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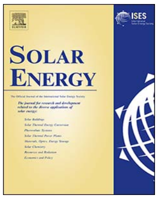

Efficiency improvement of Si quantum dot solar cells by activation with boron implantation

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ABSTRACT

The activation of Si quantum dots (QDs) in general Si QD heterojunction solar cells fabricated by the co-deposition of Si and B is typically not effective, as a high concentration of B is required for effective activation. In order to address this issue, B atoms were injected by ion implantation after the formation of Si QDs in a SiO_2 matrix. A Si QD solar cell was successfully realized when a Si QD layer was activated by the implantation of B ions followed by an annealing step. As a result, the power conversion efficiency of a Si QD solar cell realized by the ion implantation of B increased from 13.17% to 13.92%. The open-circuit voltage also increased from 523.03 mV to 529.64 mV in the Si QD solar cell created with the ion implantation of B.

1. Introduction

Over the last few decades, various new materials, new technologies and new device structures have been proposed to overcome the theoretical efficiency limits of conventional crystalline Si solar cells. It is known that the power conversion efficiency (PCE) can be improved by the effective absorption of solar light, the improvement of the charge carrier transport and by multiple exciton generation (Beard et al., 2007; Di et al., 2011; Nelson, 2003; Schaller and Klimov, 2004). Multiple junction solar cells, hot carrier solar cells and intermediate-band solar cells have been suggested as new types of solar cells which may allow researchers to overcome the theoretical efficiency limits of Si solar cells with a single p-n junction (Conibeer et al., 2009; Cuadra et al., 2004; Green, 2001; Vos, 1980).

At present, various silicon nanostructures have been investigated as new materials with which to realize new highly efficiency solar cells (Ellingson et al., 2005; Gao et al., 2008; Konagai, 2011; Kurokawa et al., 2006; Lu et al., 1995). Among them, silicon quantum dots (Si QDs) have been proposed as a promising material for next-generation solar cells because they simplify modification of the band-gap energy (Park et al., 2009; Zacharias et al., 2002; Kwak et al., 2017; Jiang and Green, 2006; Aliberti et al., 2010). Although the Si QD heterojunction solar cells have been developed, the efficiency of these cells remains low due to certain limitations inherent in them(Conibeer et al., 2011; Hong et al., 2011).

An intrinsic drawback of Si QD solar cells with Si QDs embedded in a dielectric material is the difficulty in the doping of B atoms into the Si QDs and the effective activation of the cells. In the general Si QD solar cell fabricated via the co-deposition of Si and B, a high concentration of B is required for the activation of the Si QDs (Hong et al., 2011). Although the ion implantation method is widely used to create p-n junctions in crystalline silicon solar cells, research on the activation of the Si QDs by the implantation of B into the Si QD layer remains rare.

Thus, in the present study, two types of Si QD solar cells were fabricated with p-type Si QD layers by the co-deposition of Si and B atoms and by the implantation of B ions into an intrinsic Si QD layer. At the similar B concentration of 1.0×10^{21} atoms/cm^3, the PCE was increased from 13.17 to 13.92%. The short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) were also improved in the solar cell activated by the implantation of B ions.

2. Experimental method

2.1. Growth and characterization of B-doped SiO_x films

B-doped SiO_x (SiO_x:B) layers were grown on 6″ Si (1 0 0) wafers (n-type, 1–3 O.cm) by the co-sputtering of a combination target in which a small B chip is fixed on a Si wafer. Stoichiometric SiO_2 layers were deposited at a high oxygen partial pressure of 1.7×10^{-4} Torr. The stoichiometry of the SiO_x layers was controlled by variation of the

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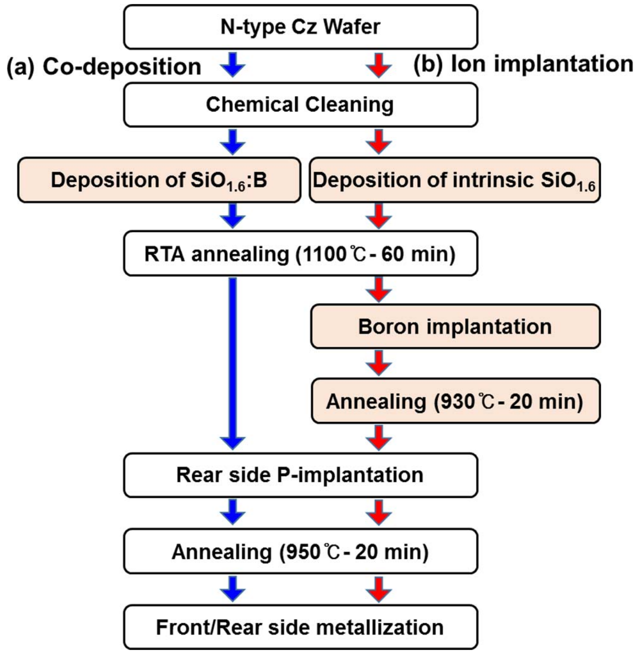

Fig. 1. Schematic procedure for the fabrication of a general Si QD solar cell by (a) the co-deposition of Si and B for a CD-QD SC (blue arrow) and of a new solar cell by (b) the ion implantation of B for a BI-QD SC (red arrow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oxygen partial pressure and was analyzed by in-situ X-ray photoelectron spectroscopy (XPS) (Kim and Moon, 1998, p. 5). The stoichiometry of the SiO_x layers was fixed at $SiO_{1.6}$, where the density of Si QDs is maximized, as reported in the literature (Kim et al., 2005). The silicon substrates were rotated during the film deposition step to ensure homogeneity of the thickness and stoichiometry.

The doping concentration of B in the B-doped Si QD layer was controlled by varying the location of the small B chip fixed on a Si wafer target from the center of the sputtering area. The concentration of B was determined from the relative sensitivity factor B as determined from the secondary ion mass spectrometry (SIMS) depth profiling of a B-implanted Si reference material (NIST SRM 2137).

2.2. *Fabrication of photovoltaic devices*

Two types of Si QD heterojunction solar cells with a B-doped Si QD layer of approximately 130 nm were fabricated to compare the activation of B atoms in the Si QD layers, as shown in Fig. 1. The first was a general Si QD solar cell with a B-doped Si QD layer grown by the co-deposition of B and Si (CD-QD SC). In this solar cell, the B atoms were diffused and activated by high-temperature annealing (1100 °C, 60 min) of the SiO_x:B layer fabricated by the co-deposition of B and Si under oxygen partial pressure.

The second type of cell was an ion-implanted Si QD solar cell with a B-doped Si QD layer fabricated by the implantation of B ions on a Si QD layer (BI-QD SC). An intrinsic Si QD (i-Si QD) layer was initially formed by the high-temperature annealing of an intrinsic SiO_x layer. Subsequently, B atoms were injected into the intrinsic Si QD layer by the implantation of B ions at the dose of 1×10^{16} atoms/cm^2 and at an energy level of 40 keV. The B-ion implanted Si QD layer was annealed again at a medium temperature (930 °C, 20 min) to activate the Si QDs. There were no remarkable differences in the size and density of the Si QDs in the Si QD layers of the CD-QD SC and BI-QD SC, as correspondingly shown in Fig. 2(b) and (c).

The B-doped Si QD layer used in this study can be supposed to be a superlattice structure of Si QD layers and SiO_2 layers. The band gap of SiO_2 is about 9 eV and that of the Si QDs in SiO_2 matrix is known to be about 3.17 eV (Jiang and Green, 2006; Löper et al., 2011). The band gap of the Si QDs formed from a $SiO_{1.6}$ layer was reported to be about 1.5 eV (Kim et al., 2005). From this information, the band diagram for B doped Si QD solar cell can be simply configured as shown in Fig. 2(d).

Fig. 3 shows the depth distributions of B in the two cells. In the case of ion implantation, B atoms were implanted by a two-step implantation with by 40 keV B ions with a dose of 1.0×10^{16} atoms/cm^2 and by 20 keV B ions with a dose of 1.0×10^{16} atoms/cm^2.

The surface-oxide layer of the BI-QD SC with low B concentration was removed by a buffered oxide etchant (BOE, 50:1) because the distribution of B is intrinsically very low in the surface range. The surface oxide layer of the Si QD layer in the CD-QD SC was also removed to control the thickness at 130 nm. As a result, the average boron concentrations of the BI-QD SC was controlled approximately at 9.4×10^{20} atoms/cm^3, which is similar with that of the CD-QD SC (1.0×10^{21} atoms/cm^3) to minimize the effect of different B concentrations on the device performance, as shown in Fig. 3.

A 2 nm $SiO_{2.0}$ layer was deposited between the B-doped Si QD layer and the n-type Si substrate to reduce the diffusion of B from the Si QD layer to the Si substrate during the high-temperature annealing process. Al films approximately 700 nm thick were grown by thermal evaporation as the front and rear electrodes. After the deposition of the electrodes, the cells were annealed at 425 °C to enhance the contact property of the electrodes. The Si QD films grown on 6 in. n-type Si (1 0 0) wafers were diced to small chips of 10 mm × 10 mm size and the area of active area was 0.19 cm^2.

2.3. *Characterization of photovoltaic devices*

The Photovoltaic properties of the solar cells were measured by a solar simulator (McScience K201) under AM 1.5G illumination with a xenon lamp at room temperature. The power conversion efficiency (η) of the solar cells is the ratio of the maximal electrical output power to the incident power density. The efficiency is calculated from the relationship of $\eta = J_{sc} \cdot V_{oc} \cdot FF/P_{in}$, where J_{sc}, V_{oc}, FF and P_{in} are the short-circuit current density (mA/cm^2), the open-circuit voltage (mV), the fill factor (%) and the incident power density (100 mW/cm^2) at room temperature, respectively. The external quantum efficiency (EQE), reflectance and internal quantum efficiency (IQE) were measured by an Oriel IQE-200 instrument in the scanning spectral range of 350–1100 nm.

3. Results and discussion

The activation of doping elements is one of the most important factors to improve the performance of electronic devices. Doping elements are generally injected into the emitter region in semiconductor devices by co-deposition, ion implantation or thermal diffusion (Arduca and Perego, 2017; Cho et al., 2016; Kwak et al., 2017; Rohatgi et al., 2012).

In the general Si QD heterojunction solar cell (CD-QD SC), the SiO_x:B layer is grown by the co-deposition of Si and B under O_2 partial pressure and the SiO_x:B layer is annealed at 1100 °C for 60 min to form Si QDs in the SiO_2 matrix (Hong et al., 2016; Kwak et al., 2017). In the early growth stage of Si QDs, it is difficult to activate the Si QDs because B atoms as impurities are expelled from the Si nano-crystals to form pure Si QDs. According to a previous study of the activation of B atoms in Si nanostructures, the activation of doped B atoms is known to be very difficult in Si QDs. For the effective activation of the Si QD layer, the doped B atoms should be substituted into the fourfold coordinated crystalline Si sites inside of the Si QDs instead of the threefold coordinated Si sites on the surfaces of the Si QDs (Hong et al., 2011). Although most of the Si sites in single-crystalline bulk Si are fourfold coordinated, the Si sites in the Si QD layer are composed of threefold coordinated Si sites on the surfaces of the Si QDs and fourfold coordinated Si sites inside the Si QDs. In the Si QD layer, the ratio of the