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MATERIAL CHARACTERIZATION FOR ADVANCED UPCONVERTER SYSTEMS

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ABSTRACT

Upconversion is a promising way to enhance the efficiency of silicon solar cells, by also using photons with energies below the bandgap of silicon. Unfortunately, promising upconverting materials, such as Erbium-doped $NaYF_4$ have only a narrow absorption range. More photons can be converted, when the upconverter is combined with a fluorescent material. The fluorescent material should absorb over a wide spectral range and emit in the absorption range of the upconverter. PbSe/PbS core-shell nanocrystal quantum dots are a promising fluorescence material for this application. In this paper we present an advanced upconverting system layout, which includes the combination of upconverter and fluorescent material, and the application of photonic structures for spectral management. We also present results from the characterization of the different materials needed for such an advanced upconverter system. An overall optical quantum efficiency of 9.4% was measured for a $NaYF_4$: 20% Er^{3+} upconverter, and it is shown that the absorption and emission characteristics of the PbSe/PbS core-shell Nanocrystal Quantum dots embedded in polymer can be tuned into to the desired spectral region. We also show, that Si/SiC multilayer systems can be used as spectrally selective mirrors for the spectral management.

Keywords: Luminescence, Upconversion, Photon Management, Silicon Solar Cell, Fluorescent Concentrator, Spectral Concentration

1 INTRODUCTION

Silicon is the dominating material for the production of commercial solar cells. Over 80% of the world's solar cell production utilize crystal and mono- and multicrystalline silicon [1]. The key advantages of silicon are its none-toxicity and its abundance. Silicon is the second most frequent element in the earth crust. Additionally, already great know how for its application exists in photovoltaic (PV) technology as well as in microelectronics.

There are two ways to reduce the costs for energy production from PV. The first is to reduce the price of solar cell production. At the moment 70% of the costs are coming from the silicon wafer. So producing thinner solar cells reduces these costs. The second way is to increase the solar cells efficiency to get more of the solar energy converted with the same amount of material.

Silicon solar cells loose about 35% of the incident power because of thermalisation losses. The energy of incoming photons which exceeds the bandgap of silicon is transformed into heat. Another 20% are lost because photons with energy below the bandgap are transmitted straight through the device. Upconversion of these photons is a promising approach reducing these losses without interfering with the electronic properties of silicon photovoltaic devices. The theoretical efficiency limit is raised from near 30% [2] up to 40.2% [3] for a silicon solar with upconverter illuminated by non-concentrated light.

2 A POTENTIAL SETUP FOR AN ADVANCED UPCONVERTER SYSTEM

The major problem of rare earth-based upconverters is their weak and narrow absorption range. One possibility to overcome this limitation is to combine the upconverter with a fluorescent material [4]. The fluorescent material should absorb all photons with wavelength between the bandgap of the solar cell and the absorption of the upconverter and emit in the narrow absorption range of the upconverting material (see Figure 1), so the light of a broad spectral range is used. Because the solar photon density over a broad range is concentrated to a smaller range, we call this process spectral concentration.

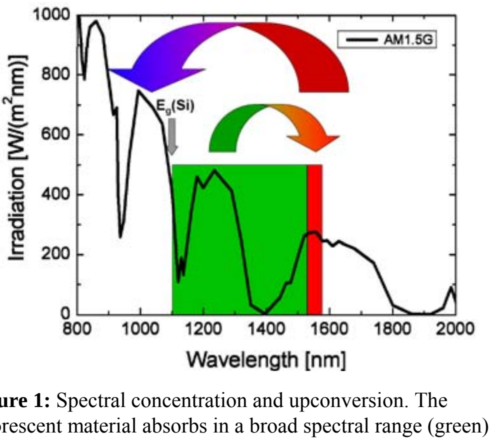

Figure 1: Spectral concentration and upconversion. The fluorescent material absorbs in a broad spectral range (green) and emits in the absorption range of the upconverter (red). The upconverter emits photons with energies above the bandgap E_G of the silicon solar cell.

Organic fluorescent dyes are available, which have quantum efficiencies above 95% for the visible spectrum. Unfortunately, there are no such dyes for the NIR [5]. Potential materials which could work in the NIR are PbSe and PbS nanocrystal quantum dots (NQDs). They show a wide spread absorption because of the semiconductor structure with a well-defined bandedge. However, these NQDs also absorb the photons emitted from the upconverter, see Figure 5. Therefore upconverter and fluorescent material have to be separated from each other. We propose an advanced upconverter system design shown in Figure 2 to achieve these requirements. The fluorescent material is embedded in a transparent matrix material to form a fluorescent concentrator. If the upconverter does not cover the entire back of the solar cell, we achieve a geometric concentration additionally to the spectral concentration. As upconversion is a nonlinear process, the quantum efficiency increases with increasing intensity [6]. So with our concept we can increase efficiency of the upconversion significantly by combining spectral and geometric concentration.

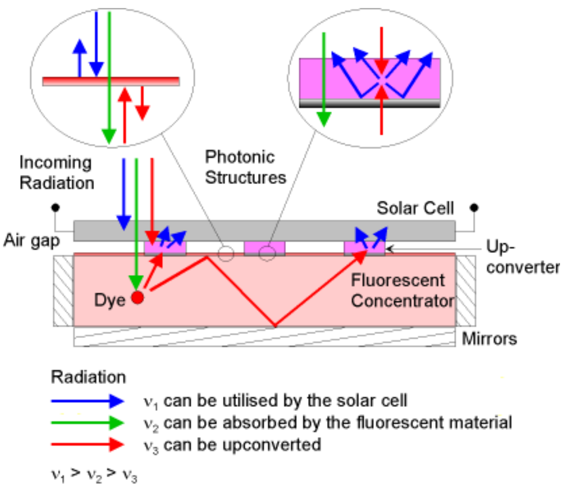

Figure 2: Potential setup of an advanced upconverter system. The solar cell absorbs photons with energies above the band-gap (ν_1). Photons with less energy are transmitted (ν_2, ν_3). The upconverter transforms especially low energy photons, with energies in the absorption range of the upconverter (ν_3), into high energy photons, which can be used by the solar cell (ν_1). Photons with energies below the bandgap but above the absorption range of the upconverter (ν_2) are absorbed in the fluorescent material, which emits photons in the absorption range of the upconverter (ν_3). The emitted radiation is guided by total internal reflection and/or photonic structures to the upconverter. As the upconverter does not cover the whole area, a geometric concentration is achieved. Radiation which is emitted from the upconverter towards the fluorescent concentrator is back reflected by a spectrally selective photonic structure.

Selective reflecting photonic structures between fluorescent concentrator and upconverter prevent upconverted light from entering the fluorescent concentrator and getting potentially lost. A second photonic structure serves as a mirror for photons with energies above the bandgap of the solar cell material and enhances the collection efficiency of the fluorescent concentrator [7].

3 MATERIAL CHARACTERIZATION

The advanced upconverter setup can be split into three parts: The upconverter, the fluorescent concentrator and the photonic structures. To determine their properties and to optimize them for their later use in the system we characterized them separately. The first focus of interest is to match spectral properties, which are the luminescence range of the fluorescent material, the absorption range of the upconverter and the reflection bands of the photonic structures.

3.1 Upconverter

Promising upconverters are rare earth-based materials, especially trivalent Erbium (Er^{3+}). The schematic configuration of Er^{3+} is shown in Figure 3. Absorption of photons with wavelengths around 1520 nm successively pumps the levels $^4I_{13/2}$, $^4I_{9/2}$ and $^4S_{3/2}$. These excited states decay to the next lower lying state or directly and radiatively to the ground state. Photons emitted by a transition process from $^4I_{11/2}$ or higher excited levels back to the ground state have more energy than the bandgap of silicon.

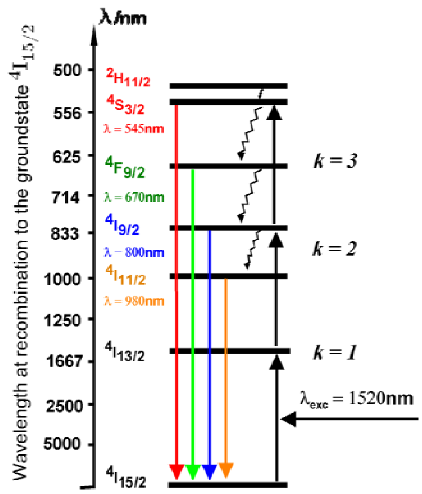

Figure 3: Schematically configuration of Er^{3+}. Radiative absorption are indicated by black, radiative emission by colored and non-radiative by wavy arrows.

Because of the low non-radiative recombination $NaYF_4$ is a good host material for the Erbium. We used $NaYF_4$: 20% Er^{3+}, which found to be an efficient upconverter from NIR to visible spectral regime [8, 9]. For our measurement a 150 µm thick $NaYF_4$: 20% Er^{3+} powder layer was pressed between two glass plates. The upconverter was illuminated with a Santec ECL-210 laser at a wavelength of 1523 nm and an irradiance of 2032 W/m^2. The emitted photons were detected with a Si and an InGaAs solar cell. The setup was calibrated with a tungsten band lamp. The lamp is used as a grey emitter at a defined temperature. Figure 4 shows the number of photons emitted at each wavelength divided by the total amount of incoming photons. We get the strongest emission for the transitions from the levels $^4I_{11/2}$ and $^4I_{9/2}$ back to the ground state with wavelengths of around 980 nm and 800 nm. For the excitation of these levels only two photons are needed. Further upconversion to higher levels requires more photons. Integration of the spectrum yields an overall quantum efficiency of 9.39%. As at least two absorbed photons are needed for the emission of one upconverted photon, nearly 20% of the incoming photons contributed to an upconversion event.

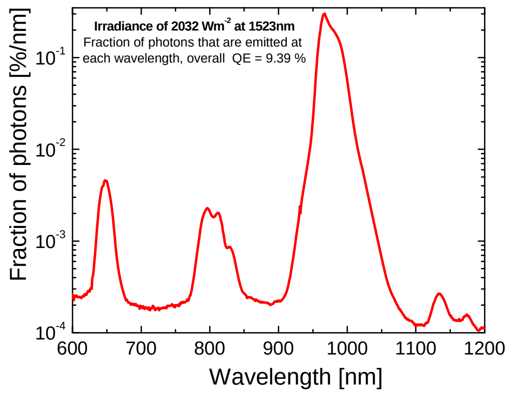

Figure 4: Calibrated photoluminescence measurement of $NaYF_4$: 20% Er^{3+} with an irradiance of 2032 W/m^2 at an incoming wavelength of 1523 nm

3.2 Fluorescent Material

As mentioned before PbSe/PbS core-shell NQDs are promising fluorescent materials for the spectral concentration. They have the additional advantage, that their spectral properties can be tuned by the variation of their diameter and their composition.

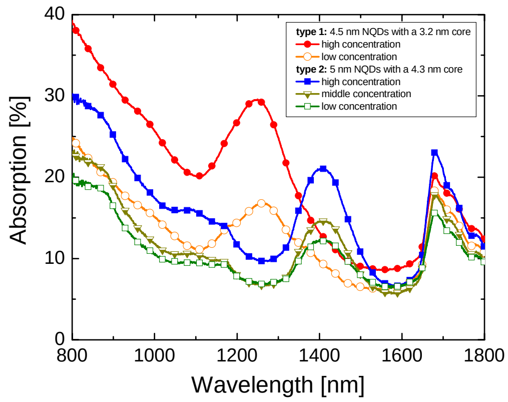

Figure 5: Absorbance of PbSe/PbS NQDs embedded in PMMA. The samples vary by NQDs concentration in polymer and different core/shell size and composition.

Transmission *T* and reflection *R* of first PbSe/PbS core-shell NQDs in $[CH_2C(CH_3)(CO_2CH_3)\text{-}]_n$ (PMMA) were measured with a Cary 500i. The absorption was calculated via 1-*T*-*R* and is shown in Figure 5. The different samples are embedded in a polymer. The samples of type 2 have a 3.2 nm PbSe core with a PbS shell whose size is about 1.5 monolayer. The total size is around 4.5 nm. The difference between the samples is the different concentration of the NQDs in the polymer. The samples of type 2 have a 4.3 nm core with a less than 1 monolayer shell. The total size is about 5 nm and the difference is again the concentration of the NQDs in the polymer. The weight fraction of the NQDs to the polymer is around 1% and decreases to nearly 0.6% for the different samples. The sizes of the samples are determined using transmission electron microscope (TEM) measurements of similar samples. Therefore the data are not absolutely exact.

The samples of type 1 have a higher and better suited absorption for our needs. The absorption peak at 1250 nm is close to a lateral maximum of the standard solar spectrum AM1.5G. Otherwise the luminescence peaks of type 2 NQDs are at higher wavelength and therefore better suited for the absorption range of the upconverter $NaYF_4$: 20% Er^{3+}.

Figure 6 shows the photoluminescence spectrum of the same samples. The NQDs were illuminated with a 3 W laser at a wavelength of 810 nm. To reduce the strong laser peak a high pass filter was built in. Nevertheless a sharp peak at 1620 nm appears which is the second harmonic of the laser wavelength. Due to the absorption range of the upconverter $NaYF_4$: 20% Er^{3+} from 1470 nm to 1580 nm the luminescence peaks are at to low wavelengths. The full width at half maximum differs from 200 nm up to 400 nm.

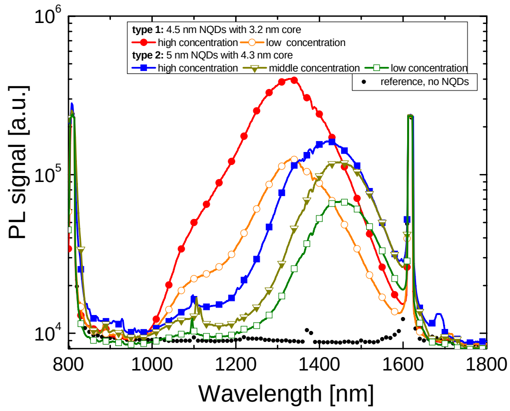

Figure 6: Photoluminescence spectrum of PbSe/PbS nanocrystal quantum dot samples embedded in PMMA. The samples vary by different concentration and core/shell size and composition. Illuminated with a 3 W laser at a wavelength of 810nm

For better efficiencies the absorption of the NQDs has to be improved over the range of 1100-1500 nm. Furthermore, the luminescence has to be narrowed and shifted to the absorption range of the upconverter.

3.3 Photonic Structure

Another important feature of the advanced upconversion setup are structures which reflect spectrally selective. Photonic structures with desired spectral selectivity can be realised by variations of Rugate structures [5,10]. These are one-dimensional photonic crystals with a continuously varying refractive index. They are realized with multilayer systems made from silicon alloys. With silicon carbide (SiC) deposited by Plasma Enhanced Chemical Vapour Phase Deposition (PECVD) it is possible to create photonic structures with very high refractive index contrasts. Depending on the composition of the SiC, the refractive index of the deposited material can be varied between 1.8 and 4.0. A high refractive index contrast is important because some of the optical properties only occur, if the refractive index contrast inside the structure is sufficiently high. The reflection of first photonic structure made from PECVD-deposition SiC at Fraunhofer ISE is shown in Figure 7.

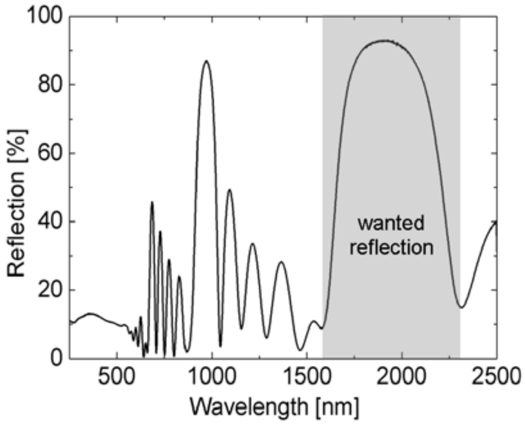

Figure 7: Reflection of a first photonic structure made from PECVD-deposited SiC at Fraunhofer ISE.

The wanted spectral selectivity is already visible. However, the potential of such structures is not utilized so far. One reason is that the refractive index contrast is not high enough yet. The extension of SiC alloys with other elements such as nitrogen and oxygen leads to higher index contrast and should enable to reach the desired quality.

Other promising photonic structures are the three dimensional photonic crystals with an opal-like symmetry. The opal consists of spheres that are arranged in a hexagonal closest package. This structure can be produced on large areas with a self-organisation process.

4 SUMMARY

In this paper we characterized potential materials for an advanced upconverter system concept. It comprises spectral concentration with a luminescent material with additional geometric concentration by utilizing the fluorescent concentrator effect. Additionally spectral management with selectively reflective structures is applied. A quantum efficiency of 9.39% was measured for the upconverter $NaYF_4$: 20% Er^{3+} at an irradiance of 2032 W/m^2. Absorption and photoluminescence spectra of PbSe/PbS core-shell NQDs embedded in PMMA serving as a fluorescent material were shown. For these samples the absorption between the bandgap of silicon and the absorption of the upconverter at around 1520 nm has to be improved as well as the luminescence range shifted to higher wavelengths. The reflection of first photonic structures made from SiC has been measured. High reflection in the wanted spectral region was achieved, but the performance of the structure has to be improved by the incorporation of other elements such as nitrogen and oxygen into the alloy.

5 ACKNOWLEDGEMENTS

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