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High Efficiency Si Quantum Dot Heterojunction Solar Cells using a Single SiO$_x$:B layer

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Abstract

Most of the Si quantum dot (QD) has been fabricated from SiO$_2$/SiO$_x$ multilayer structure in order to create a homogeneous size. However, this structure achieved much lower efficiencies than expected in the Si QD photovoltaic field. It is because the Si QD generation and the photoexcited carrier transport is restricted by adjacent SiO$_2$ layer. In this study, we applied a single SiO$_x$:B layer fabrication method to the Si QD heterojunction solar cells. The number of generated Si QDs and the photo-excited carrier lifetime was maximized when the oxygen partial pressure and boron doping concentration parameters were $2.7 \times 10^{-5}$ Torr and $2.27 \times 10^{17}$ atoms/cm$^2$, respectively. As a result, over than 17% power conversion efficiency of Si QD heterojunction solar cell was achieved using the single layer method.

Supplementary material for this article is available.

Keywords: Silicon quantum dot, Single layer method, Heterojunction Solar cell

(Some figures may appear in colour only in the online journal)

1. Introduction

Nowadays, various kinds of next-generation solar cells have been developed to overcome the Shockley-Queisser limit of conventional solar cells [1-3]. Among these, Si QD solar cell has been studied as one of the promising candidates [4-6]. The Si QD, whose size is smaller than Bohr radius of Si, has a large band-gap due to quantum confinement effect [7]. These Si QD can extensively absorb the solar energy than bulk Si. Martin group at the University of New South Wales (UNSW) utilized these merits and firstly achieved a Si QD heterojunction solar cell with an efficiency of 10.6 % from SiO$_x$/SiO$_2$ multilayer structures on a p-type Si wafer [8]. After that, various fabrication parameters, such as size, stoichiometry, and matrix materials, have been studied to improve the efficiency of Si QD heterojunction solar cells with multilayer structures [4, 9-11]. The highest power conversion efficiency has been reported as 13.4% [12]. However, photoexcited carrier transport and number of generated Si QDs in this structure has a restricted by adjacent SiO$_2$ layer, which has a crucial impact on the efficiency in Si QD based photovoltaic cells [8, 13].

Recently, we have fabricated Si QD heterojunction solar cells with 14.8 % efficiency from a boron-doped single SiO$_x$ layer (SiO$_x$:B) [14]. In addition, we have studied the importance of the B doping concentration for the effective electronic band engineering of the absorption layer in Si QD heterojunction solar cells [15]. In this study, first, we compared the number of generated Si QDs from a single SiO$_x$ layer structure and a SiO$_2$/SiO$_x$ multilayer structure. Second, we optimized the oxygen partial pressure (PO$_2$) and doping concentration as an independent variable in the single layer method for high-efficiency Si QD heterojunction solar cells. As a result, the short circuit current ($J_{sc}$) was nearly maximized to 40 A/cm$^2$, and its power conversion efficiency was highly improved from 15.00 to 17.04 %.

2. Experimental
2.1 Characterization of single SiO$_2$:B layer

The SiO$_2$:B layers with a thickness of about 100 nm were grown on 6 inches n-type Si (100) substrates (<10 $\Omega$cm, CZ) by an ion beam sputtering deposition (IBSD) method [16]. The stoichiometry of the SiO$_2$:B layer was controlled by varying the oxygen partial pressure (PO$_2$) and analyzed by in-situ x-ray photoelectron spectroscopy as shown in Figure 1(a) [17, 18]. When the B chip was located at the center of the sputtering area, the doping concentration was maximized. We denoted as C+0. The concentration of B at the C+0 position was 1.51×10$^{22}$ atoms/cm$^3$, which value was confirmed by using a secondary ion mass spectroscopy (CAMECA, IMS-7f) and reference material (NIST SRM 2137). The variation of B concentration as a function of distance from the sputtering position is shown in Figure 1(b).

2.2 Characterization of Si QD

The size and distribution of Si QDs in the single SiO$_2$:B layer was observed by high-resolution transmission electron microscopy (JEOL, JEM-ARM200F). The crystallographic characterization of Si QDs was measured by Raman spectroscopy (Thermo, DXR). Raman sample was prepared on quartz substrate to minimize the signal from the c-Si substrate itself. The power of the 532 nm laser was kept below 5 mW to avoid the laser-induced local crystallization during measurements.

The effective minority carrier lifetime was evaluated using the Quasi-Steady-State Photo-Conductance (Sinton, WCT-120). The Si QD layers were deposited on both sides of the n-type Si wafer due to symmetrical lifetime. The detail data evaluation was suggested by Sinton et al. [19].

2.3 Fabrication of Si QD heterojunction solar cells

The SiO$_2$:B /n-Si wafer was annealed by using rapid thermal annealing (UniTemp, RTP-1200) at 1100 °C for 60 min in high purity nitrogen (N$_2$, 99.9999%) atmosphere to form Si QDs. It was hydrogenated at 600 °C for 20 min in forming gas (H$_2$ in N$_2$, 5%) to passivate defect states. For the improvement of contact property, m$^2$ layer was formed at the rear side by implantation of phosphorus (P) ions with a dose of 1.0 × 10$^{16}$ ions/cm$^2$ at 15 keV. After that, it was annealed for activating the dopants at 910 °C for 20 min. The surface oxide layer formed during the annealing process was removed by dipping it in a buffered oxide etchant (BOE, 50:1). The front and rear Al electrodes of about 500 nm were deposited and then annealed at 425 °C for 20 min in an ambient atmosphere to improve the electrical contact property. The front electrode comprises a busbar with 3.2mm$^2$ area and 9 finger lines of 0.95 mm$^2$ area. Wherein the busbar is vertically placed in the center of unit cells and the finger lines are horizontally connected to the busbar.

2.4 Evaluation of Si QD heterojunction solar cells

The photovoltaic properties of the devices were characterized with a solar simulator (McScience, Polaronix K201) under AM 1.5 G illumination with an incident xenon lamp power density of 100 mW cm$^{-2}$ at room temperature. During the current-voltage measurement, the light directly illuminates the Si QD top layer of the 36 mm$^2$. The external quantum efficiency (EQE), reflectance, and internal quantum efficiency (IQE) were measured with an Oriel IQE-200 instruments in a scan spectral range from 300 to 1100 nm at intervals of 10 nm.

3. Results and discussion

3.1 Configuration of the Si QDs

![Figure 1](image)

Figure 1. (a) Conceptual scheme of single and multilayer structure on a one specimen. (b) Energy filtered TEM image of conceptual scheme. High-resolution TEM images of (c) multilayer and (d) single region. The red circles indicate generated Si QDs.

The size and number of generated Si QDs are critical for the performance of Si QD based photovoltaic devices. Two structures were prepared on a one specimen as shown in Figure 1(a) to compare the size and number of generated Si QDs at the same fabrication conditions. The energy-filtered TEM image (Figure 1(b)) and high-resolution TEM images (Figure 1(c), (d)) were used. In Figure 1(b), the bright region is related with nano-sized crystalline Si while the dark background is related with the amorphous SiO$_2$ matrix. Figure 1(c) and (d) show that spherical Si QDs surrounded by a speckle pattern in the amorphous SiO$_2$ matrix. The
average size of the Si QDs were similar as below 4 nm in both structures. However, the number of generated Si QDs in the single layer is relatively higher than that in the multilayer region. This result suggests that the solar energy absorption and photocarrier transport through the Si QD fabricated from a single layer structure is relatively higher than the multilayer structure.

3.2 Effects of oxygen partial pressure
We regulated the relative ratio of oxygen to silicon (O/Si ratio) to control the number of the generated Si QDs in a single layer because the formation of the Si QDs depends on the excess Si in the layer [20, 21]. HR-TEM images depending on the PO₂ were displayed in Figure 2. Figure 2(a) shows the size of some Si QDs exceed 10 nm. In this case, the quantum confinement effect cannot be expected and carrier transport can also be limited due to the enlarged inter-dots tunneling distance. On the other hand, Figure 2(b) and (c) shows average size of the Si QDs is less than 4 nm. Especially, Figure 2(b) shows higher number of the generated Si QDs than the others.

Raman spectroscopy has been widely used to characterize the properties of nanomaterials through monitoring the peak shift and intensity [10]. Figure 3 shows Raman spectra of the single layers grown at the three different PO₂. The Raman peak was deconvoluted with four Gaussian peaks (Longitudinal acoustic (LA), Longitudinal optical (LO), Matrix, and Interface) and one Lorentzian peak (nc-Si QD) [22-25]. All of the Lorentzian peaks (517.3–518.7 cm⁻¹) show downshifts from that of bulk c-Si (521 cm⁻¹). This can be explained by the phonon confinement model and the tensile strain between the nc-Si QD and SiO₂ matrix [26-29]. In addition, as the PO₂ decreased, the intensity of the matrix peak was reduced, and the intensity of the QD peak was increased.

![Figure 2. High-resolution TEM images of the Si QD grown at three oxygen partial pressures. The red circle is a virtual line for recognizing Si QD.](image)

![Figure 3. Raman spectra of Si QD in a single layer deposited on a quartz substrate. The full-width at half maxima of the Lorentzian peak (nc-Si QD), and Gaussian peaks (interface, matrix) were fixed to 11.56, 36.51, and 71.96 cm⁻¹, respectively.](image)
Figure 4 shows a great difference in quantum efficiency at the UV light region. It is closely related with the properties of Si QD layers. The IQE value (yellow) of the Si QD solar cell fabricated at a low PO$_2$ (1.6x10$^{-5}$ Torr) is much lower than that (red) fabricated at an optimized PO$_2$ (2.7x10$^{-5}$ Torr). It is due to insufficient absorption of light in the short wavelength region by the Si QD layer with large QDs and an irregular size distribution as shown in figure 2. While, the IQE value (black) of the Si QD solar cell fabricated at a high PO$_2$ (3.5x10$^{-5}$ Torr) is also lower than that fabricated at the optimized condition. It is because the number of Si QDs was decreased. That is, IQE response with different PO$_2$ conditions in the short wavelength region is mainly originated from the quantum confinement effect of Si QD.

3.3 Effects of Doping Concentration

In this experiment, three type of single layers with different doping concentrations were fabricated. During fabrication, the PO$_2$ was maintained at 2.7x10$^{-5}$ Torr. The exact doping concentration was estimated by the SIMS depth profile (Figure S1(b)). The doping concentration of 1.3 x 10$^{21}$ atoms/cm$^3$ (C+5) was chosen as the minimum doping concentration because it is close to the concentration limit of active doping (1.1 x 10$^{21}$ atoms/cm$^3$) [12]. The other SiO$_x$:B layers were fabricated at C+3.5 (2.27x10$^{21}$ atoms/cm$^3$) and C+2.5 (5.61x10$^{21}$ atoms/cm$^3$) positions.

Figure 5. Effective minority carrier lifetimes of the Si QD solar cells depending on B concentration

Each carrier lifetime was measured by quasi-steady-state photo-conductance (QSSPC). The carrier lifetime ($\tau_{eff}$) was calculated by the continuity equation (eq.1), where $\Delta n(t)$ is

\begin{equation} \tau_{eff} = \frac{\Delta n(t)}{\Delta P(t)} \end{equation}
the time-dependent excess minority carrier density, which can be directly monitored via photo-conductance.

\[ \tau_{\text{eff}} = \frac{\Delta n(t)}{G(t) - \frac{d\Delta n(t)}{dt}} \] (eq. 1)

The \( G(t) \) is the electron-hole pair generation rate. In the QSSPC measurement, the sample was under quasi-steady-state conditions because the flash lamp decay time is always longer than the carrier lifetime of the sample \( (G(t) >> \frac{d\Delta n(t)}{dt}) \). The effective minority carrier lifetime was measured at an injection carrier density of 2.0 \times 10^{15} \text{ cm}^{-3} (vertical black dash line) [31]. The carrier lifetimes of the Si QD layer/n-type Si wafer are much shorter than a conventional n-type Si of several hundreds microseconds because of high-temperature annealing damage, recombination site in SiO\(_2\) matrix, and Si QD-SiO\(_2\) interface defects [32, 33]. However, the measured lifetime values are sufficiently meaningful to compare to the effects of the relative doping concentration. Figure 5 shows that the carrier lifetime of the Si QD/n-type Si wafer was maximized to be 45.19 \mu s at the doping concentration of 2.27 \times 10^{11} \text{ atoms/cm}^3 (blue dot, C+3.5). It is because the yield of photocarrier recombination increases as the doping concentration increases. For the precise understanding of the correlation between the doping concentration and photovoltaic performance, we obtained the photovoltaic parameters from each 10 devices under the doping conditions. Figure 6 shows the photovoltaic parameters. The improvement in power conversion efficiency is highly related to the variations in \( V_{oc} \) and FF. It is because the photocarrier lifetime is maximized and increased active doping effect enhances the electrical property. On the other hand, there is no difference in the \( J_{sc} \) and IQE spectra across the full wavelength region as shown in Figure S2. These results indicate that the variation of doping concentration does not affect the size and the number density of Si QDs.

![Figure 6. Summary of photovoltaic parameters (\( J_{sc}, V_{oc}, FF, \) and \( \eta \)) with B doping concentration. Black-line indicates standard fitting curve on histograms.](image)

### 4. Conclusions

In this study, Si QDs fabricated from a single SiO\(_2\) layer structure and SiO\(_2\)/SiO\(_2\), multilayer structure were compared. The number of generated Si QDs in a single layer could simply be adjusted by oxygen partial pressure. In addition, the number of generated Si QDs from the single SiO\(_2\) layer structure is larger than that from the multilayer structures under the same conditions. Based on these results, we have applied a single SiO\(_2\) layer to fabricate Si QD heterojunction solar cells. The \( J_{sc} \) parameter correlated with the number of generated Si QDs in the absorption layer was maximized to be 39.9 mA/cm\(^2\) at the 2.7x10\(^{-3}\) Torr. Furthermore, the power conversion efficiency of the Si QD solar cell was maximized at the B doping concentration of 2.27 \times 10^{11} \text{ atoms/cm}^3 due to enhancement of \( V_{oc} \) and FF by activated doping effect. As a result, the best power conversion efficiency of Si QD solar cells was reached up to 17.04\%. This result can be related
with the improvement of short carrier life time problem in the Si QD based photovoltaic cells with SiOx/SiO2 multilayer structure.

**References**


