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Towards upconversion for amorphous silicon solar cells

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ABSTRACT

Upconversion of subbandgap light of thin film single junction amorphous silicon solar cells may enhance their performance in the near infrared (NIR). In this paper we report on the application of the NIR–vis upconverter β-$NaYF_4$:Yb^{3+}(18%) Er^{3+}(2%) at the back of an amorphous silicon solar cell in combination with a white back reflector and its response to infrared irradiation. Current–voltage measurements and spectral response measurements were done on experimental solar cells. An enhancement of 10 μA/cm^2 was measured under illumination with a 980 nm diode laser (10 mW). A part of this was due to defect absorption in localized states of the amorphous silicon.

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 subbandgap 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 subbandgap photons are absorbed and re-emitted at higher energy; these can subsequently be directed to the solar cell using an optical reflector behind the cell and absorbed in the active layer.

Much research is done on crystalline silicon solar cells using upconverters with lanthanide ions [1–3]. However, for amorphous silicon solar cells this has not been undertaken yet even though the potential gain is much higher for a-Si solar cells as the transmission losses are larger due to the wider bandgap in comparison with c-Si. In this paper we report on application of a UC layer to the back of a thin film amorphous silicon solar cell and experiments are performed to verify the enhanced solar cell response in the NIR.

UC of lanthanide ions has been extensively investigated since the1960s and an overview is given by Auzel [4]. 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 most efficient upconversion material based on lanthanides is $NaYF_4$:Yb, Er [5,6]. A systematic study has been performed, varying Er^{3+} ($4f^{11}$) and Yb^{3+} ($4f^{13}$) concentrations, and it revealed that the most efficient UC is obtained for β-$NaYF_4$ doped with 18% Yb^{3+} and 2% Er^{3+} [7]. For amorphous silicon this is a suitable UC process since it absorbs NIR radiation around 980 nm and emits around 522, 540 and 653 nm (see Fig. 1), for which amorphous silicon solar cells have high internal collection efficiency.

Different mechanisms are responsible for UC luminescence. The dominant UC mechanism in β-NaYF4 18% Yb^{3+} 2% Er^{3+} 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+}. Excitation of the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition of Yb^{3+} leads to energy transfer to a nearby Er^{3+} ion. The Er^{3+} ion is then excited to the $^4I_{11/2}$ state. Subsequent energy transfer to the same erbium ion in the excited state excites it to $^2F_{7/2}$. As a result of the fact that at least two photons are required to obtain upconverted light the emitted power is quadratically related to excitation power. The maximum upconversion efficiency (defined as P_{out}/P_{in}; 5%) occurs when the excitation power at 980 nm is more than 20 W/cm^2 [9,10]; 23% of

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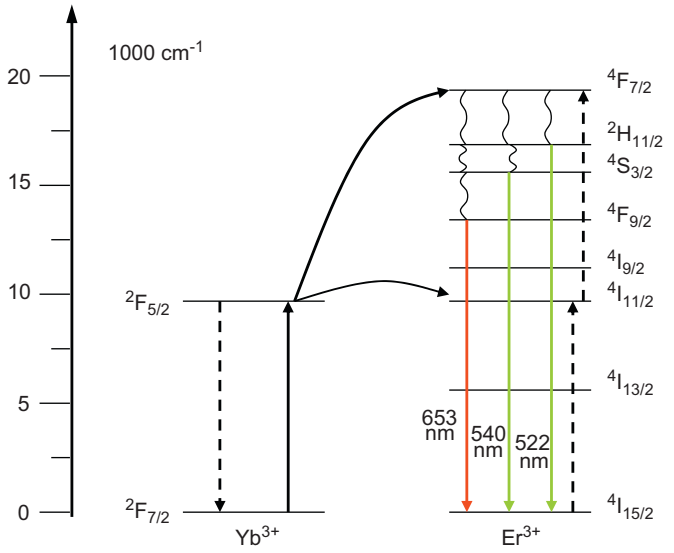

Fig. 1. Energy transfer between Yb^{3+} and Er^{3+} ions. The dashed lines represent non-radiative energy transfer, the full lines radiative and the curly lines cross-relaxation and multi-phonon relaxation processes. A two-step energy transfer leads to excitation of the $^4F_{7/2}$ state of the Er^{3+} ion. Emission from this state is not detected. After relaxation from this state towards lower states, the Er^{3+} ion falls down to the ground state. For the two-photon energy transfer the photons with energies higher than the amorphous silicon band gap are emitted. Figure taken from [8].

the absorbed photons is then converted to 522/540 nm and 24% to 653 nm [11]. At lower power densities the green emission becomes more dominant.

2. Experimental

The β-NaYF4:Er(2%),Yb(18%) phosphors were made 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 obtained. Excitation of the phosphors at 980 nm was done with a Lambda Physic LPD3000 tunable dye laser filled with a Styrile 14 dye solution. It is pumped by a Lambda Physic LPX100 excimer (XeCl) laser.

The UC powder mixture was applied to the rear of the solar cells by first dissolving it in a solution of PMMA in chloroform after which it was spincoated. As a back reflector a white paint was used. Standard p–i–n amorphous silicon solar cells were made by plasma enhanced chemical vapor deposition (PECVD) with an area of 0.16 cm^2 and an intrinsic layer thickness of 500 nm. As the back contact, 1 μm sputtered ZnO from a ZnO:Al 0.5% target was used. Front side illumination yields a power conversion efficiency of 8% and back side illumination (through the n-layer) an efficiency of 5%.

To show the enhancement of solar cell performance due to UC, current–voltage measurements and spectral response measurements were performed. The solar cells were illuminated with a diode laser, with a power of 10 mW. The laser emits light at wavelengths of 981 and 986 nm, which are suitable wavelengths for absorption by Yb^{3+}. In amorphous silicon the density of states within the band gap is much higher than that for crystalline silicon; therefore part of the light is already absorbed before it reaches the backside of the cell, where it can be upconverted. To distinguish the response to upconverted light from the primary response to subbandgap light response, the response of the solar cell for subbandgap light was measured as well.

3. Results

3.1. Emission spectra

Emission spectra of excitation in the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} are performed for different samples. Fig. 2 shows the emission spectra for two β-$NaYF_4$ and α-$NaYF_4$ samples at the same excitation power. The major emission is in the green and red, as expected. For variations in the laser intensity, neutral density filters were used. With decrease in excitation intensity the 653 nm emission band decreases stronger than the 522/540 nm emission band, see Fig. 3; the slope in the double logarithmic plot is 1.7 for the 522/540 nm emission band and 1.9 for the 653 nm emission band. This is in good agreement with the quadratic dependence on excitation density. Note that a small deviation from 2 is commonly observed and marks a transition to a slope of

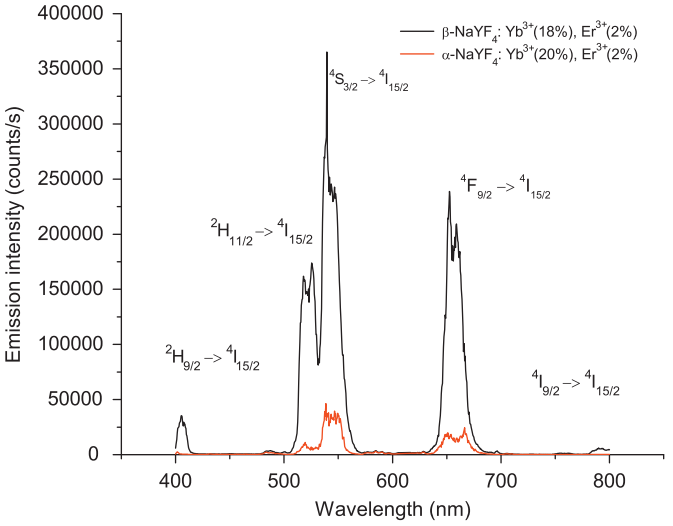

Fig. 2. Emission spectra of two phases of $NaYF_4$ under the same excitation density. The cubic α-phase is less efficient than that of the hexagonal β-phase of $NaYF_4$. The excited $^4F_{7/2}$ state does not emit light but relaxation occurs to the $^2H_{11/2}$, $^2S3_{/2}$ and $^4F_{9/2}$ states. The main emission is in the green and red; however for the β-phase also the blue 405 nm is significant under high excitation power. This represents a three-step upconverted photon. All emissions are in the absorption range of a-Si.

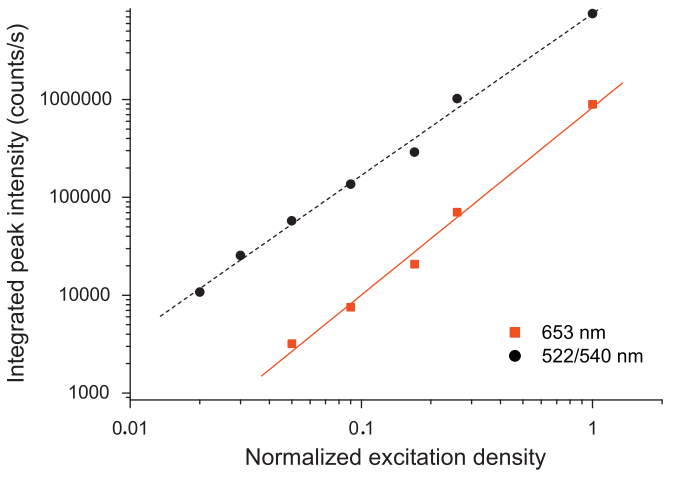

Fig. 3. Power dependence of emission bands in β-NaYF4. The slope in the double logarithmic plot gives the dependence of emitted light on excitation power density. The slope of the 522/540 nm emission is 1.7 (dashed line) and of the red one is 1.9 (full line), revealing a quadratic dependence of emitted power on excitation density.

1 in the high power regime; the $^4F_{7/2}$ excited state is further excited to the 400 nm level, i.e. 3-photon absorption.

3.2. Subbandgap absorption

To investigate the subbandgap response of the solar cell, spectral response measurements were performed with a Fourier transform photocurrent spectroscopy (FTPS) [12] set-up. The FTPS set-up has a NIR/vis source with a low intensity light beam. The sample is excited with broadband light and the detected signal is converted from time domain to frequency domain by a fast Fourier transform technique. For normalization of spectral response, a reference solar cell without back reflector is used; Fig. 4 gives a schematic overview of the solar cells used. Fig. 5 (top) shows the normalized response of the solar cell for red and subbandgap light (in the range 600–1100 nm). As expected, a back reflector increases mainly the response in the red and NIR region. Higher energy photons are efficiently absorbed in the intrinsic layer after a single pass of light. The subbandgap response is increased when a back reflector is applied, as shown in Fig. 4b; however the increase is smaller when a UC layer is attached to the cell, as shown in Fig. 4c. This is due to absorption in the PMMA/UC layer. Absorbance of β-$NaYF_4$ is shown in Fig. 5 (bottom); there is a clear correlation between the subbandgap response and the absorbance of $NaYF_4$. This shows that for the low excitation intensities used in this experiment the upconversion efficiency is low and the overall effect of the application of the UC layer is absorption of 980 nm NIR. The absorbed 980 nm light is not reflected back into the solar cell and this explains the observed reduction in the subbandgap response around 980 nm for solar cell c compared to solar cell b (Fig. 4). We conclude that there is a minimum intensity of incoming light needed to have a positive effect of the UC layer.

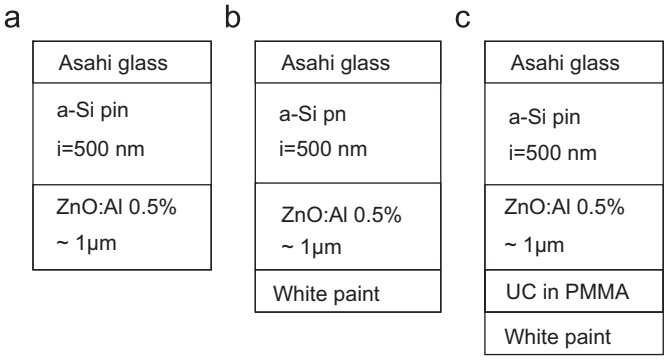

Fig. 4. Schematic overview of different back contact designs of the solar cells used in this experiment.

3.3. Upconversion

For the second set of experiments reference cells were made either with only a white back reflector or with a UC/white back reflector combination (solar cells b and c of Fig. 4) to be able to distinguish between the long-wavelength response due to the UC and that due to direct subbandgap absorption of localized states. Measurements were performed where the solar cells were illuminated by the diode laser. The measurements were performed in a dark enclosure to avoid the influence of any background light. Solar cells b and c were measured. A clear difference between solar cells b and c was measured, see Fig. 5. The solar cells with an upconverter had a higher response (Fig. 6). The current density increase due to the UC is ~5 μA/cm^2. The intensity of the light was high enough to overcome the low efficiency under low illumination densities and the upconversion effect to become dominant over (passive) absorption.

Spectral response measurements were performed when the cells were illuminated by the diode laser. The laser light was chopped (just like spectrally scanned monochromatic light), which causes an offset of spectral response. The response is only due to absorption of the 540 and 653 nm light emitted by the

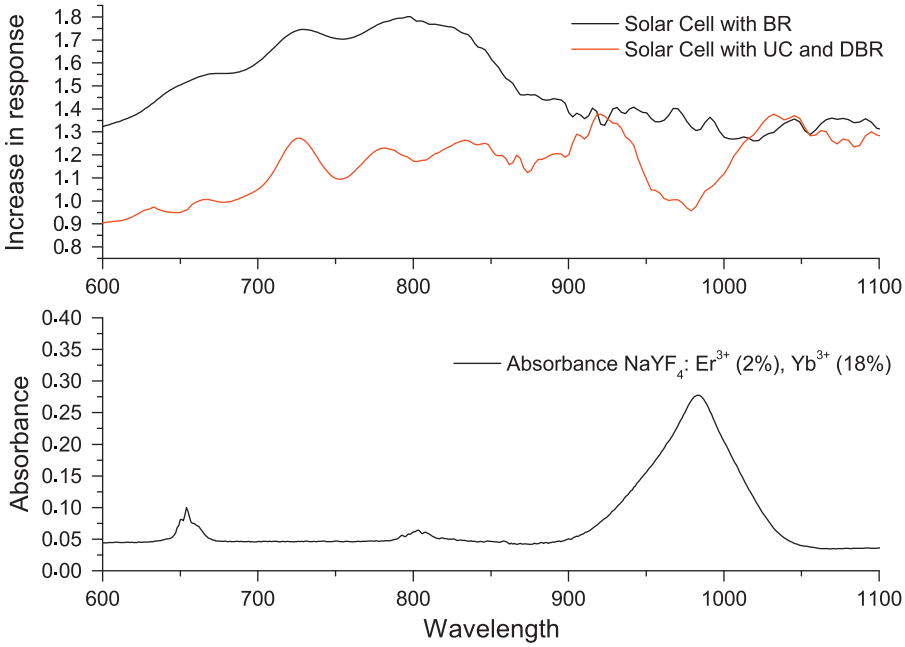

Fig. 5. Upper graph shows the normalized spectral response of the solar cell for red and sub-band gap light. The spectral response is normalized with respect to a cell without back reflector. A solar cell with white back reflector increases the response from 30% to almost twice at the band edges (800 nm), compared with a solar cell without any back reflector. The solar cell with UC, however, increases the response in the NIR by approximately 20%. This is slightly lower due to absorption in the PMMA/UC layer. Around 653, 800 and 980 nm there is a decrease in the response, which is consistent with the peaks in absorbance of β-NaYF4:Er(2%),Yb(18%) depicted in the lower graph.

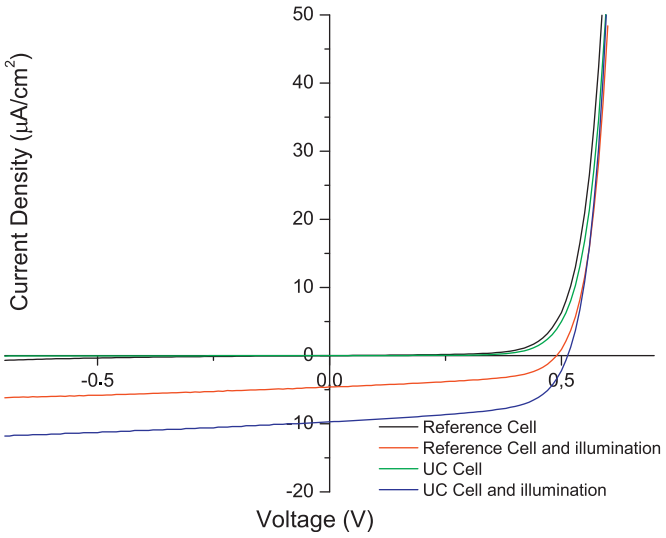

Fig. 6. *I–V* curves of solar cells with and without UC attached at the back. The reference cell has only a white back reflector. In the dark the solar cells have the same *I–V* curve; however when illuminated with the diode laser, with a power of 10 mW, current is generated in both solar cells. The current in the cell with UC is twice the current generated in the cell without UC.

upconverter, but detected at every wavelength setting of the monochromator as the laser light is present at every setting. Taking into account a direct subbandgap absorption of 5 μA/cm^2, and assuming that the laser light is converted to 540-nm light only, the current density improvement due to the offset is 10 μA/cm^2, again amounting to a current of 5 μA/cm^2 due to upconversion.

4. Discussion

Proof-of-principle experiments were performed demonstrating the effect of a UC material on subbandgap response of amorphous silicon solar cells. We have shown that the principle of upconversion is suitable also for amorphous silicon solar cells; clearly improvements are required to make it more significant. Nevertheless, the potential for UC in amorphous silicon is higher than that for crystalline silicon solar cells, considering the major losses associated with amorphous silicon cells due to the high band gap. The β-NaYF4:Er(2%), Yb(18%) phosphor is presently the most efficient upconverter, and the maximum efficiency of the upconverter is reached at 20 W/cm^2 of monochromatic light. The AM 1.5 solar spectrum yields a power density of 1.8 mW/cm^2 between 960 and 1000 nm. Thus concentration of light is necessary.

Light reaching the UC is of smaller intensity than the incoming light; a part is reflected at the front, a part is absorbed in the TCO layers and in the solar cell itself, which was proven by the appreciable subbandgap response. Only 40% of the incoming light reaches the UC layer. The subbandgap response was lower for the solar cell with UC than that for the solar cell with only a back reflector. This is mainly caused by the absorption of light in the UC layer, which would otherwise be reflected by the back reflector. Approximately 4 mW of incoming laser light reaches the UC layer, leading to a current enhancement of 5 μA/cm^2. Since the response is lower with UC, the current of 5 μA/cm^2 found with only the white back reflector that we subtracted from the 10 μA/cm^2 found with UC to find the net improvement was probably too high. Thus the current increase of 5 μA/cm^2 represents a lower limit. Light that is absorbed in the intrinsic layer leads also to current improvements and it is difficult to distinguish the direct photogenerated current from the photocurrent due to upconversion. Intensity dependence measurements, however, will clearly distinguish UC from subbandgap response because of the non-linear behaviour of the UC layer; this will be treated in detail elsewhere [13].

Another loss factor is the fact that upconverted light is illuminating the cell from the back side. Backside illumination leads to a smaller response than frontside illumination. This is mainly caused by the fact that the major part of the unconverted light (~540 nm) is absorbed in the vicinity of the n-layer; thus generation of the electron–hole pairs is close to the n-layer. Holes therefore have to travel a much larger distance if generated at the back, which also means that they are more likely to be lost by recombination events, in particular because our present cells are rather thick. Adjusting the *i*-layer thickness to smaller thickness may thus not only be helpful for interference purposes but also increase the response for backside illumination.

5. Conclusion

We have applied the upconverter β-$NaYF_4$:Yb^{3+}(18%), Er^{3+}(2%) at the back of an amorphous silicon solar cell and have demonstrated that upconversion of NIR light leads to a doubling of the current density due to 980 nm illumination compared with a cell without upconverter. Loss factors have been identified, and will be further investigated.

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