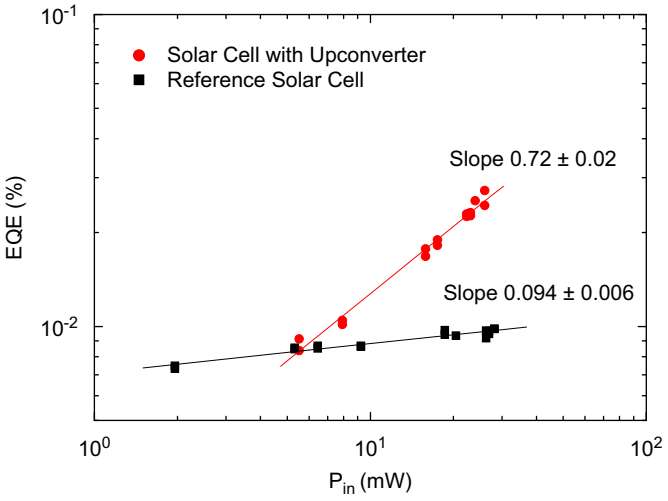

Fig. 5. Double logarithmic plot of EQE as a function of excitation power. The slope in case of the solar cell with upconverter (dashed line) matches the expected power dependence of P_{in}^{n-1}, with $n=1.65$ as found earlier (Fig. 2). EQE of the reference cell is approximately constant, which is expected for a one-photon process.

We find that EQE increases with increase in intensity, with a slope of 0.71 (see Fig. 5) from which the value of $n=1.71$ is deduced. This matches closely with the slope of 1.65 found earlier for the green emission, which is the most significant part of the upconverted light. In order to distinguish direct response and response due to upconverted light reference measurements were also done. A very weak dependence on the illumination intensity of the reference cell was found, inferring that the sub-bandgap response is almost a linear process and the relative contribution of UC becomes more significant at higher excitation powers.

4. External quantum efficiency and upconversion efficiency

The efficiency of the upconverter can be calculated from the measured EQE and compared with expected efficiencies for lower

excitation densities. Here two things have to be taken into consideration: (1) the incoming light has a wavelength of 980 nm, and the upconverted light has a wavelength of predominantly 540 nm; (2) the upconverted light enters the solar cell through the *n*-layer at the back of the cell. Furthermore it is assumed that all light is reflected back into the solar cell, which is reasonable to assume due to the high reflectivity of the diffusively white back reflector. Considering only the green light emission simplifies the equations and is a reasonable approximation since at lower light intensities it is at least 10 times stronger than emission at other wavelengths. EQE due to illumination from the back by the upconverted photons does not depend on the upconversion efficiency. The EQE can thus simply be measured by spectral response measurements. EQE from backside illumination at 540 nm was measured to be 0.62.

The efficiency of the upconverter is defined as P_{out}/P_{in}. Recalling Eq. (1), and rewriting I_{sc} as $P_{out}q/h\nu_{bs} \times EQE_{bs}$, where EQE_{bs} is the measured quantum efficiency at the specific wavelength (here 540 nm) for backside illumination, the efficiency of the upconverter P_{out}/P_{in} can then be written as

$$\eta_{uc} = \frac{EQE_{uc} q/h\nu_{bs}}{EQE_{bs} q/h\nu_{uc}} \quad (3)$$

where $q/h\nu_{bs}$ and $q/h\nu_{uc}$ are the energies of the emitted and incoming photons from the upconverter, respectively. An upconversion efficiency of 0.05% is found this way, whereby the EQE_{uc} is corrected for the sub-bandgap response.

To compare with the expected efficiency of the upconverter it is important to know the power density. The power density was measured to be 3 W/cm^2. However, not all light reaches the upconverter layer due to absorption in the localized states of the semiconductor layers and in the front and back TCO layers. Therefore, only 40% of the incoming light is transmitted and reaches the upconverter layer, leading to a power density of 1.2 W/cm^2. A decrease in the upconverter efficiency of $\eta = \eta_{max}(P_{in}/P_{max})^{1.65}$, with η_{max} and P_{max} taken from Refs. [9,10], leads to an upconverter efficiency of $\sim$0.05%, consistent with the measured EQE.

This very close match of experimentally determined efficiency and theoretical efficiency means that the approximation that all light is reflected back into the solar cell is a good one. We are close to theoretical values may be because EQE_{bs} is higher than measured. This can be explained by the diffuse back reflector that diffusively scatters the light back into the solar cell, which leads to a longer path length of the incoming light and consequently a higher chance that the light will be absorbed.

5. Conclusion

In conclusion, proof-of-principle experiments were performed, demonstrating the effect of an UC material on the response of amorphous silicon solar cells to the sub-bandgap spectral region. We have shown that the principle of UC can be exploited in thin film solar cells, with an amorphous silicon solar cell as the experimental example. Theoretical calculations have shown a consistent EQE between experiment and theory, which can only be achieved if all emitted photons are reflected back into the solar cell.

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