Cell concept for thin film a-Si:H solar cells including photon upconversion

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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 subbandgap infrared irradiation. Current-voltage measurements and spectral response measurements were performed on experimental solar cells. Spectral response measurements showed a current increase of 6% for a silver back reflector and 10% for a diffuse white back reflector with respect to a cell with just a single-layer ZnO:Al back contact. An enhancement of 6.2 μA was measured under illumination with a 980 nm diode laser, at 28 mW. A part of the current was due to subbandgap absorption. Further, 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.
Keywords: a-Si:H, back contact, optical losses, photoluminescence, ZnO

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 1.7 - 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 two or more low energy photons are converted to one higher energy photon. Thus far, research is concentrated 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 than for c-Si solar cells as the transmission losses are larger due to the wider bandgap in comparison with c-Si.

The most efficient UC materials rely on lanthanide ions. UC of lanthanide ions is extensively investigated since the 1960s 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 partially 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 presently 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 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 for which amorphous silicon solar cells have high internal collection efficiency.

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, see Figure 1. As a result of the fact that at least two photons are required to obtain upconverted light the emitted power is quadratically dependent on the excitation power. The maximum upconversion efficiency (5.5%) occurs when the excitation power at 980 nm is more than 20 W/cm^2 [9, 10]; 23% of the absorbed photons is then converted to 522/540 nm and 24 % to 653 nm [11].

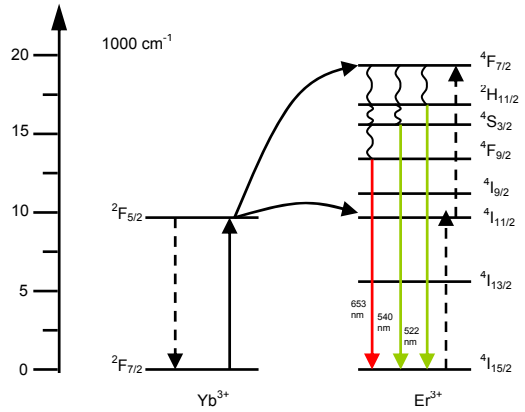

Figure 1: Upconversion in the (Yb^{3+}, Er^{3+}) couple. The dashed lines represent non-radiative energy transfer, the full lines radiative and the curly lines multiphonon relaxation processes. A two-step energy transfer leads to excitation to the $^4F_{7/2}$ state of the Er^{3+} ion. After relaxation 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 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 hours at 750°C. 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 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 back contact a ZnO:Al layer was used.

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 28 mW. The laser beam was not focussed and the area was 1 mm^2 which results in a power density of 2.8 W/cm^2. 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 in 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 for subbandgap light of the solar cell without upconverter was measured as well.

3 RESULTS

3.1 Back contact and back reflector

To have a new solar cell with upconverter layer at the back, the usual 80 nm ZnO/Ag back contact had to be replaced by a thicker layer of TCO that serves as the new back contact. This TCO layer has to be highly transparent for NIR photons and highly conductive to minimize resistance losses. A good TCO is ZnO:Al that is transparent in the NIR. Figure 2 shows the transmission curves for ZnO:Al layers prepared from three ZnO:Al targets with different concentrations of Al. A significant increase of transparency with decreasing aluminum concentration is found. Table I gives the absorption coefficients at 980 nm for the layers obtained at different Al concentrations in the targets. From the viewpoint of transparency only the lower aluminum concentration is very suitable for our solar cells.

To have a TCO layer that serves as back contact a sheet resistance of $R_{\square} < 10\ \Omega$ is required. Figure 3 shows the sheet resistance depending on the thickness. A layer thickness of approximately 1 µm fulfills this requirement for all targets. Table 1 gives the mobility for a layer thickness of approximately 1 µm. A high charge carrier mobility leads to good conductivity and high transparency, making ZnO:Al 0.5% (ZnO with 0.5 wt.-% Al_2O_3) the best option. Therefore, for further experiments the 80 nm ZnO/Ag back contact is replaced by a 1 µm TCO layer from a ZnO:Al 0.5% target. Figure 4 shows the different structures. Front side illumination yields an efficiency of 8% and back side illumination (through the n-layer) an efficiency of 5% of solar cell structure 2a.

By applying a back reflector the current increases. Two different back reflectors were applied, a specular silver and diffuse white reflector. It is expected that a diffuse back reflector increases the current more than a specular reflector, because diffusively scattered light will be better absorbed in the solar cell due to increased path length. Figure 5 shows the spectral response of the solar cell with a 1 µm ZnO:Al 0.5% layer without a back reflector and with a silver and white back reflector (solar cells 2a and b) . Moreover, surface plasmon related absorption loss is absent with the white paint. The current increase is 6% for the silver and 10% for the white back reflector.

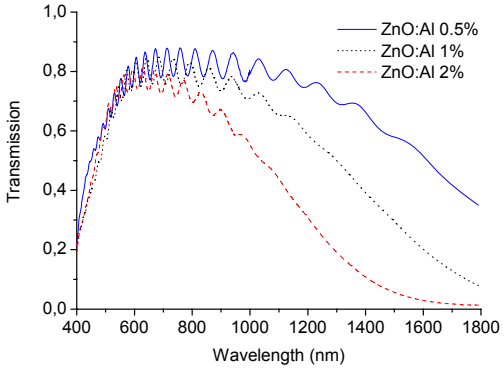

Figure 2: Transmission for 3-µm thick layers obtained from different ZnO targets. The transmission of infrared light is dependent on the aluminum concentration in the targets.

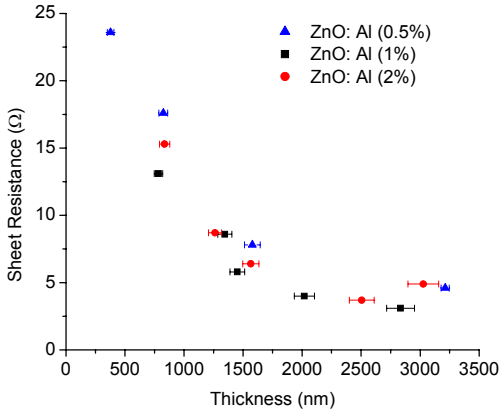

Figure 3: The sheet resistance of layers obtained from different ZnO:Al targets versus thickness of the layers. To have a TCO layer that serves as back contact a sheet resistance of $R_{\square} < 10\ \Omega$ is required, leading to a thickness of at least 1 µm.

Table I: Absorption at 980 nm and charge carrier mobility for layers obtained different ZnO:Al targets

ZnO:Al	Absorption (cm^{-1})	Mobility (cm^2/Vs)
0.5%	13 ± 1	28 ± 2
1%	126 ± 14	21 ± 1
2%	625 ± 40	16 ± 1

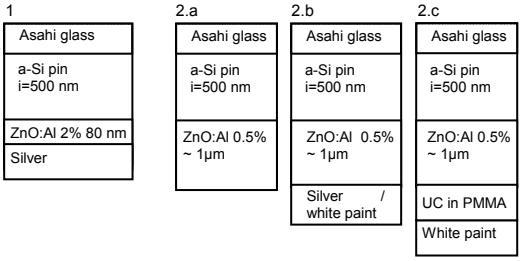

Figure 4: Schematic overview of the different solar cells. Solar cell 1 has the conventional ZnO/Ag back contact/reflector. This is replaced by a thicker ZnO:Al layer and to have upconverter layer at the back (solar cells 2a and 2c).

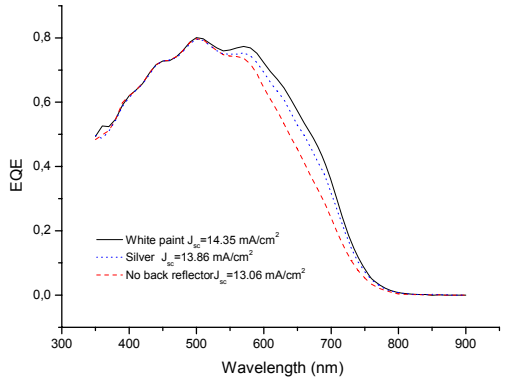

Figure 5: Spectral response measurements for solar cells with 1 µm ZnO:Al 0.5% layer as the back contact and different back reflectors.

3.2 Solar Cells with Upconverter layer

For the second set of experiments reference cells were made either with only a white back reflector on top of the ZnO:Al layer or with an UC/white back reflector combination (solar cells 2b and 2c) to be able to distinguish between the long-wavelength response due to the UC and that due to direct subbandgap absorption of localized states. Current-voltage measurements were performed where the solar cells were illuminated by the diode laser. The solar cells were mounted in a box in which no light from outside could penetrate, so that the response of the solar cell is only due to the diode laser. A clear difference between the solar cell with upconverter layer and reference was measured, see Fig. 6. The reference cell shows a current of 2.1 µA. There is a clear three-fold improvement due to UC leading to a current of 6.2 µA. The EQE is calculated as $I_{sc}/(qP_{in}/h\nu_{980}) = 0.03\%$, where I_{sc} is the short circuit current, q the electron charge, and $h\nu_{980}$ the energy of the 980 nm photon. This EQE is dependent on the UC efficiency, the carrier photogeneration efficiency, and the collection efficiency of the device.

3.3 Power Dependence

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. Intensity dependent measurements have been done on UC material and solar cells by varying the intensity of laser light with neutral density filters. The slope of a log-log curve is used to find the power dependence of the emission by the UC layer. Figure 7 shows the dependence for the red (653 nm) and green (522 and 540 nm) emissions. The slopes are 1.9 ± 0.1 and 1.65± 0.06, respectively. This is consistent with a two-photon absorption process.

The external quantum efficiency (EQE) of solar cells due to non-linear processes like UC is strongly dependent on the illumination intensity. Because EQE is proportional to I_{sc}/P_{in} while the current I_{sc} itself is proportional to $P_{out} \propto P^{n}_{in}$ a power dependence of $P^{n}_{in}/P_{in} = P_{in}^{n-1}$ is expected. We find that EQE increases with increasing intensity, with a slope of 0.72, see Figure 8, from which a value of n of 1.72 is deduced. This matches closely the slope of 1.65 found earlier (figure 7) 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 done. A very weak dependence on the illumination intensity of the reference cell was found, identifying that the sub-bandgap response is almost a linear process and the relative contribution of UC becomes more significant at higher excitation powers.

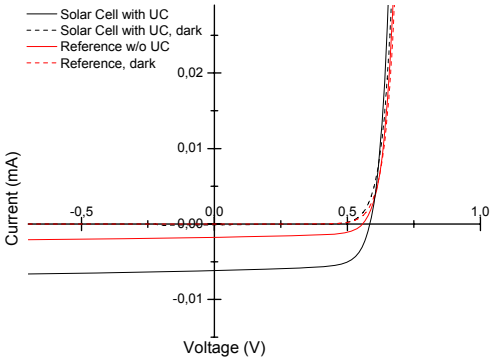

Figure 6 I-V curves of a-Si:H solar cells with and without UC layer attached at the back. In the dark the solar cells have the same I-V curve, however when illuminated with the NIR diode laser (~980 nm), current is generated in both solar cells. The current in the cell with the UC phosphor is a factor of three larger.

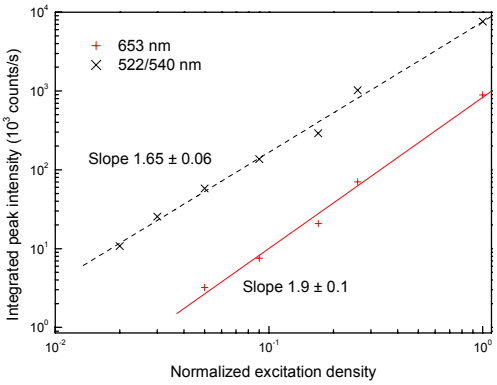

Figure 7: Power dependence of the UC emission intensity in β--$NaYF_4$. The slope in a double logarithmic plot gives the dependence of the emitted light on the excitation power density. The slope of the 522/540 nm emission is 1.65 ± 0.06 (dashed line) and of the 653 nm emission is 1.9 ± 0.1 (solid line), revealing a higher order dependence of the emitted power on the excitation density.

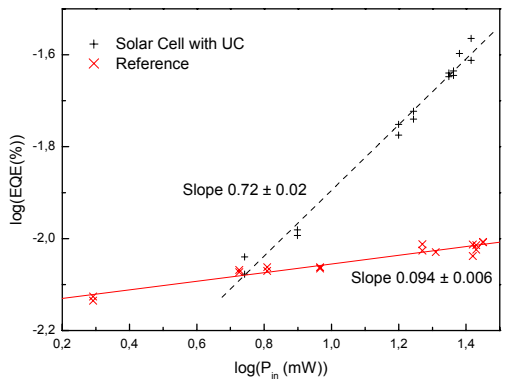

Figure 8: Double logarithmic plot of EQE as a function of excitation power. The slope in case of the solar cell with upconverter (dashed line) matches the expected power dependence of P_{in}^{n-1}, with n equalling 1.65 as found earlier (Fig. 7). The EQE of the reference cell is approximately constant, which is expected for a one photon process.

4 CONCLUSION

A new solar cell concept with upconversion layer is proven to be suitable for thin film amorphous silicon solar cells. The new solar cells were adapted in various ways to apply an upconverter at the back. A silver back contact was replaced by a transparent TCO layer. It was experimentally determined that ZnO:Al from a ZnO target with 0.5 wt.-% Al_2O_3 is a suitable TCO and that white paint is beneficial as back reflector. Proof-of-principle experiments were performed demonstrating the effect of an UC material on the long-wavelength response of amorphous silicon solar cells. We have shown that the principle of upconversion is also suitable for thin film amorphous silicon solar cells.

5 REFERENCES

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