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Application of NaYF₄:Er³⁺ up-converting phosphors for enhanced near-infrared silicon solar cell response

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Erbium-doped sodium yttrium fluoride (NaYF₄:Er³⁺) up-conversion phosphors were attached to the rear of a bifacial silicon solar cell to enhance its reponsivity in the near-infrared. The incident wavelength and light intensity were varied and the resulting short circuit current of the solar cell was measured. A close match between the spectral features of the external quantum efficiency and the phosphor absorption is consistent with the energy transfer up-conversion process. The peak external quantum efficiency of the silicon solar cell was measured to be (2.5±0.2)% under 5.1 mW laser excitation at 1523 nm, corresponding to an internal quantum efficiency of 3.8%. © 2005 American Institute of Physics. [DOI: 10.1063/1.1844592]

Up-conversion (UC) is the generation of one higher energy visible (400–750 nm) or near-infrared (NIR, 750 nm–3 μm) photon from at least two lower energy (NIR) photons. UC has been studied extensively since the 1960's, with a recent in-depth review by Auzel¹ discussing the history, mechanisms, and applications of UC. To date, UC research has been dominated by applications requiring the UC of NIR to visible light and has also been restricted mainly to the UC of monochromatic light. Silicon solar cells only absorb NIR light with energies greater than the band gap of 1.12 eV corresponding to wavelengths (λ) shorter than 1100 nm and could benefit from the UC of sub-band-gap NIR light (λ > 1100 nm) to visible/NIR light (λ < 1100 nm). Trupke *et al.* have determined that the upper limit of the photovoltaic conversion efficiency of a single junction solar cell coupled to an ideal UC device is 47.6%, when the sun is modeled as a 6000 K blackbody² and 50.7% under the standard air-mass (AM1.5) terrestrial spectrum.³ An efficiency of 63.2% is calculated for concentrated 6000 K blackbody illumination. The optimal band gap for such an UC layer is about 2 eV, with a radiative level lying roughly one third of the way between the valence and conduction bands. In this work, an UC layer is placed on the rear of a bifacial buried contact silicon solar cell and experiments are performed to verify the enhanced solar cell response in the NIR.

Excited state absorption (ESA) occurs when infrared photons are absorbed sequentially within a single ion raising its energy to a higher energy state. The energy transfer up-conversion (ETU) mechanism occurs when an excited ion transfers its energy to a nearby neighboring ion (also in an excited state) raising it to a higher energy excited state, this is denoted by ①, ②, or ③ for a one, two and three step ETU process respectively in Fig. 1. For a two step ETU process, both ions must be in their first excited state before energy can be transferred. This first excited state can be achieved by ground state absorption (GSA, denoted by the solid upwards

arrow in Fig. 1), or by energy transfer from a neighboring ion (denoted by ① in Fig. 1). Since the probability of a two step ETU process depends on the product of the probability of both ions being in their excited state, a quadratic relationship between the resulting luminescence and excitation power exists.⁴

Trivalent erbium (Er³⁺) is an ideal candidate for single wavelength NIR up-conversion due to its ladder of nearly equally spaced energy levels that are multiples of the ⁴I_{15/2} → ⁴I_{13/2} (~1540 nm) transition, as shown in Fig. 1. Erbium is also suitable for photovoltaic UC purposes since the spectral power from the normalized 1000 Wm⁻² AM1.5 spectrum yields over 20 Wm⁻² between 1500 and 1580 nm.

In this work, polycrystalline phosphors of erbium-doped sodium yttrium fluoride (NaYF₄:20% Er³⁺) were fabricated using the method of Krämer *et al.*⁵ Similar phosphors co-doped with ytterbium (NaYF₄:18% Yb³⁺, 2% Er³⁺) have exhibited a NIR to visible UC efficiency (emitted visible power per absorbed NIR power) of 5% with 980 nm pulsed laser (200 W/cm²) excitation.⁶ Yb³⁺ has an excited meta-

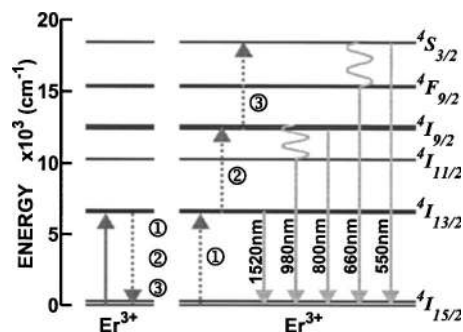


FIG. 1. Three-step UC process between two erbium Er³⁺ ions. Energy relaxation from one Er³⁺ ion (the sensitizer) can result in energy transfer to a neighboring Er³⁺ ion (activator) giving rise to higher energy photons. Solid lines represent photon absorption (up) and emission (down), dotted lines represent energy transfer, wavy lines represent phonon emission. For the two step process, photons with energies greater than the band gap of silicon are emitted.

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stable energy level and is often used as a sensitizer for NIR to visible UC, absorbing photons with wavelengths in the range of 920–980 nm with an emission between 980 and 1030 nm. Since silicon also absorbs at these wavelengths, Yb^{3+} was not added to the phosphor samples utilized here. The yttrium ion is not optically active, however it is effective in providing sufficient dispersion of the Er^{3+} ions thus preventing the onset of saturation. Studies using high Er^{3+} concentrations in $\text{Cs}_3\text{Lu}_2\text{Cl}_9$ have demonstrated the onset of saturation at lower incident pump powers, however, increasing the dopant Er^{3+} concentration increases the absorption and also the relative luminescent emission at these lower powers.^{7,8} Higher wavelength emission intensities are known to increase with higher doping levels due to efficient cross-relaxation (similar to the reverse of the ETU mechanism) processes between Er^{3+} ions.⁴ The energy ETU mechanism is usually the dominant mechanism at high doping ($>2\%$) and low incident excitation intensities ($<200\text{ mW m}^{-2}$).

The polycrystalline UC samples were mixed into an optically transparent (refractive index similar to that of the phosphors) acrylic adhesive medium (weight ratio 0.4:0.6) and adhered to the rear of a bifacial buried-contact silicon solar cell. The solar cell without the phosphor adhered to the rear exhibited an efficiency of 15% and 12% when illuminated from the front and rear, respectively. Reflective white paint was used as a reflector on the rear of the system. The absorption coefficient (α) of a cast 1.5-mm-thick planar UC layer ($\text{NaYF}_4:20\% \text{Er}^{3+}$ phosphors mixed with the transparent acrylic medium) was calculated by measuring the transmission and reflectance using a Varian Cary 5G spectrophotometer. The external quantum efficiency (EQE) was calculated from the short circuit current (I_{sc}) of the solar cell using standard lock-in techniques with a modulation frequency of 1 Hz. A collimated (1.8 mm diameter grin lens) beam from a Santec TSL-210 tunable laser (1510–1590 nm) was used as the excitation source. The power of the incident beam was measured using a calibrated germanium detector both before and after the experiment and adjusted using the internal automatic power control of the laser. In the spectral range $\lambda < 1510$ nm the EQE was measured using a quartz-tungsten-halogen (QTH) lamp in combination with a 1/4 m monochromator as light source. In both cases, a white light bias on the cell was not used.

The similarity between the phosphor absorption coefficient (α) and the EQE response from the solar cell is illustrated in Fig. 2. This similarity suggests that the number of up-converted photons with energies above or near the silicon band gap is almost directly proportional to the number of sub-band-gap 1480–1580 nm photons absorbed. Such a reproduction of the Stark structure from the initial excited state ($^4I_{15/2} \rightarrow ^4I_{13/2}$) is typical for the ETU mechanism since other cooperative effects would show the convolution of all the states involved.¹

Calculating the slope of a double-logarithmic plot of luminescent emission intensity (at a given energy) versus incident excitation power (P_{in}) is a common method used to investigate the power dependence of UC mechanisms.⁴ Since I_{sc} is dependent on the number of electron-hole ($e-h$) pairs and therefore UC emission intensity, a double-logarithmic plot of I_{sc} vs P_{in} can also be used to investigate power dependent mechanisms. This is plotted in Fig. 3 where, at low incident pump powers, a slope of 2.00 ± 0.01 exists, implying

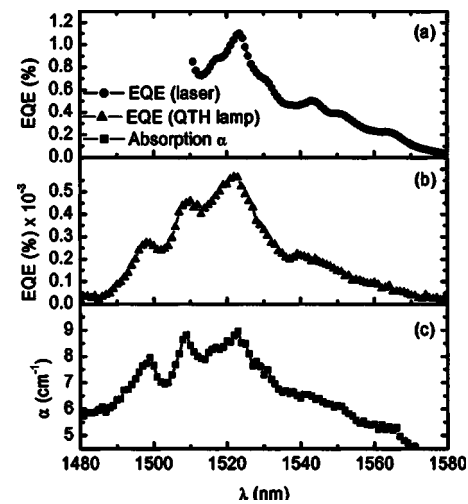


FIG. 2. Similarity between the EQE using constant 3.3 mW laser excitation (a), EQE using QTH lamp excitation (b) and the absorption coefficient of $\text{NaYF}_4:\text{Er}$ (20%) phosphors (c).

that a two-step (quadratic) UC process dominates. It is important to realize that due to carrier thermalization within the silicon, the actual energies of the absorbed photons are unknown. At increasing excitation intensities the slope deviates as predicted when the rate equations of a three-level UC system are solved.⁴

EQE measurements from solar cells are usually independent of incident light intensities since the number of $e-h$ pairs generated is directly proportional to the absorbed number of photons. As a result, the EQE is proportional to the short-circuit current I_{sc} of the solar cell divided by the incident optical power P_{in} ($\text{EQE} \propto I_{sc}/P_{in}$). However, UC is not linearly dependent on incident light intensities and as a result, EQE measurements generally also depend on the incident light intensity. Assuming a quadratic relationship of I_{sc} with incident optical power, a linear EQE dependence is predicted with increasing excitation intensities. Figure 4(a) shows measured EQE values as a function of excitation intensity, while Fig. 4(b) demonstrates that a linear relationship for EQE vs P_{in} indeed exists at lower excitation intensities—in the same range as where the quadratic relationship exists for I_{sc} vs P_{in} (see Fig. 3). The onset of a slope change in double log representation seems to occur at excitation intensities close to 1.7 mW. Another mechanism resulting in the appearance of a slope change in this particular study is that at higher excitation intensities ($>2.2\text{ mW}$),

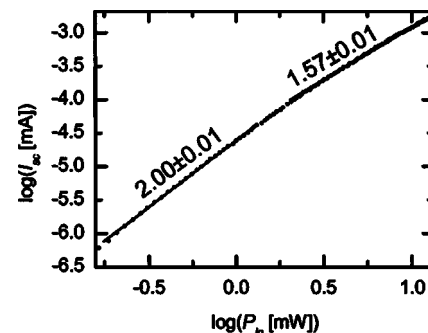


FIG. 3. Current-versus excitation intensity graph where, at low excitation, a two step UC process dominates (with slope close to 2). The excitation wavelength is 1523 nm corresponding to the dominant peak of the absorption spectra.

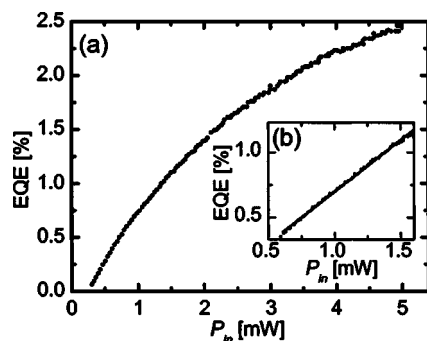


FIG. 4. (a) EQE vs excitation power; (b) close-up showing linear relationship at lower P_{in} (at these powers, $I_{sc} \propto P_{in}^2$).

green luminescence from the phosphors can be seen using the naked eye implying three-step up-conversion to the $^4S_{3/2}$ energy level; see Fig. 1. The emission of these higher energy photons also contribute to the decreased slope since three incident photons are absorbed while still only one $e-h$ pair is generated within the silicon by absorption of the up-converted photon.

Since both Figs. 3 and 4 show the same experimental data in different representations, the deviation from a slope close to 2 in Fig. 3 is equivalent to the deviation from linearity in Fig. 4.

EQE's up to 2.5% have been measured from a silicon solar cell illuminated by a 1523 nm laser source. Taking into account reflection losses from the front and rear surface of the solar cell and absorption losses in the polymer, a peak internal quantum efficiency of 3.8% is calculated. The EQE values achieved with the UC-solar cell combination could be significantly increased by: first, minimizing 1480–1580 nm reflection losses from the bifacial silicon solar cell; second, using phosphors with a higher rare-earth doping level; third, using a transparent medium with a higher refractive index; and finally, using a solar cell with higher rear-side efficiency.

One of the fundamental advantages of the combination of solar cells with UC is that the efficiency of existing solar cells can be improved with no significant modification of the solar cell itself. Fundamentally an UC-layer attached to the rear surface of a solar cell can only lead to an efficiency improvement even if the UC-efficiency is very small. In practice, however, an UC layer attached to the rear surface of a high efficiency silicon solar cell will lead to some parasitic losses due to absorption of near-band-gap light within the different components of the UC-layer and also due to a deterioration of the rear reflectivity and thus of the light trapping properties for near- and sub-band-gap light. The EQE values at wavelengths around 1520 nm of a few percent reported here are still too small to overcompensate such losses. However, these figures are orders of magnitude higher than quantum efficiencies that have been achieved, for example, with the impurity photovoltaic effect in erbium-doped silicon solar cells.⁹ The EQE values reported here indicate that by a further optimization of the UC materials and of the UC system as described above net improvement of the cell efficiency appear to be within reach.

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