Si-quantum-dot heterojunction solar cells with 16.2% efficiency achieved by employing doped-graphene transparent conductive electrodes

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\section*{A B S T R A C T}

To overcome small- and indirect-bandgap nature of crystalline bulk Si, a lot of efforts have been made to utilize Si quantum dots (SQDs) in optoelectronic devices. By controlling the size of Si quantum dots (SQDs), it is possible to vary the energy bandgap based on quantum confinement effect, which can maximize the power-conversion efficiency (PCE) of solar cells due to the energy harvesting in a broader spectral range. Here, we first employ graphene transparent conductive electrodes (TCEs) for SQDs-based solar cells, showing a maximum PCE of 16.2%, much larger than ever achieved in bulk-Si solar cells with graphene TCEs. In this work, the graphene TCEs are doped with two kinds of materials such as AuCl\textsubscript{3} and Ag nanowires for efficient collection of the carriers photo-induced in SQDs. The encapsulation of the doped-graphene TCE with another graphene layer prevents the doping elements from being desorbed or oxidized, thereby making the PCE higher, its doping dependence more evident, and the long-term performance more stable. The observed unique solar cell characteristics prove to be dominated by the trade-off effects between doping-induced variations of diode quality, transmittance/sheet resistance of graphene, energy barrier at the graphene TCE/SQDs interface, and reflectance.

\section*{1. Introduction}

Compared to bulk Si, the relaxation of the carriers excited in Si quantum dots (SQDs) \cite{1} is slowed down due to the widening of the distance between their energy states. If the carriers can be extracted from SQDs before the relaxation, the open circuit voltage of the solar cells can be increased. An electron-hole pair with an energy much larger than the bandgap tends to split into multiple electron-hole pairs before thermalization or recombination. If these electrons and holes are successfully collected from SQDs, it will enhance the current of the solar cells. SQDs-based solar cells \cite{2-5} have been fabricated principally in a structure of metal/SQDs-embedded oxide (SQDs: SiO\textsubscript{2})/Si wafer by using Al, Au, ITO, Au/Ni, and Au/Sb as metal transparent conductive electrodes (TCEs). However, the power conversion efficiencies (PCEs) \cite{10.4 - 14.8%} that are optimized in metal/SQDs: SiO\textsubscript{2} wafer solar cells \cite{2-6} are still much smaller than those of commercially-available bulk-Si solar cells \cite{7}.

Perfect transparency, high carrier mobility, and tunable work function of graphene \cite{8,9} have made it play a key role as TCEs in optoelectronic devices including solar cells. Recently, a lot of studies have been done on graphene/bulk-Si heterostructure solar cells \cite{10,11}. In this structure, the graphene film not only enhances light transmission into Si substrate but also forms an interface Schottky junction with Si, thereby producing the built-in electric field, resulting in well separation of photoexcited electron–hole pairs \cite{11,12}. Much efforts have been made to enhance the PCE of the graphene/bulk-Si solar cells. The PCE reached nearly 4\% by employing a pristine monolayer graphene \cite{13}. High efficiency over 10\% was obtained from the graphene/bulk-Si solar cells containing a surface-passivation layer or an electron-blocking polymer \cite{14,15}. However, their performance still remains far below that of commercial Si solar cells. One of the main issues to be solved for high-efficiency graphene/Si solar cells is low Schottky barrier height, resulting in large leakage current and low open circuit voltage \cite{12}.

As another issue for the use of graphene in Si solar cells, the sheet resistance of chemical-vapor-deposition (CVD)-grown graphene films is...
usually in the range 125–1000 Ω/□ [16], originating from its polycrystalline nature, much larger compared to conventional TCEs (40–60 Ω/□) used in commercial Si solar cells. Such high sheet resistance cannot meet commercial requirements of solar cells. Chemical-doping techniques [11,12,17–19] have been utilized as one strategy to reduce the sheet resistance of graphene films, thereby improving the PCE of graphene/Si solar cells. A maximum PCE of 8.6% has been reported in graphene/Si solar cells by using doped graphene layers [12,17], but this value is still under 10% (a criterion for commercialization possibility) and also much lower than carbon nanotube/Si solar cells (15%) [20]. In addition, the degradation (or stability) of graphene/Si solar cells is a challenge to overcome before commercialization.

Recently, we have reported graphene/SQDs: SiO2-heterojunction tunneling diodes [21] showing high photoresponse that is less-noise, faster, and near-UV sensitive compared to commercially-available crystalline-Si photodetectors. These results suggest that if graphene is employed for SQDs-based solar cells it can lead to dramatic improvements in their PCE. Below we focus on structural, electrical, and optical control of CVD-grown graphene by doping with AuCl3 or Ag nanowires (NWs), known to be one of the major dopants for p- or n-type graphene, respectively, at various concentrations, thereby enhancing the PCE of graphene/SQDs: SiO2 solar cells up to 16.2%, and possible explanations of the unique solar cell behaviors.

2. Results and discussion

Fig. 1a shows a schematic diagram of graphene/p-type SQDs: SiO2/n-type crystalline Si wafer (p-SQDs/n-Si) heterojunction solar cell, where the graphene is pristine or doped and the thickness of the p-SQDs layer is about 120 nm. High-resolution transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy proved densely-distributed SQDs of ~ 3.5 nm average size within SiO2 matrix in our previous reports [6,22] (see also Fig. S1). The graphene layer was shown to be single layer by Raman/transmittance spectra (Fig. S1). The upper and lower optical images, as shown in Fig. 1b, clearly show the mesa-type Al electrodes deposited on the bare SQDs or graphene/SQDs, respectively. A reflection mapping image in Fig. 1b confirms that the mesa pattern of the Al electrode on the graphene is well-defined. The p-SQDs in the solar cell are actually alternating layers of p-SQDs and SiO2, across which the electrical conduction is dominated by the tunneling of charge carriers, as detailed theoretically and experimentally in our previous studies for the similar structures [21,23]. Here, the p-SQDs are simply regarded as an effectively-single layer to focus on the photovoltaic functions without describing the tunneling of charge carriers in the layer.

Fig. 1c shows dark current density-voltage (J-V) characteristics of the solar cells without/with pristine graphene layer on the SQDs. At low voltages (region I, V < 0.1 V), the forward and reverse currents are...
almost the same for both devices, and a linear J-V relationship is observed, consistent with the Ohm's law. The Ohmic shunt resistances \[24\] are estimated to be 4362 and 4800 Ω cm\(^2\) for the solar cells without/with pristine graphene layer, respectively. At intermediate voltages (region II, V = 0.1 ~ 0.6 V), the J-V characteristics of the nonideal diode is governed by the thermionic emission model \[25\] expressed by the following equation: \(J = J_s \exp(eV/nkT) - 1\), as well applied to SQDs-based diodes with metal or graphene electrodes \[21,26\], where \(J_s\) is the ideal reverse saturation current, \(e\) is electron charge, \(T\) is temperature, \(k\) is the Boltzmann constant, and \(n\) is diode ideality factor. The \(n\) is estimated to be 1.98 and 2.92 for the solar cells without/with graphene, respectively, from the slope of the dark J-V curves derived through curve fitting. At large voltages (region III, V > 0.6 V), the slopes of the J-V curves are reduced and deviate from the exponential behavior. From log J-log V plots, the J-V characteristics show a power-law dependence in the range of bias voltages up to 2 V. This suggests that the current is limited by a space-charge limited current conduction described by \(J \propto V^m\), as reported before \[26,27\], where \(M\), depending on the density of states in the layer of SQDs, is estimated to be 1.8 ± 0.5 for both cases.

Fig. 1d shows photocurrent (PC) mapping images for various powers of a laser line at 532 nm. The estimated external quantum efficiency (EQE) (~ 78%) is almost the same, irrespective of the position on the graphene and the laser power, indicating extremely uniform production of electron/hole pairs in the solar cell by the illumination. Fig. 1e and f show J-V curves under dark and illumination, where series resistances are estimated to be 6.28/3.72 Ω cm\(^2\) for the solar cells without/with graphene, respectively. The variations of the series and shunt resistances explain why the photovoltaic parameters such as short-circuit current density (Jsc), the fill factor (FF), and PCE are enhanced with the use of graphene, as shown in the insets of Fig. 1e and f. These results are also consistent with the reduction of the reflectance (Fig. S2) and the enhancement of the EQE not only in the near-ultraviolet but also in the near-infrared region, as shown in Fig. 1g.

Fig. 2a shows a band diagram of the AuCl\(_3\)-doped graphene/p-SQDs/n-Si heterojunction solar cell (for the pristine graphene, see Fig. S3). Here, the p-SQDs are simplified like a single layer to well describe the band structure of the solar cell, as explained above. The p-type characteristics of graphene by the AuCl\(_3\) doping were demonstrated by measuring transmittance, Raman spectra, sheet resistance, and work function (Fig. S4). The measured work function of the pristine graphene is ~ 4.4 eV (Fig. S4), and the Fermi level of the p-SQDs is determined to
be located below ~ 4.7 eV from the vacuum level because the electron affinity and bandgap of SQDs are 3.8 eV \[28\] and ~ 1.7 eV (from the PL peak energy of SQDs, Fig. S1), respectively. This suggests that the work function of the pristine graphene is smaller than that of the p-SQDs, resulting in the formation of the energy barrier at the graphene/p-SQDs interface (Fig. S3), which the holes should overcome to transport to the graphene electrode. Therefore, the graphene should be p-type-doped to increase its work function, thereby facilitating the collection of the photo-induced holes to the graphene, as shown in Fig. 2a.

This expectation, however, was not realized in the solar cells. Fig. 2b shows the enhanced reflectance (R) of graphene by AuCl3 doping, especially in the broad visible range. With increasing the doping concentration of AuCl3 \(n_D\), the photo-J-V curve and resulting photovoltaic parameters such as \(J_{sc}\), open-circuit voltage \(V_{oc}\), FF, and PCE are monotonically degraded, as shown in Fig. 2c (see also Table S1 and Fig. S5). In addition, the doping effect was almost negligible in the dark J-V curves (Fig. S6). These results are closely related to the fabrication processes of the solar cells. Annealing should be done after completing the fabrication of the solar cell structure, as shown in Fig. 1a, to enhance the contacting properties between p-SQDs, graphene layer, and Al mesa electrode. The optimum annealing temperature was found to be 540 °C for the pristine graphene (Fig. S6). In case of AuCl3-doped graphene, it has been previously known that the doping effect almost disappears at this annealing temperature, mostly due to desorption of the doping elements \[29,30\]. This explains why the AuCl3 doping was not effective for enhancing the photovoltaic properties.

To solve this problem, we employed an approach of encapsulation with another graphene layer. A pristine graphene sheet was transferred on the AuCl3-doped graphene/p-SQDs/n-Si solar cells before depositing the Al mesa electrode on the doped graphene, resulting in the completion of the encapsulation structure: graphene/AuCl3/graphene. The transmittance was reduced about 2.3% by the encapsulation, irrespective of \(n_D\) (Fig. S7). The \(n_D\)-dependent behaviors of transmittance, sheet resistance, work function, and electron/hole mobilities are similar irrespective of the encapsulation (Fig. S4). Fig. 2d and e show photo-J-V curves and EQE spectra of the encapsulated solar cells for various \(n_D\). Fig. 2f-h show the enhanced EQE of the AuCl3-doped graphene/p-SQDs/n-Si solar cell by the encapsulation and resulting upshift of the PCE in the full range of \(n_D\). The EQE spectra strongly depend on \(n_D\), and their \(n_D\)-dependent variation is very much consistent with that of \(J_{sc}\) (Table S2), resulting from strong correlation of \(J_{sc}\) with integrated the EQE \[31\]. The PCE shows a clear \(n_D\) dependence with its magnitude being peaked at \(n_D = 10\) mM, which is consistent with the expectation based on the band diagram, as shown in Fig. 2a. As \(n_D\) increases, the energy barrier at the graphene/p-SQDs interface and the sheet resistance are reduced, more useful for the collection of the photo-induced holes to the graphene, while the electron/hole mobilities and transmittance are reduced (Fig. S7). Due to this trade-off, the solar cell shows best performances (FF and PCE) at \(n_D = 10\) mM (see also Table S2 and Fig. S8) (i.e., optimized doping concentration), which is also evidenced by the \(n_D\)-dependent behaviors of the diode ideality factor and series resistance (Fig. S9 and Table S2).

The work function of graphene is reduced to ~ 4.2 eV with increasing the concentration \(n_A\) of Ag NWs to 0.3 wt% (Fig. S10), indicating n-type doping, resulting in the enhancement of the energy barrier at the graphene/p-SQDs interface, opposite to the case of AuCl3 doping. Therefore, it is expected that the doping of Ag NWs deteriorates the collection of the photo-induced holes to the graphene in view of the energy barrier at the graphene/p-SQDs interface, but this effect is not so big as the reduction of the energy barrier by the AuCl3 doping, judging from the reduced transmittance around 2.3% and increased sheet resistance by the encapsulation.
from the only 0.2 eV variation in the work function of Ag NWs-doped graphene over the full range of $n_A$. The sheet resistance and transmittance of the Ag-NWs-doped graphene show monotonically-decreasing behaviors with increasing $n_A$ (Fig. S11), possibly resulting from the enhanced networking of the Ag NWs on the graphene at larger $n_A$, as confirmed by scanning electron microscopy images (Fig. S12).

Fig. 3a and b show $n_A$-dependent dark J-V curves and resulting ideality factors, indicating best diode quality at $n_A = 0.1$ wt%. As $n_A$ increases, the density of states at the Fermi level of graphene increases and the sheet resistance decreases, thereby facilitating the collection of electrons at the graphene/p-SQDs interface under forward bias, resulting in the current increase at higher $n_A$, as shown in Fig. 3a. However, the increased networking of the Ag NWs can hinder the current flow at higher bias, leading to the optimization of the diode properties at $n_A = 0.1$ wt%, as shown in Fig. 3b. Fig. 3c and d show $n_A$-dependent photo J-V curves and PCEs. The PCE shows a maximum of 16.2% at $n_A = 0.1$ wt% (see also Fig. S13 and Table S3), consistent with the $n_A$-dependent behaviors of the shunt resistance and ideality factor, as shown in Fig. 3b. The reflectance and EQE show almost monotonically-decreasing behaviors with increasing $n_A$ from 0.05 to 0.3 wt %, as shown in Fig. 3e and f. Due to the trade-off correlation between the $n_A$-dependent reflectance, EQE, sheet resistance, transmittance, and graphene/SQDs energy barrier, the PCE becomes eventually largest at $n_A = 0.1$ wt%.

The long-term stability tests were done for the solar cells with pristine-, AuCl3-doped-, encapsulated-AuCl3-doped-, and Ag-NWs-doped-graphene TCEs (Fig. S14). The stability is degraded by doping with AuCl3 or Ag NWs, possibly due to desorption or oxidation [32] of the dopant elements, respectively, but remarkably improved by the encapsulation of the doped graphene with another graphene.

3. Conclusion

These results are very promising in view of the first fabrication of the SQDs-based heterojunction solar cells with AuCl3 or Ag NWs-doped graphene layers as TCEs, showing a maximum PCE of 16.2%. We believe this achievement, in combination with the existing technologies for improving the front/back sides of the solar cells, will also open exciting opportunities for the creation of the SQDs-based solar cells that can overcome the PCE limit of commercially-available bulk-Si solar cells.

4. Experimental section

4.1. Preparation of Si quantum dots (SQDs)

B-doped SiO2 films were grown on 6-in. n-type Si(100) wafers at room temperature (RT) by ion beam sputtering using an Ar+ beam with ion energy of 800 V. The deposition chamber was evacuated to a pressure of $1.2 \times 10^{-8}$ mbar. Details of the system are described elsewhere [33]. The SiO2 layers were deposited by sputtering of a Si wafer at a high oxygen partial pressure of about 2.1 $\times 10^{-4}$ mbar. The growth rate and the stoichiometry of the SiO2 layers were controlled by varying the oxygen partial pressure and analyzed by in-situ x-ray photoelectron spectroscopy [33]. The B doping of the SiO2 layers was achieved by co-sputtering using a combination target where a small boron chip was fixed on a p-type Si wafer. The B concentration ($n_B$) was controlled by varying the size of the boron chip. The doping level of the SiO2 layers was estimated by secondary ion mass spectroscopy (Cameca, model IMS-7 F) using an oxygen-ion beam of 5 keV. The quantifi- cation of the B-doped SiO2 layers was performed using a B-implanted certified reference material. In this work, the $n_B$ was fixed to 5.7 $\times 10^{13}$ atom cm$^{-2}$. After deposition, the samples were heated at 1100 °C for 20 min in ultra-pure N2 ambient by rapid thermal annealing to form SQDs in the SiO2 layers (SQDs: SiO2). During the formation of Si QDs in the SiO2 layer by the high-temperature annealing, the doping elements are spontaneously diffused into the SQDs [34] because B is thermo-dynamically more stable in Si than in SiO2 [35]. The thickness of the resulting p-SQDs: SiO2 layer is about 120 nm. The size of SQDs strongly depend on the x value, as intensively studied in our previous reports [33,36]. Here, $x$ was fixed to 1.6 (the size of SQDs = 3.5 nm, as analyzed by TEM), at which the optical properties including PL were opti-mized based on the quantum confinement effect, as shown in the previous reports [6,33].

4.2. Growth, transfer, and characterization of graphene

Graphene layers were grown on 70-μm-thick Cu foils (Wacopa, 99.8 purity) in a graphite-heater-based chemical-vapor-deposition quartz tube furnace at a growth temperature of 1000 °C with 10-sccm H2 and 20-sccm CH4 flowing at a pressure of 3 Torr. The graphene/Cu stack was spin-coated with poly(methyl methacrylate) (PMMA), and the Cu was then etched in a 1 M ammonium persulfate for 10 h. The graphene/PMMA stack was then placed in deionized water before transferring to the 120 nm p-SQDs: SiO2/n-type Si wafers and blow-dried with dry N2. The PMMA/graphene/p-SQDs: SiO2/n-Si stack was then heated on a hot plate in air at 180 °C for 2 h to cure the PMMA. After the samples were cooled to RT, the PMMA was stripped by soaking them in acetone for 1 h at RT. Subsequently, the graphene/p-SQDs: SiO2/n-Si stack was put in isopropyl alcohol (IPA) for 10 min and dried by blowing N2 to minimize the water traps possibly present at the graphene/p-SQDs: SiO2 interface, and annealed at 400 °C for 1 h in vacuum to remove the surface adsorbates. After the transfer, the graphene layers were characterized by Raman spectroscopy, and PL. The Raman intensity ratio ($I_G/I_D$) of the G and 2D bands peaked at ~1585 and ~2683 cm$^{-1}$, respectively, was about 0.45 on the graphene/SQDs: SiO2, indicative of single-layer graphene.

4.3. Doping of graphene

Gold chloride powder used for p-type dopant was dissolved in ni-tromethane for preparing AuCl3 doping solution. For the doping of graphene, the dopant solution was dropped on the surface of graphene sheet and after 1 min (this time is defined as doping time) elapsed, it was spin-coated at 2000 rpm for 1 min. The doped graphene sheets were annealed at 100 °C for 1 min for uniform doping. Further details on the preparation and characterization of the AuCl3-doped graphene were described in our previous reports. [37,38]. Ag NWs powder (Nanopysix, Korea) was dissolved in IPA to prepare Ag NWs solution for doping of graphene. The Ag NWs solution was dropped/spin-coated on the surface of the graphene, and annealed at 100 °C for 2 min to remove the solvent, resulting in the formation of the Ag-NWs network. The handling and analysis of the Ag NWs appeared in more detail elsewhere [32,39].

4.4. Fabrication of graphene/p-SQDs:SiO2 solar cells

For the electrical contacts, Al was deposited on the top of 1 $\times$ 1 cm2 AuCl3- or Ag NWs-doped graphene/p-SQDs: SiO2/n-Si as a mesa pattern of 7.76 mm2 area and on the bottom of n-Si substrate as a film, thereby completing the graphene/SQDs: SiO2 solar cells. In case of the en-capulsated solar cells, the Al deposition was done after another gra- phene was transferred on the AuCl3-doped graphene. The $n_D$ and $n_A$ were varied from 5 to 30 mM and from 0.05 to 0.3 wt%, respectively. The pristine graphene/SQDs solar cells were also fabricated for comparison. Annealing was done after completing the fabrication of the solar cell structure to enhance the contacting properties between p- SQDs, graphene layer, and Al mesa electrode. The optimum annealing temperature was found to be 540 °C for the pristine graphene
4.5. Measurements

PL spectra were measured at RT by using the 325 nm line of a HeCd laser as the excitation source. Emitted light was collected by using a lens and analyzed using a grating monochromator and a GaAs photomultiplier tube. Standard lock-in detection techniques were used to maximize the signal-to-noise ratio. The laser power for the PL excitation was about 3 mW. The sheet resistance of the graphene was determined by the 4 probe van der Pauw method and its surface morphology was characterized using atomic force microscopy with a monochromator (Agilent Model). The laser power for the PL excitation was 0.1 ~ 2.2 mW for reflection and collection of the emitted light. The optical properties of the solar cells were characterized by Raman spectroscopy with a laser excitation energy of 532 nm (2.33 eV) and a laser as the excitation source. Emitted light was collected by using a grating monochromator (McScience, K201) under illumination of 1 Sun (100 mWcm$^{-2}$ AM 1.5 G) and a calibrated Si reference cell certified by Korea Industrial Standards (LG company). EQE was measured by a power source (Newport 300 W xenon lamp, 66483-300XF) with a monochromator (Newport, CS260).

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Appendix A. Supporting information

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References