Enhancing the power conversion efficiency of solar cells employing down-shifting silicon quantum dots

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Abstract. We report the synthesis and characterization of silicon quantum dots that exhibit down-shifting, photo luminescent characteristics. We also discuss the fabrication and characterization of single crystal Silicon (c-Si) Solar cells with and without the influence of the previously mentioned QDs. The incorporation of these nanostructures triggers improvements in the performance of the fabricated photovoltaic devices, especially in the open circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$). Specifically, the experimental results showed increments in the $V_{oc}$ from 532.6 to 536.2 mV and in the $J_{sc}$ from 33.4 to 38.3 mA/cm$^2$. The combined effect of those improved $V_{oc}$ and $J_{sc}$ values led to an increment in the power conversion efficiency (PCE) from 11.90 to 13.37%. This increment represents an improvement of the order of 12.4% on the power conversion efficiency of this type of solar cells. The observed results could be conducive to promoting the proliferation of photovoltaic structures.

1. Introduction.

Even though the wavelength distribution of the solar spectrum extends from the infrared (2500 nm) to the ultraviolet (280 nm) one of the major problems in solar energy conversion is the relatively small absorption range of the materials employed in solar cells [1-4]. The underlying reason is that in principle only photons with energy greater than the bandgap can be absorbed by the material leading to the loss of relatively low energy photons. But even photons with energies much larger than the bandgap have a non-negligible probability of interacting with crystal phonons, in a process referred to as thermalization, rather than producing electron-hole pairs [3].

These fundamental losses can be ameliorated by the utilization of luminescent materials. To promote the absorption of low energy photons, near and below the bandgap, particles with up-conversion properties can be employed [5, 6]. On the other hand, in the case of energetic photons that contribute to thermalization, the alternative is to employ down-shifting materials, such as silicon quantum dots (Si-QDs) [7-9], able to emit lower energy photons that fall within the range of absorption by the underlying solar cell.
2. **Experimental.**

2.1. **Silicon Quantum Dots Synthesis.**

Silicon quantum dots (Si-QDs) were synthesized following the method described by Wang et al. [10] to achieve water-dispersible Si-QDs at room temperature. The Si-QDs were prepared by adding (1.5, 1.75 and 2.0) mL of (3-Aminopropyl) triethoxysilane 99% (APTES) to 4 mL of deionized (DI) water and stirred for 10 minutes. After that, 1.25 mL of 0.1 M (+)-Sodium L-ascorbate ≥ 98% (SA) was added to the previous mixture and stirred by an additional 30 minutes. The synthesis of Si-QDs was carried out using different amounts of APTES to achieve a batch of samples in order to characterize their photo-luminescence under UV radiation and the performance of solar cells in the presence of the aforementioned QDs.

2.2. **Silicon Solar Cell Fabrication.**

The silicon solar cells under study were fabricated from 4-inch, n-type, <100> silicon wafers with resistivity of 10–20 Ω-cm employing a spin on dopant technique (SOD) that has been described elsewhere [11].

The wafers were cut into pieces of approximately 30 x 30 mm; subsequently the samples were cleaned employing an extended 4-steps RCA cleaning process. To create the p-type emitter and the n+ back surface field (BSF) for charge collection, Boron and Phosphorous spin-on-dopant (SOD) solutions were prepared by the sol–gel method [11]. The Boron (SOD) solution was spin coated on the window side of the silicon sample and the Phosphorous (SOD) was deposited on the opposite side. Then, the samples were baked at 120°C for 10 min to remove the organic solvents. Subsequently, an annealing of 10 minutes at 1000°C was performed to diffuse the dopants and create the p–n junction and the BSF. To make the electrical contacts, a layer of 200 nm of aluminum was deposited on each side of the device by thermal evaporation. A shadow mask was used on the window side to make a pattern of finger electrodes, while a blanket deposition was performed in the back side. Then, the samples were annealed at 585°C for 10 min to promote the formation of an ohmic Al/Si contact.

Subsequently, Si-QDs films were spin cast on the window side of the solar cell. To this end, 200 μl of Si-QDs solution was dispersed with an angular velocity of 4000 rpm during 60s. All the samples were characterized by the same method in order to compare the performance of the device with and without the influence of the Si-QDs. Figure 1 show the flowchart of the fabrication and deposition process.

![Figure 1. Flowchart of the fabrication of c-Silicon solar cell and Si-QDs deposition: 1) Extended RCA cleaning, 2) Diffusion of the emitter layer and BSF, 3) Front and back electrode deposition and 4) spin casting of a Si-QDs layer.](image)

3. **Results and Discussion.**

3.1. **Characterization of Silicon Quantum Dots.**

The UV-Vis absorption spectra of the synthesized Si-QDs were measured using a Varian Cary 5000 UV-Vis spectrometer, while the photoluminescence effects were recorded using an Ocean Optics Flame-S-UV-VIS spectrometer. The absorption and photoluminescence spectra of the different synthesis process of Si-QDs are shown in Figure 2. All the synthesized Si-QDs show an absorption spectrum tapering off beyond ~500 nm. The photo-luminescence spectra consist of broad bands extending from 450 to 650 nm in all cases with variations in the maximum intensity and the peak position. Figure 2 shows that the variation in the amount of APTES used in the synthesis has a relatively minor effect on peak position that fluctuates from 521 nm to 526 nm, for 1.5 ml and 2.0 ml of APTES, respectively.
A Zetasizer Nano Series using a dynamic light scattering method (DLS) was employed to perform measurements of the average size of the synthesized silicon nanoparticles. As shown in Figure 3, the amount of APTES has a relatively minor influence on the size of the QDs whose diameter is centred around 2.6 nm. For subsequent characterization efforts, the samples with the highest photoluminescence intensity were selected, namely, 2.0 ml APTES (with 0.1M SA and 30 min of reaction).

3.2. Solar Cell Characterization.

A set of three c-Si solar cells were fabricated with the previously described approach. Si-QDs with 2.0 ml APTES were deposited on the set of solar cells to determine the influence of synthesis variable. I–V characteristics of the devices were measured before and after the deployment of the Si-QDs. In all cases, the utilization of Si-QDs improved the performance of the solar cells. In general the short circuit current had a more pronounced improvement than the open circuit voltage as shown in Figure 4.

The averages of the solar cell performance parameters are listed in Table 1. The application of these nanostructures on the c-Si solar cells lead to increases in two of the three main parameters that contribute to solar cell efficiency, namely, the open circuit voltage ($V_{oc}$) and the short circuit current density ($J_{sc}$). An improvement was observed in all the solar cells after the deposition of the Si-QDs synthesized, where the solar cell $V_{oc}$ increased from an average of 532.57 to 536.20 mV, the $J_{sc}$ went from 33.42 to 38.28 mA/cm$^2$ and although the fill factor (FF) decreased from 66.87 to 65.20%, the combination of all these parameters led to an improvement of the power conversion efficiency (PCE) from 11.90 to 13.37% for an overall PCE improvement of 12.4%.

| Solar cell performance | Voc (mV) | $J_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|------------------------|---------|---------------------|--------|---------|
| c-Si Solar cell set    | 532.57  | 33.42               | 66.87  | 11.9 ± 0.27 |
| c-Si Solar cell set + Si-QDs | 536.2  | 38.28               | 65.20  | 13.37 ± 0.19 |

Figure 5 shows the spectral response of the c-Si solar cell with the application of Si-QDs. EQE measurements indicate that the QDs are improving the photocurrent generation specially in two segments, namely, (i.) below 600 nm, in agreement with the photo-luminescence spectra, and (ii.) a broad contribution with maxima ranging from 850 to 950 nm which could be attributed to a change in the reflectance due to the Si-QDs layer. These EQE improvements are thought to be responsible for the current increase measured during the current – voltage analysis.
4. Conclusions.
In the present work it was studied the influence of Si-QDs in c-Si solar cells as photovoltaic response improvers. The Si-QDs were synthesized using a water-dispersible method. Different amount of APTES were used in order to obtain different emission spectra. Experimental results showed that the incorporation of Si-QDs as down-shifting material on the window side of a solar cell improves the photocurrent generation which can be seen from the current density and open circuit voltage increase. Even though the FF was observed to decrease in all cases, the overall power conversion efficiency achieved after the application of Si-QDs was increased from 11.90% to 13.37 %. This result represents an improvement of 12.4% in the photovoltaic performance. The experimental results evince that this strategy represents a promising way to improve the efficiency of existing solar cells, which could promote the proliferation of photovoltaic energy harvesting.

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