論文の内容の要旨

論文題目　Theoretical Analysis and Characterization of Quantum-Dot Solar Cells with Multiple-Intermediate Bands
(複数中間バンド型量子ドット太陽電池の理論解析とその特性評価に関する研究)

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Intermediate band solar cells (IBSCs) are a promising technology for realizing ultrahigh efficiency of solar energy conversion. An IBSC forms an intermediate band (IB) inside the bandgap between the conduction band (CB) and the valence band (VB). In the solar cell, the first photon pumps an electron from the VB to the IB and the second photon excites an electron from the IB to the CB *i.e.* two-step photon absorption process. Thus, the photocurrent can be enhanced in comparison to the conventional solar cell without IB. One of the most promising IBSCs is based on semiconductor quantum dots (quantum dot-intermediate band solar cell/quantum dot solar cell : QD-IBSC/QDSC). The QDs have discrete confined energy levels which are ideally isolated from the CB and the VB, and therefore they can be available as IB.

The QDSCs have been widely studied because the growth techniques of the high density of QDs with highly stacked layers by the Stranski-Krastanow mode have dramatically progressed. Most of the works reported so far deal with the research of QDSCs with single IB. However, in order to open new paths toward ultrahigh energy conversion efficiency, we should investigate QDSCs with multiple IBs in detail.

The performance of QDSCs reported to date by many groups is far from the ideal characteristics. The open circuit voltage is significantly reduced and the increase of photocurrent is extremely small, in comparison to the reference cell (solar cell without QDs). One of the reasons is considered to be the low probability of two-step photon absorption, in particular the optical transition from the IB to the CB (intraband transition), which is essential for QDSCs. The demonstration of the two-step photon absorption has been performed in samples with ensemble of QDs. They detect a small increase of photocurrent when two sub-bandgap energy photons are absorbed simultaneously. However, in order to get clearer evidence, to achieve a deeper understanding of fundamental mechanisms and to find clues for enhancing two-step photon absorption, sophisticated spectroscopy using a single QD is required.

This thesis focuses on those research issues and original research conclusions for the QDSCs with multiple IBs are presented in the following.

First, using the simulation based on the detailed balance limit model, the upper limit of the thermodynamic efficiency for IBSCs with 4 IBs is found to be 74.6%, which far exceeds 63% for the single IB case.

Second, from the simulation based on the drift diffusion model, the maximum energy conversion efficiency of 6-level IBSCs is obtained around half doping in IB layer.

Third, from the k·p calculation, we find that the presence of QD largely affects the intensity of the intraband transitions and hence, the quantum states engineering is indispensable for the realization of QD-IBSCs.

Finally, we have demonstrated for the first time that the two-step photon absorption occurs in a single QD. We estimate the absorption coefficient for the intraband transition to be of the order of 100 cm^{-1} for the 0.20 eV (6.13 μm) transition energy and of the order of 10 cm^{-1} for the 0.27 eV (4.56 μm) transition energy. These estimated values are in agreement with the theoretical calculations.

This thesis is organized into nine chapters.

Chapter 1 provides an overview of the solar cell research field.

In chapter 2, the basis for solar energy conversion and photovoltaic cell is briefly reviewed. Carnot engine produces entropy-free energy with an energy conversion efficiency, the so-called Carnot efficiency, of 95.0%. However, we can only obtain a negligible amount of work. The highest efficiency from the solar energy to electricity is 86.8% *e.g.* for multijunction solar cells with infinite number of cells. While the upper limit of the thermodynamic efficiency for a single junction solar cell is 40.7%, a higher efficiency of 63.2% is obtained for an intermediate band solar cell with single IB under full concentration. The advantages of a QD-IBSC and its current status are also presented.

In chapter 3, we describe the simulation methods based on the detailed balance limit model and the drift diffusion model for QDSCs with multiple IBs. For the detailed balance limit model, the thermodynamic upper limit efficiencies are estimated using the equations for the optical transition and the balance equations in each IB. As for the drift diffusion model, the energy conversion efficiencies in the actual device structures are simulated by solving the continuity equations for the electron and the hole, the Poisson equation and the balance equations in each IB, self-consistently. In the latter model, practical energy loss processes are included: radiative recombinations, non-radiative recombinations and surface recombinations.

In chapter 4, we evaluate the efficiency for IBSCs with multiple IBs by optimizing IB's energy levels, using the simulation based on the detailed balance limit model. The thermodynamic limit efficiency of IBSCs with 4 IBs is estimated to be 74.6% which far exceeds 63.2% calculated in a previous study for the single IB case. By further increasing the total number of IBs, the thermodynamic limit of IBSCs can approach nearly 80%. These results show the high potential of IBSCs with multiple IBs and promise ultrahigh solar energy conversion.

Chapter 5 is devoted to presenting the evaluation of the energy conversion efficiency for actual device structures of QDSC with multiple IBs. The simulation based on the drift diffusion model is utilized. We find that the efficiencies of IBSCs with 4 IBs have stronger dependence on the doping concentration than those of IBSCs with single IB. On one hand, for non-optimal doping conditions under 1 sun, the efficiencies of IBSCs with 4 IBs can be inferior to those of IBSCs with single IB and even single junction solar cells. On the other hand, at around half occupation of electrons in the IBs, the efficiency of IBSCs with 4 IBs has a maximum (66% under 1000 suns), approaching the thermodynamic upper limit. These results indicate the importance of optimizing the doping concentrations in the IB regions for the IBSCs with 4 IBs.

In chapter 6, the intraband transitions, which are essential for QDSCs, are theoretically investigated by estimating the matrix elements for a structure with a quantum dot embedded in a matrix. We find that the QD pushes away the electron envelope functions (probability densities) from the QD region in almost all quantum states above the matrix conduction band minimum. As a result, the matrix elements of the intraband transitions in the QD/matrix structure are largely reduced, compared to those calculated assuming the envelope functions of free electrons (*i.e.* plane-wave envelope functions) in a matrix structure as the final states of the intraband transitions. The result indicates the importance of quantum states engineering in CB.

In chapter 7, in the former part, we present the fabrication method of an *n-i* Schottky QD photodiode, which is used for a single QD spectroscopy. We fabricate the QD photodiode by using electron beam (EB) lithography techniques so that the small apertures on top of a metallic mask can be formed. The metal with the apertures works as a shadow mask and limits the number of QDs which are irradiated by the laser light. Therefore, it enables a single quantum dot spectroscopy, *i.e.* photoluminescence (PL) spectroscopy and photocurrent (PC) spectroscopy for two-step photon absorption. In the latter part, we address a single quantum dot spectroscopy techniques. By utilizing the quantum confined Stark effect and the resonant excitation (*i.e.* an exciton is resonantly excited between the electron and hole ground states of a single QD), we can perform the single quantum dot spectroscopy.

In chapter 8, we demonstrate for the first time that the two-step photon absorption occurs in a single QD. This is a significant result for the proof of concept in QD-IBSC, the comprehension of fundamental mechanism and the improvement of the performance of QD-IBSCs. First, spectroscopy for one-step photon absorption/emission in a single QD is performed using PL and PC measurements (one-step photon absorption/emission mean the absorption from VB to IB and the emission from IB to VB). As a consequence, the tunneling current and the emission from a single QD are confirmed, meaning the successful observation of a single QD. Then, we perform spectroscopy for two-step photon absorption in a single QD by irradiating the primary and secondary lasers simultaneously to a single QD. The increased photocurrent is observed only when an exciton is resonantly excited in a single QD, depending on the power of the secondary laser. In addition, the continuous Stark shift is confirmed for one-step photon absorption/emission and two-step photon absorption. These results prove that the two-step photon absorption occurs in a single QD. We also confirm that the two-step photon absorption occurs up to at least 55 K. From the experimental results, we estimate the absorption coefficients for the in-plane polarized intraband transition to be of the order of 100 cm^{-1} for the 0.20 eV (6.13 μm) transition energy and of the order of 10 cm^{-1} for the 0.27 eV (4.56 μm) transition energy. These estimated absorption coefficients are in agreement with those from the theoretical calculations.

We compare the energy conversion efficiency estimated from the drift diffusion model, using either the ideal value of the intraband transition absorption coefficient 10^4 cm^{-1} or its experimental value 500 cm^{-1}. The efficiencies of ideal 3-level IBSC and 6-level IBSC are respectively 55% and 66%. In the case of a 500 cm^{-1} absorption coefficient, they decrease down to 30% and 27%, respectively. This indicates that further work on enhancing the intraband transition is indispensable for realizing IBSC with high energy conversion efficiency.

In chapter 9, we present conclusions to this thesis. We also give an outlook for future research and development.