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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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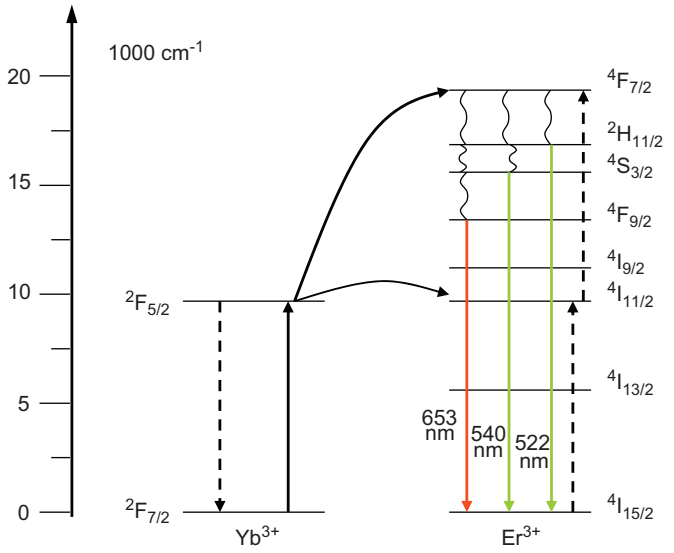

Fig. 1. Energy transfer between Yb^{3+} and Er^{3+} ions. The dashed lines represent non-radiative energy transfer, the full lines radiative and the curly lines cross-relaxation and multi-phonon relaxation processes. A two-step energy transfer leads to excitation of the $^4F_{7/2}$ state of the Er^{3+} 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

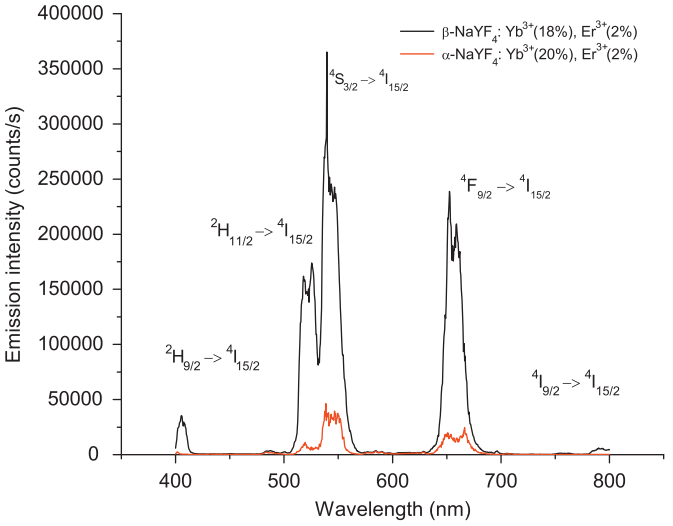

Fig. 2. Emission spectra of two phases of $NaYF_4$ under the same excitation density. The cubic α-phase is less efficient than that of the hexagonal β-phase of $NaYF_4$. The excited $^4F_{7/2}$ state does not emit light but relaxation occurs to the $^2H_{11/2}$, $^2S3_{/2}$ and $^4F_{9/2}$ states. The 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.

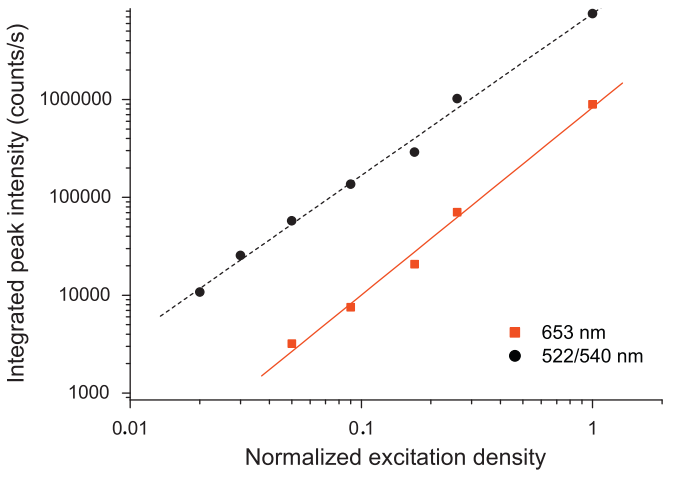

Fig. 3. Power dependence of emission bands in β-NaYF4. The slope in the double logarithmic plot gives the dependence of emitted light on excitation power density. The slope of the 522/540 nm emission is 1.7 (dashed line) and of the red one is 1.9 (full line), revealing a quadratic dependence of emitted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