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Purcell effect and luminescent downshifting in silicon nanocrystals coated back-contact solar cells

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ABSTRACT

Silicon nanocrystals show a significant shift between the strong absorption in the blue–ultraviolet region and their characteristic red–near-infrared emission as well as space separated-quantum cutting when short wavelength photons are absorbed. These two effects can be used to increase the efficiency of crystalline silicon solar cells. We fabricated high quality interdigitated back-contact crystalline silicon solar cells in an industrial pilot line and coated them with optimized silicon nanocrystals layers in a cost effective way. Here we demonstrate an increase of 0.8% of the power conversion efficiency of the interdigitated back-contact cell by the silicon nanocrystals layer. In addition, we prove that this increase is due to a combination of a better surface passivation, a better optical coating, and of the luminescent downshifting effect. Moreover we demonstrated that the engineering of the local density of photon states, thanks to the Purcell effect, is instrumental in order to exploit this effect.

1. Introduction

Production of photovoltaic cells is dominated by single junction devices based on crystalline silicon [1], which account for about 90% of the world total photovoltaic cell production. Considerable progresses in increasing the efficiency of crystalline silicon solar cells have been made by minimizing photon, carrier and electrical losses through new cell structures and processes, such as interdigitated back-contact cells (IBC) or heterojunction cells with intrinsic thin layer [2]. At the same time, enormous interest raised in novel approaches–third generation photovoltaic–aimed at increasing the efficiency with new concepts [3]: improved light harvesting [4–7], minimization of hot carrier losses by promoting fast and non-dissipative recombination mechanisms [8–12], and modification of the solar spectrum through photon conversion [13,14]. In this context the exploitation of luminescent downshifting effect (LDS) and space separated-quantum cutting (SSQC) [12] is of special interest, allowing the combination of different concepts to improve the cell efficiency with practical production technologies.

The basic idea of LDS is to move short-wavelength photons to long wavelength photons [13]: a range where silicon solar cell has almost 100% internal quantum efficiency (IQE). In this way, the short circuit current density (J_{sc}) is increased while the open circuit voltage (V_{oc}) is barely affected [13]. Up to now, LDS has not been engineered in an effective way. A few successful reports demonstrated industrialization of LDS by using phosphor doped ethylene vinyl acetate with an increase of 0.3% in module efficiency [15] or by using inkjet printing with a relative increase in the cell efficiency of 2% [16]. Interestingly, many reports address the use of silicon nanocrystals (Si-NCs) as suitable candidates for LDS [16–19]: these nanoparticles are stable, bright, show a significant red-shift between emission and absorption [20], and can be manufactured by using standard deposition techniques. In addition, SSQC in Si-NCs has also been reported [8–12]. This process involves the transformation of a high-energy photon into two or more photons of lower energy, hence "cutting" the energy quantum [12]. Ideally, the down-converted photons are in a suitable range of the spectrum and can be further used without

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loss of energy. A similar idea involves the generation of multiple electron–hole pairs by a single high-energy photon absorbed in a nanocrystal. This process, called multiple exciton generation, can be used as an internal gain process in the solar cell. Indeed, a peak external quantum efficiency exceeding 100% has been reported for PbSe quantum dot solar cells exploiting multiple exciton generation [21].

In this paper, an innovative method is presented to fabricate interdigitated back contact silicon crystalline solar cells in an industrial pilot line [22] coated by an optimized Si-NCs layer in a cost effective way [23]. An improvement in the power energy conversion efficiency of 0.8% was measured. We prove that this increase is due to a combination of different effects: a better surface passivation, a better optical coating, LDS effect, and that the engineering of the local density of photon states is instrumental in order to exploit this effect.

2. Materials and methods

To exploit LDS stemming from Si-NCs implemented directly on solar cells, we fabricated interdigitated back contact solar cells on 25 Ω•cm n-type doped float-zone silicon wafers with bulk minority carrier lifetime higher than 5 ms coated with Si-NCs in an industrial process [22]. The wafer thickness (160 μm) guarantees a high collection efficiency of the minority carriers. All wafers were saw-damage etched in a 22% NaOH solution, resulting in chemically polished surfaces. Prior to the diffusion processes, the wafers were cleaned in a 5% HCl, 2% HF and a piranha solution (i.e., 6:1 mixture of concentrated H_2SO_4 and 30% H_2O_2), with DI water dips in between every step. The subsequent process involved the formation of the front surface field (FSF) and the back surface field (BSF) by phosphorus doping with oxychloride ($POCl_3$) as a diffusion source in an industrial-size quartz tube furnace, followed by a plasma enhanced chemical vapour deposition (PECVD) of a dielectric mask on the BSF side and etching of the phosphorus silicate glass. At this stage of the process the solar cells were coated, on the FSF side, with an optimized 55 nm-thick SiO_2 and 65 nm-thick silicon rich oxide (SRO) double-stack antireflection coating (ARC) to fabricate Si-nanostructured solar cells or by an optimized 75 nm-thick SiN_x and 5 nm-thick SiO_2 double ARC layer to develop industry-standard IBC solar cells. In the next process step, the interdigitated pattern on the backside was accomplished by laser ablation of the mask layer followed by a laser-damage etch and surface cleaning (as described before). A p^+ emitter was then formed in the ablated areas by boron tribromide (BBr_3) tube diffusion. After borosilicate glass etching and another surface cleaning, the backside of the IBC cells was passivated by a 20 nm-thick thermal SiO_2 and about 60 nm-thick SiN_x double-layer stack. The cell fabrication was then completed by metallization using standard screen-printing of an Ag paste (for BSF) and an Ag/Al paste (for emitter), with a subsequent contact-firing step. For more details on the used process flow, see the Supplementary information.

Si-NCs in a SiO_2 matrix were produced by thermally induced phase separation of the SRO layer. During the high temperature-annealing step (1100 °C for 1 h), Si-NCs nucleate within the SRO layer [24]. The main problem concerning the integration of this active element into the cell manufacturing process is the high temperature-annealing step necessary for the nanoparticles formation. This additional thermal treatment takes place at significantly higher temperature than the typical diffusion temperature used to form the emitter or the back/front surface field regions. As a consequence the whole IBC cell process will be affected, resulting in lower solar cell performances. In order to overcome this drawback, we integrated the annealing within the IBC cell process steps. Particular care was taken in order to depart as little as possible from the standard industrial process used to produce the IBC cells [22]. For that matter the SiO_2/SRO double-stack layer was deposited at the stage when in the standard process the passivation layer was deposited on the front side, while the annealing step used to drive in the dopants was adapted to be also used to induce the Si-NCs in the SRO. In more detail, by carefully adapting the temperature profile during initial $POCl_3$ diffusion, we successfully incorporated the annealing of Si-NCs in-situ during the subsequent BBr_3 diffusion, thus further reducing the number of process steps and fabrication cost of the solar cells. The entire IBC cell process presented here uses only fabrication techniques readily available in most pilot production lines, making such an approach relevant for commercialization. Reference industry-standard solar cells (named REF in the following) were also fabricated with the same batch processing. In this case, an optimized 75 nm-thick SiN_x and 5 nm-thick SiO_2 double stack ARC layer was used on the front side, as described above. This layer was made via PECVD deposition. For more details on the thickness optimization, see the Results and discussion section. In addition it should be mentioned that these cells are fabricated on flat surface (not textured), resulting in a lower photocurrent generation. It was not possible to fabricate Si-nanostructured IBC textured solar cells due to technical issues in processing textured surfaces together with the nanoparticles formation.

The total reflectance spectra of the Si-nanostructured and reference IBC solar cells were measured with a Perkin-Elmer Lambda 950 spectrometer using an integrated sphere to 150 mm. The measured total reflectance R was converted to the total absorption (1–R) and used to extract the internal quantum efficiency from the external quantum efficiency measurement. In order to study the optical properties of the different double stack ARC layers, we used a variable angle spectroscopy ellipsometer (VASE) to measure the refractive index and their thicknesses. The ellipsometric spectra were measured from 0.28 to 1.2 μm at different angles and the dielectric function, and then the refractive indices were obtained by a standard least square regression analysis. The Si-NCs photoluminescence spectra were obtained by using the 355 nm line of a Nd:YVO_4 laser to excite the samples at normal incidence.

To isolate the LDS effect from the other contributions to the short circuit current increase, we used two different approaches. In the first approach we have deposited, via PECVD, an optimized 130 nm of SRO layer on 500 μm thick amorphous quartz substrate. In the second method a colloidal suspension of Si-NCs in glycerol, obtained from sonification of porous silicon as described in [25], was used. In this study the J_{sc} measurements were performed using an ABET sun 2000 solar simulator class AAB and a Keithley source-meter series 2612 A. A Peltier element coupled with a Pt100 was used to control the temperature of the cell (23 ± 1 °C) during the experiments.

3. Results and discussion

Optimization of the layer thicknesses with respect to low reflectance, high absorbance and maximum emission is needed to maximize the solar cell performances [18]. Using the model presented in [18], we have optimized a SiO_2/SRO double layer stack on top of a silicon substrate in order to yield maximum short circuit current density. To perform this optimization, we used the measured internal quantum efficiency of the IBC cell. Further, we used the measured refractive index of an annealed SRO layer (Fig. 2d). The refractive indices of the other materials were taken from the database of the thin film modelling software Scout® [26]. Fig. 1 shows the results of these calculations for both the REF and