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Enhanced carrier collection efficiency and reduced quantum state absorption by electron doping in self-assembled quantum dot solar cells

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Reduced quantum dot (QD) absorption due to state filling effects and enhanced electron transport in doped QDs are demonstrated to play a key role in solar energy conversion. Reduced QD state absorption with increased n-doping is observed in the self-assembled $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}$ QDs from high resolution below-bandgap external quantum efficiency (EQE) measurement, which is a direct consequence of the Pauli exclusion principle. We also show that besides partial filling of the quantum states, electron-doping produces negatively charged QDs that exert a repulsive Coulomb force on the mobile electrons, thus altering the electron trajectory and reducing the probability of electron capture, leading to an improved collection efficiency of photo-generated carriers, as indicated by an absolute above-bandgap EQE measurement. The resulting redistribution of the mobile electron in the planar direction is further validated by the observed photoluminescence intensity dependence on doping. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907348>]

Interest in using III-V quantum dots (QDs) to raise the sub-gap photocurrent at the same time maintaining the open circuit voltage has arisen following the proposal for an intermediate band solar cell (IBSC)¹ by Luque and Marti more than 15 years ago. We have recently investigated several different contributions to below-bandgap photocurrent of a quantum dot solar cell, which includes transitions via the quantum confined energy states and a continuum background density of states (Urbach tail).^{2,3} We believe that this continuum distribution of tailing states superposed with the QD and WL (wetting layer) confined energy states facilitates carrier relaxation and acts as an escape pathway for below-bandgap photogenerated carriers. In this work, a much narrower Urbach tailing distribution compared with our previous work was designed and led to less coupling between the quantum states and the background continuum states.⁴ The composition of 50% In and 50% Ga has created less strain than that at the interface of InAs/GaAs quantum dots. Furthermore, in the current devices, 50 nm spacing was used to minimize tunneling effect. Thermal energy is far from sufficient to excite carriers from the QD ground state to the GaAs matrix of continuum states. Moreover, due to the requirement of momentum conservation,² there exists an inconsequential number of photons in the one-sun solar spectrum that can excite carriers from the bound quantum states to the unbound continuum states of the conduction band directly. It is worthwhile to note that the quantum potential for holes is too shallow, so that holes can readily escape from the quantum states with thermal energy. For all the above reasons, there is a lack of carrier escape pathways for electrons from the QD states to the conduction band in our $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}$ QD devices. Thus, when mobile electrons are transported through the QD layers, the strain potential at

the interface of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ and GaAs drives them towards confined lower states. In this way, QDs can be considered as “multi-electron” trapping centers.

For the realization of IBSC, doping has been considered as a desirable method to half-fill the quantum dots, which facilitates a sequential two-photon absorption process from valence band to confined states and from confined states to the conduction band. Consequently, it is important to investigate the role of electron-doping in QD devices, especially its potential impact on both the electron capture potential which affects (1) carrier collection efficiency and (2) below-bandgap photon absorption via transitions to quantum confined states. In this paper, we will detail these two key aspects, respectively.

Self-assembled $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}$ QDs solar cells were grown on n^+ -GaAs substrate by metal organic chemical vapor deposition (MOCVD).^{5,6} The resulting quantum dots are truncated pyramids in shape. The undoped QDs structure consists of n^+ -doped substrate, n -GaAs base layer, ten layers of 6 monolayers of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ QDs separated by 50 nm of GaAs barrier with a dot density of $\sim 4.5 \times 10^{10} \text{ cm}^{-2}$, and a $p\text{-Al}_{0.45}\text{Ga}_{0.55}\text{As}$ window layer and is terminated with a p^+ -doped GaAs contact layer. For the modulation-doped QDs solar cell, Si dopants were placed within a 4 nm thick GaAs barrier layer that is 10 nm below each QD layer, with a dopant sheet densities of $\sim 9 \times 10^{10} \text{ cm}^{-2}$ and $\sim 1.8 \times 10^{11} \text{ cm}^{-2}$ to provide ~ 2 and ~ 4 electrons per dot, respectively. Our fabrication recipes have been carefully calibrated to ensure uniform device performance. The details can be found elsewhere.²

Standard solar cell characteristics were tested by an Oriel Solar Simulator. The external quantum efficiency (EQE) measurement was performed with a 250 W halogen lamp as a light source. A biased Ge diode was used as detector. In order to filter out the grating second order contribution to the transmitted light going through a 1/3 m spectrometer,

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a 650 nm long pass filter from Thorlabs was placed in front of the fiber bundle of the light source at the entrance slit of the spectrometer. A low noise current preamplifier SR 570 from Stanford Research Systems was connected to the external circuit of the device prior to the EG&G 5210 lock-in amplifier. For photoluminescence (PL) measurement, the same light source was used with a 950 nm long pass filter. The emitted photons were collected through the spectrometer and detected with the same Ge detector. We have also utilized a 1310 nm laser to accurately measure the linear photocurrent response and further evaluate the background density of states below the QD ground states.

The current-voltage characteristics of the fabricated solar cells are shown in Figure 1(a). A gradually enhanced J_{sc} is observed with increased doping. The 0e/dot, 2e/dot to 4e/dot devices exhibit a short circuit current density of 10.1 mA/cm², 11.8 mA/cm², and 12.6 mA/cm², respectively. To evaluate the origins of the enhancement of J_{sc} with increasing n-doping, we performed an absolute EQE measurement to measure the bandgap photoresponse, as shown in Figure 1(b). The results show that the 4e/dot device has higher external quantum efficiency than the one for the undoped device. From the integration with the solar spectrum data provided by Oriel, we found that the above bandgap photons contribute ~ 12.3 mA/cm² for the 4e/dot device and ~ 10 mA/cm² for the 0e/dot device. The results indicate that the measured total J_{sc} for both 4e/dot

(12.6 mA/cm²) and 0e/dot (10.1 mA/cm²) devices mostly comes from above bandgap photocurrent. We have also used a bulk GaAs wafer as a natural filter to filter out the above bandgap light from the solar simulator to roughly estimate the below-bandgap photon contribution to the photocurrent. The resulting photocurrent is around 0.15 mA/cm² for all studied devices, which is comparatively small. The below-bandgap photocurrent mostly comes from the wetting layer and band edge tailing states contribution, while the QD state contributed absorption is comparably much smaller due to its low density and low absorption coefficient. As a result, it is understandable that not much difference has been observed in the measured photocurrent under GaAs wafer filtered AM1.5 spectrum for different sets of devices. We therefore conclude that in this set of devices, the extra absorption of sub-bandgap photons by QDs is only a very small contribution to the total J_{sc} . Similarly, Polly *et al.* have also reported that QD doping had no positive effect on sub-bandgap photocurrent generation.⁷

The agreement of the overall J_{sc} and the absolute above bandgap EQE integration with the solar spectrum leads us to believe that the enhancement of the J_{sc} with doping is mainly due to carrier collection efficiency difference between the doped and undoped devices. When the photocarriers are generated within the active region, including the depletion region and the electron and hole diffusion region, they need to be transported to their respective electrode via drift and diffusion. Generally, the band offset of strained In_{0.5}Ga_{0.5}As and GaAs appears mainly in the conduction band, while the hole-confined states are thermally connected to the valence band. Thus, the QDs mainly operate as efficient electron capturing centers and draw the mobile electrons into the conduction band potential well.

To explain the impact of electron doping on carrier collection efficiency, we would like to make a comparison between confined quantum energy states occupation and impurity deionization process. The quantized quantum dots behave like electron traps in a similar way to impurities/defect centers in the forbidden band. An impurity band will form as a consequence of increased impurity concentration when the trapped electron/hole wavefunctions overlap. Similarly, the evolution of the discrete quantum states into intermediate band happens when electrons in the quantum dot confined states become delocalized with an interspacing of less than 10 nm. For an electron trapping center, the trapping potential from this impurity disappears when fully occupied. Most of the impurities are one-electron trap. That is to say, after one electron has been trapped, the trap state no longer exists for trapping a second electron. The process is explained as a carrier screening effect. We found that the model is also applicable to explain the screened Coulomb potential energy of n-doped quantum dots.⁸ The In_{0.5}Ga_{0.5}As/GaAs quantum dots, without any intentional doping, have unoccupied ground or excited states. They potentially act as electron capturing centers.⁹ When the quantum dot levels are partially occupied by electrons, not only the available states for electron trapping have been reduced but they have also electrically weakened the trapping potential and even have exerted a repulsive force on the

FIG. 1. (a) Current-voltage characteristics of undoped, 2e/dot, and 4e/dot devices and (b) above bandgap absolute EQE of 0e/dot and 4e/dot.

FIG. 2. The absorption coefficient for high energy photons quickly decay exponentially into the device. Generated electrons need to transport through 10 layers of QDs and finally reach to the n-GaAs while generated holes are collected at the top p-type electrode. (a) Device structure. (b) Electrons transport through a single QDs layer. (c) Electrons transport through one quantum dot that affected by both QD capturing potential and negatively charged excitons repulsive Coulomb potential.

surrounding mobile electrons.¹⁰ The process is illustrated in Figure 2(b). When above-bandgap photo-generated electrons move through the QDs layer, the repulsive force exerted by the negatively charged QDs can alter the electron trajectory in such a way to reduce the probability of electron trapping. The Coulomb potential exerted by the negatively charged QDs is a competing process that acts on the mobile electrons and competes with the QDs trapping potential. When electrons are captured, the trapping effects are progressively de-activated.¹¹ The theory is in agreement with our experimental results. With further doping, the trapping effect of the quantum dots is further reduced, thus leading to improved electron collection efficiency.

As opposed to what we observed, a recent publication has also discussed the role of doping in InAs/GaAs QDs solar cells¹² and attributed the observed enhancement of J_{sc} to enhanced below-bandgap single photon absorption. In that work, the author claims a sub-bandgap photocurrent as large as 9 mA/cm^2 for a 6e/dot device and 4 mA/cm^2 for undoped device, while above bandgap photons generate around 10 mA/cm^2 . Given the total available number of above and below bandgap photons in the solar spectrum and the fact that the EQE drops substantially when going from higher energy to lower energy photons across the band edge, we estimate that the sub-bandgap photocurrent will account for only a slight enhancement of J_{sc} , less than 1 mA/cm^2 . A two-photon absorption with infrared (IR) photons is even less likely due to the small two-photon absorption coefficient in InAs/GaAs QD system and the fact that the Oriel Solar Simulator's output photons with wavelength larger than $2.5 \mu\text{m}$ are almost absent due to absorption in the silica wall of the lamp. What's more, our present results indicate that electron doping actually reduces the total number of transitions from valence band to quantum dot states as a result of the reduction of the total available density of states in quantum dots. Further analysis will appear later in the paper. Compared to the I-V results obtained by Sablon *et al.*,¹² we

do not observe a large photocurrent due to sub-gap absorption, as predicted from our EQE measurements, and we do not expect a contribution from IR photons at $4.5 \mu\text{m}$ (inter-subband transitions) since there are no such long-wavelength photons in the Newport Oriel simulation source.

The most straightforward verification of sub-bandgap photocurrent generation is by performing an external quantum efficiency measurement. By an integration of the spectral photon flux under 1 sun condition, both above- and below- bandgap, the different contribution to the photocurrent can be accurately extracted. The below-bandgap EQE measurement results are shown in Figure 3(b). The wetting layers transition is centered around 1.30 eV and the QDs transition is centered around 1.08 eV . As can be directly observed, the 0e/dot device has a much higher EQE value measured at the QD transition energy (1.1 eV) as compared to the doped QD devices. The explanation is quite straightforward. The available number of unoccupied confined electron states is reduced with further doping. According to the Fermi's Golden rule, the total transition rate decreases correspondingly and the reduction of absorption in QDs in the presence of doping is a direct manifestation of the Pauli Exclusion Principle, as illustrated in Figure 3(a). Due to the existence of tailing states, the electric field for undoped sample over the intrinsic region does not vary linearly. A slight band bending is expected. With further doping of the QDs embedded region, the effective thickness of the depletion region will be reduced, and more layers of QDs will be in the flat band region with quantum states partially filled. Thus, the overall transition strength from valence band to quantum states will be greatly reduced. This is what we directly observed (see Figure 3(b)). It is also worthwhile to note that the electron-doping of the QDs increases the initial electron density of states for the transition from quantum dots to conduction band energy states with more QD layers being occupied.

We also compared the PL of the 0e/dot, 2e/dot, and 4e/dot devices. From the results shown in Figure 4, the intensity

FIG. 3. (a) Illustration of the effect of band bending on quantum dot states absorption. (b) Measured EQE (normalized) for evaluating below bandgap photon response, which shows a reduced quantum dot states contribution with enhanced electron-doping.

of quantum dots emission reduces as the doping increases. The Si dopants were incorporated in the GaAs barriers 10 nm below the QDs layer and thus should not affect the size, composition, and crystal quality of the dots. It was recently suggested that Si dopants might have a positive impact on improving the crystal quality around quantum dots.¹³ Our

FIG. 4. Photoluminescence of 0e, 2e, and 4e/dot devices. With further electron-doping, the PL signal at quantum dot ground state (centered at 1.08 eV) reduces while PL signal at wetting layer state (centered at 1.27 eV) enhances.

measurements do not indicate an improvement in the crystal quality as the Si doping increases. This can be seen from the fact that the slope of the Urbach tail does not change much as the doping increases from 0e/dot to 4e/dot. However, the consideration that defect states such as electron traps are “inactivated” by electrons from ionized dopants is in agreement with our work.^{11,13} The drift and diffusion fields drive the mobile electrons along the film growth direction. When electrons move across the doped QDs layers, not only they find less empty quantum dot states but they are also driven by the repulsive Coulomb force. Consequently, the electrons tend to circumvent the quantum dots. The doped QDs thus trap fewer electrons. Our proposed theory is again in agreement with the PL results. The 0e/dot shows the highest emission intensity at the QDs ground state transition energy simply because the undoped QDs trap more electrons into the confined states. On the other hand, we cannot eliminate the possibility that Auger recombination quenching of the luminescence can also play an important role at high doping levels ($\geq 1\text{e/dot}$).

To conclude, we have evaluated the n-type modulation doping effects in $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}/\text{GaAs}$ quantum dot solar cell. We found that electron doping of QDs leads to reduced quantum dot absorption as expected from the Pauli exclusion principle. Also, through careful investigation, we have shown that the enhanced J_{sc} observed in doped samples results from a higher carrier collection efficiency of above bandgap photogenerated electrons. This was confirmed by an integration of the above bandgap absolute EQE with AM 1.5G solar spectrum. Besides functioning as electron trapping centers, the negatively charged quantum dots exert a repulsive force in the planar direction on the mobile electrons that are transported through the QDs layers. This repulsive Coulomb force correlates with the QDs doping level and competes with the QDs trapping potential. This theory was further validated by PL measurements where the reduced ground state emission in doped dots can be explained by the reduced total number of electrons that are trapped by QDs. Our results show that the inclusion of doped quantum dots improves the solar conversion efficiency over an undoped structure. On the other hand, we anticipate that the overall conversion efficiency of a thickness optimized bulk solar cell will still demonstrate a higher conversion efficiency as compared to a thickness optimized doped solar cell, largely because of the reduced V_{oc} in samples with quantum dots.

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