

## Research Article

# Improvement of Solar Cell Characteristics Using PbS Quantum Dot Superlattice Prepared by Sedimentation

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We report the characteristics of organic solar cells on Si substrates using quantum dot superlattices (QDSLs) prepared by sedimentation. When colloidal quantum dots (QDs) are deposited on a substrate in a solvent, they are closely packed and form multiple grains in a film. We found that the PbS QD grains grew into a large superlattice when the deposition proceeded for a long period of time. A solar cell was fabricated using the QD superlattice film as an absorbing layer. When the deposition was slow, the short-circuit current density of the solar cell doubled compared with that of the rapid deposition case. Simulations based on the superposition model suggest that the superlattice formation process is responsible for the observed change in the cell characteristics.

## 1. Introduction

Renewable energy continues to attract attention as it reduces current environmental problems like global warming and increased energy demand. Photovoltaic power generation is one renewable energy technology. The maximum power conversion efficiency (PCE) of crystalline Si (c-Si) solar cells, which are currently mainstream, is theoretically approximately 29%. Higher PCE is required if solar cells are to meet future energy demands, requiring a technical breakthrough. The PCE limit is due to heat loss and transmission loss. Electrons and holes excited by photons with energy larger than the band gap of Si (absorption layer) relax to the band edge, releasing their energy as heat. Also, photons with energy smaller than the band gap transmit without being absorbed. It was theoretically predicted that intermediate band-type solar cells with a quantum dot superlattice (QDSL) structure can reduce these losses and yield greater than 60% PCE [1, 2]. Other researches have attempted to fabricate QDSL solar cells with Stranski-Krastanov-type quantum dots (QDs) [3–5]. However, formation of Stranski-Krastanov-type QDs is based on crystal strain; thus, it is difficult to grow QDs with

high uniformity and high density while simultaneously stacking them in three dimensions [6, 7]. On the other hand, colloidal QDs prepared by chemical synthesis are also expected to be a viable material for the organic solar cells [8, 9]. Colloidal QDs have been mixed into a photon-electron conversion material instead of dye to expand the absorption band in solar cells. In another case, colloidal QDs were used as an absorption layer in Schottky junction organic semiconductor solar cells. In organic solar cells, colloidal QD films are prepared by spin coating on a substrate, and the QDs accumulate randomly. We proposed using a superlattice of colloidal QDs in solar cells [10–12]. It is known that, after the evaporation of a solvent, colloidal QDs self-assemble and pack densely in the area with electron-microscopic order [13–17]. The structure functions as a polycrystalline structure in which small single-crystal regions are connected via amorphous regions. We found that the very slow QD sedimentation in a solvent enlarged each single crystalline area in the polycrystalline structure [18]. The single-crystal region can be regarded as a superlattice. By forming a film with a wide QDSL, the absorption band is broadened and the average carrier mobility increases by the generated intermediate

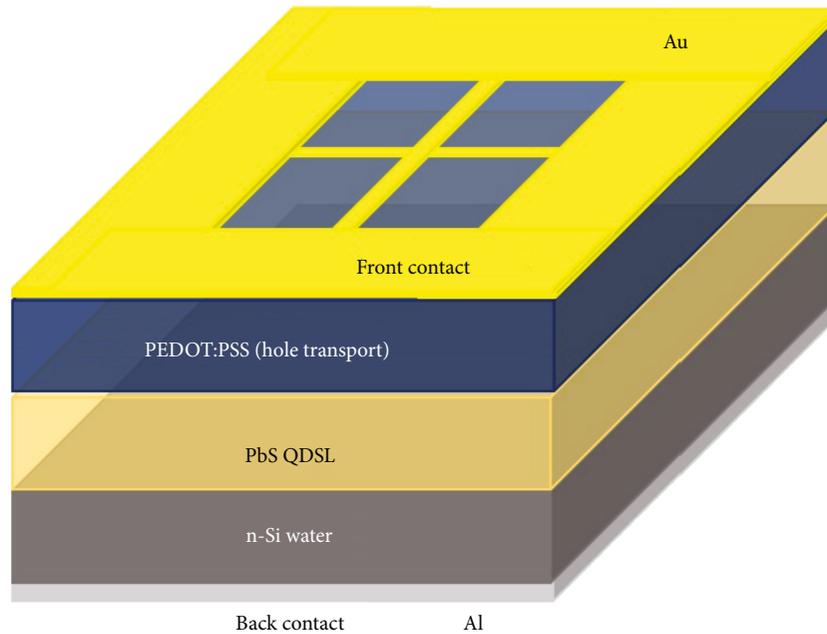


FIGURE 1: Schematic of QD solar cell structure.

band. In this work, we investigated the characteristics of an organic solar cell using PbS QDSL taking into account the sedimentation speed of QDs during QDSL formation.

## 2. Experimental

QD solar cells were fabricated using organic materials on a Si substrate. Figure 1 schematically shows the structure of the fabricated solar cell. After removing organic contamination with piranha solution, washing with buffered HF solution was applied to the n-type (100) c-Si substrate, which was a recycled product (resistivity was 1–10  $\Omega$ ·cm). Commercially available PbS QDs were used in our device (EviDot, Evident Thermoelectrics Inc.). The sedimentation time of colloidal QDs was adjusted by changing the evaporation speed of the solvent by controlling the atmospheric vapor pressure. Rapid sedimentation was carried out by leaving QD droplets on the Si substrate dry in a nitrogen gas atmosphere. Slow sedimentation occurred by setting the sample in a sealed container with a reservoir of solvent. It has been confirmed in previous studies that free QDs precipitate in a solvent to the substrate over a period of several days [4]. The thickness of the QD layer ranged from several microns to 20 microns. Thereafter, the QD layer was covered with a 40 nm thick poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) hole transport layer, which was mixed with 5 wt% dimethyl sulfoxide to improve the electric conductivity [19]. The mixture was spin-coated on the QDSL layer at 6000 rpm for 2 minutes and was subsequently annealed for 15 minutes. An aluminum electrode was deposited on the back Si surface, and a cross-shaped gold electrode was deposited on the hole transport layer by vapor deposition.

The QD layers were examined with scanning electron microscopy (SEM) and photoluminescence (PL) measurements. PL at room temperature was evaluated using a

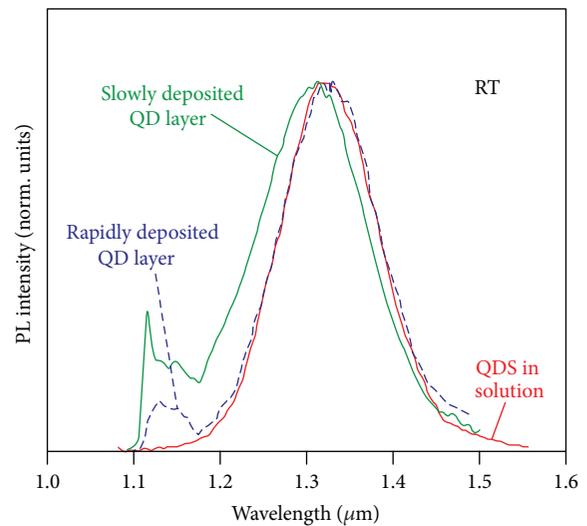


FIGURE 2: Photoluminescence spectra from the colloidal PbS QDs at room temperature.

670 nm diode laser with a monochromator (Jobin Yvon, HR320) and lock-in amplifier (Seiko EG&G Corp., 5210). The PL spectra are shown in Figure 2. Properties of QDs in solution and QD layers were compared. We can see that the QDs have a band gap in the infrared region and will be the complement to the absorption of Si in the solar cell. Evaluation of the solar cell characteristics was conducted with a lab-made apparatus. A conventional variable-illuminance halogen lamp was used as the light source. The irradiation intensity was calibrated using a solar power meter (AS ONE Corp., ST530) and standard Si solar cell. The change in the current with respect to the voltage of the solar cell was evaluated using a measurement power supply (Advantest

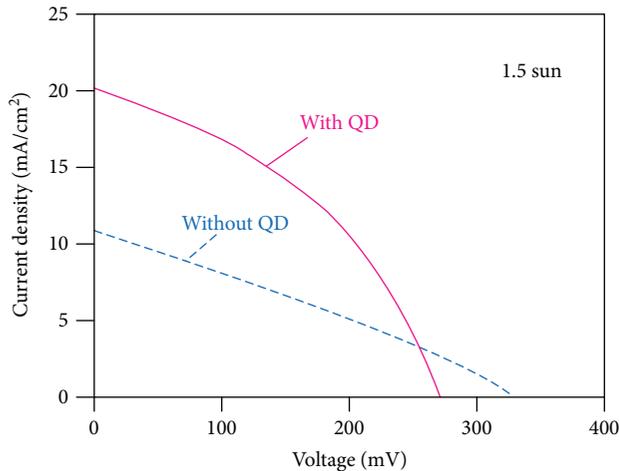


FIGURE 3: Current-voltage characteristics of solar cells. Devices with and without a QD layer are compared.

Corp., TR6134), which was controlled via UBS with a self-built VBA macro in Microsoft Excel.

### 3. Results and Discussion

The current-voltage characteristics of the fabricated QD solar cell at 1.5 suns are shown in Figure 3. A solar cell without the QD layer was prepared and its characteristics were investigated for comparison. The QD layer was formed after several minutes of solvent evaporation from the QD solution. The short-circuit current density improved from 10.4 mA/cm<sup>2</sup> to 20.1 mA/cm<sup>2</sup> after introducing the QD layer. This could occur due to a broadened absorption band in the cell. The solar cell without the QD layer was inferior to a general Si cell. This is probably because the Si substrate we used was a recycled one. PCE increased by a factor of 1.5 (0.92 to 1.42%) after incorporation of the QD layer, although the open-circuit voltage decreased slightly. The filling factor (FF) was 38% and 27% with and without QDs, respectively.

The QD sedimentation time was controlled while fabricating the QD layers. When depositing QDs slowly, free QDs have enough time to reach a stable position in the solvent and, as a result, the size of the densely packed single-crystal region is expected to grow. When the solvent evaporates rapidly, QDs accumulate on the surface of the descending solvent and adhere to the substrate. Figure 4 shows SEM images of the surface of the QD layer deposited for several minutes and that for over 3 days. A random pattern formed on the surface after rapid sedimentation. In the case of slow sedimentation, many clear steps can be seen on the surface. The step structure suggests that QDs were periodically arranged in an area of several hundred square microns. We saw that the wide QDSLs formed in the QD layer after depositing QDs for a long period of time. The PL characteristics also suggest that the unique structure appeared due to slow sedimentation. In Figure 2, one can see that the emission peak from the QD layer shifted slightly towards shorter wavelengths due to slow sedimentation. In addition, the emission intensity at short wavelengths increased and the spectrum

became asymmetric. We deduced that quantum confinement in QDs was weakened due to the formation of intermediate bands in some areas of the QD layer.

Figure 5(a) shows the current-voltage characteristics of the QD solar cell fabricated using rapid and slow deposition at 1 sun. There was almost no difference in the open-circuit voltage between the two deposition times, but the short-circuit current density nearly doubled when QD layers were deposited slowly. As a result, the PCE more than doubled when the QD layers were deposited slowly. Slow deposition caused the FF to increase by approximately a factor 1.5 times. As the irradiation power increased in a solar cell, the short-circuit current density increased. The increase was greater in the solar cell with the QD layer prepared by slow sedimentation. This may be due to the better performance of QDSLs. Comparing the results for rapid sedimentation in Figures 3 and 5(a), it seems that stronger excitation intensity leads to a lower open-circuit voltage. This is because the cells used in the measurement were different. In particular, the reproducibility of the cell performance was not good when sedimentation was rapid. The thickness of the QD layer was somewhat different, and the problem might degrade the quality of the interface between the QD layer and the hole transport layer.

The QD layer fabricated by sedimentation improved the solar cell performances. Since an improved current was observed, the measured current-voltage data from the QD solar cells were compared with simulation results from the standard superposition model [20]. The current density in the superposition model is defined as follows:

$$J = J_{SC} - J_0 \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right], \quad (1)$$

where  $J_{SC}$  is the saturation current density and  $J_0$  is the reverse saturation current density. The reverse saturation current is due to the minority carriers at the depletion layer edge and at the  $i$  region by thermal excitation. During the calculation, we used the measured  $J_{SC}$  value with  $J_0$  as a fitting parameter. The simulation results are shown in Figure 5(b). The experimental results were reproduced very well, i.e., improvements of short-circuit current density, PCE, and FF were explained by the model. The values used were  $J_0 = 2.5$  mA/cm<sup>2</sup> for slow deposition and  $J_0 = 1.3$  mA/cm<sup>2</sup> for rapid deposition. These values of  $J_0$  are very large. The most likely reason for this is that more minority carriers were generated at the depletion layer edge. Considering that the Si substrate we used was a recycled product, we cannot deny the potential adverse effects of the Si substrate. The poor results from the solar cell without QDs support this speculation. Since two types of QD cells suffer from the same performance deterioration due to the fabrication process, there must be a reason why  $J_0$  was larger in the case of slow deposition. A possible reason for the large  $J_0$  value is that minority carriers in the QDSL layer increased due to the formation of intermediate bands. It has been suggested that a wide QDSL, i.e., a broad intermediate band, formed during slow sedimentation. The intermediate band in the

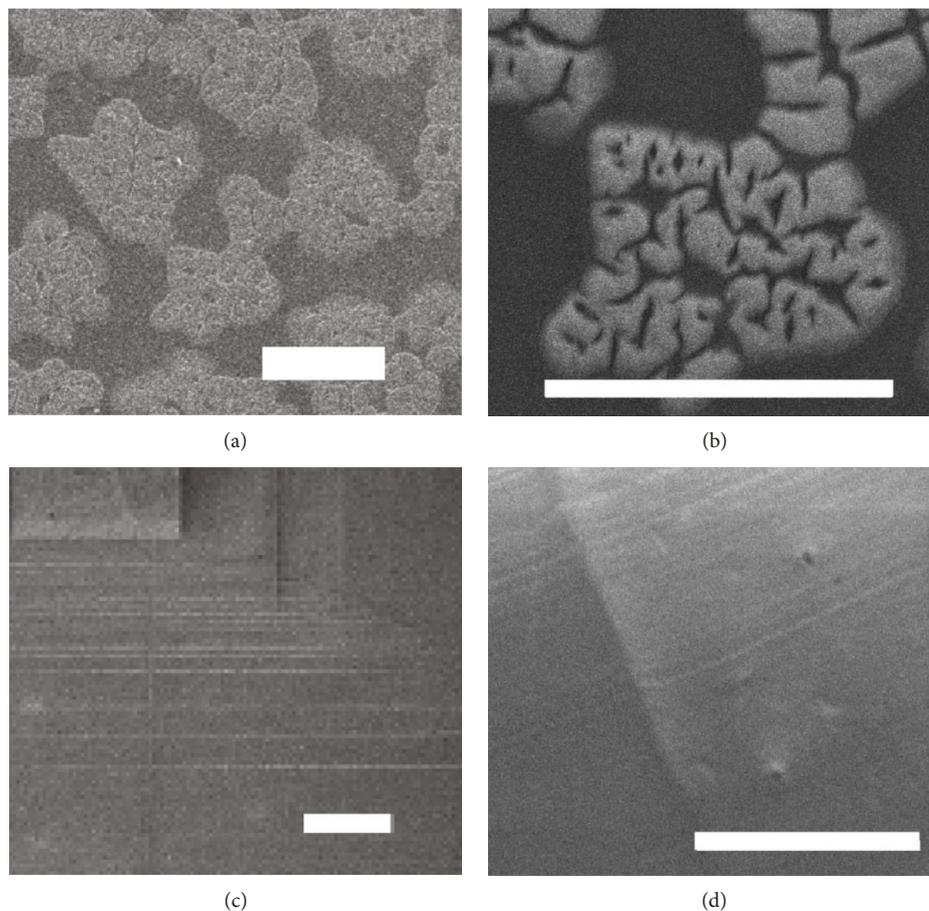


FIGURE 4: SEM images of the QD layer surfaces. (a, b) QD sedimentation time of several minutes and (c, d) sedimentation time greater than 3 days. Scale bars are 100  $\mu\text{m}$ .

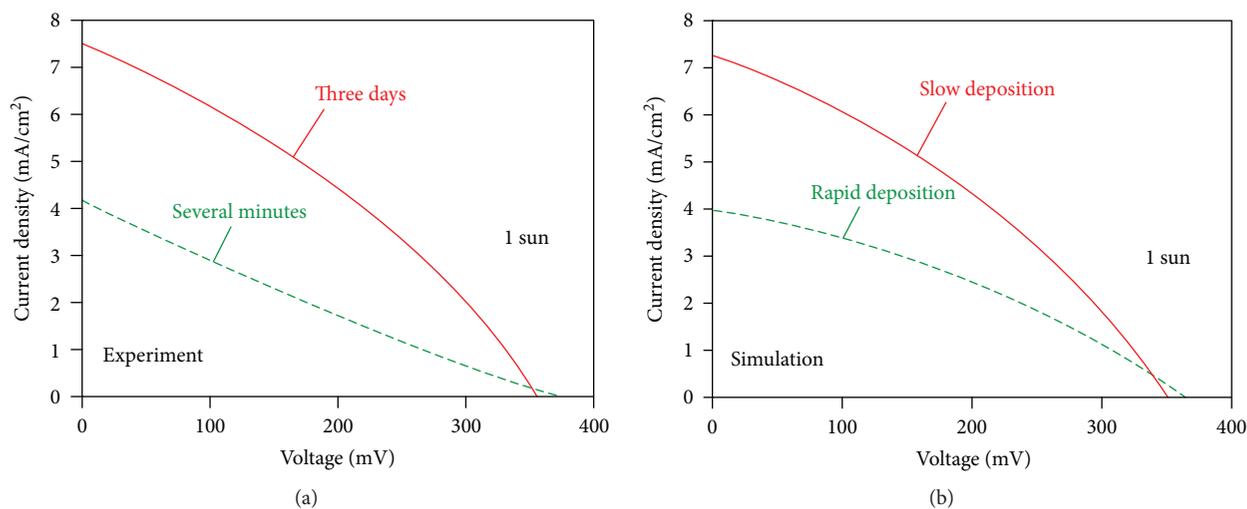


FIGURE 5: (a) Experimental current-voltage data from QD solar cells. Devices with QDs deposited over 3 days and those with QDs deposited for 20 minutes are compared. (b) Simulated current-voltage characteristics in QD solar cells.

infrared region will increase the number of minority carriers due to thermal excitation. The carrier mobility may have also improved in the intermediate band. As a result, the generated minority carriers can reach the electrode more easily, thus increasing the reverse saturation current.

It is also conceivable that  $J_0$  was apparently large due to the cell resistance values. The cell resistance was calculated from the current-voltage data in Figure 5(a). In the case of rapid sedimentation, the series and parallel resistance values were 114 and 79  $\Omega\text{-cm}^2$ , respectively. In the case of slow

sedimentation, they were 29 and 83  $\Omega\text{-cm}^2$ , respectively. The series resistance was very high in the case of rapid sedimentation, and in both cases, the parallel resistance was about one order of magnitude lower than the common value. The series resistance is the sum of various electric resistance sources encountered in the course of carrier transport. For holes, the contributing series resistances are the resistance of the QD layer, the resistance during lateral transport in the p-type layer, and the contact resistance between the electrode and the hole transport layer. Carrier scattering at the uneven PEDOT:PSS/QD layer interface is also presumed to be the cause of series resistance, and one can infer that scattering was more likely to occur in the case of rapid sedimentation. The sedimentation speed likely affects the resistance in the QD layer. For electrons, the resistance in the QD layer and Si substrate and the contact resistance at the back electrode contribute to series resistance. Among them, only the resistance in the QD layer may be influenced by sedimentation speed. Parallel resistance is a component of the leakage current. The parallel resistance is low when insulation between the positive and the negative electrodes is poor. Impurities and defects in the absorption layer lower the parallel resistance, and our cell may have problems in this respect. In particular, the PEDOT:PSS/QD layer interface and the QD layer/n-Si interface were exposed to air during fabrication, and this possibly caused contamination and/or chemical degradation.

It has been shown that QDSLs improved the characteristics of our solar cells. Our QDSL solar cells had three major problems that should be solved in order to further improve their properties. The most effective and immediate way would be to use a solar grade or better Si substrate. Another problem to be solved is control over the thickness of the QDSL layer. First, thickness should be reduced to a few microns or less. It is expected that many carrier recombination events occur since the QDSL layer was too thick to extract carriers before recombination. Also, the nonuniformity of the QDSL film should be improved. By reducing the area of the interface, deterioration in the cell fabrication process will be suppressed during atmospheric exposure. In order to improve the flatness of the film, it is necessary to homogenize the QD solution and to control the affinity between the solution and the substrate. The third point to be improved is the quality of the QDSL itself. By exchanging the QD ligand for a shorter one, the carrier transport property will be further improved [11, 12] and the number of intermediate bands will increase [21]. One would expect that carrier transport would be improved further by matching the crystal orientation of individual QDs. The aligned direction of the wave functions in a QD results in strong coupling between QDs. It has been reported that interactions between QD facets occur during sedimentation in a solvent, thus forming a so-called perfect superlattice from the colloidal QDs [21, 22].

#### 4. Conclusions

We have reported an improved organic solar cell on a Si substrate by using a PbS QDSL prepared by sedimentation.

The short-circuit current density in the solar cell with a QD layer was higher than that without a QD layer. When the QD layer was prepared via slow sedimentation, the short-circuit current density nearly doubled compared to the case of rapid sedimentation. SEM images indicate that a wide QDSL formed when QDs were deposited for a period of time longer than three days. The simulated current-voltage characteristics helped illustrate measures that could further improve the properties of the QDSL solar cells.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Disclosure

The basis of this study was reported in the 65th JSPS Spring Meeting, 2018 (in Japanese).

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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