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Feasibility of submonolayer ZnTe/ZnCdSe quantum dots as intermediate band solar cell material system

S. Dhomkar [a,b,*,1], U. Manna [c,1], L. Peng [b,d], R. Moug [d], I.C. Noyan [c], M.C. Tamargo [b,d], I.L. Kuskovsky [a,b]

[a] Department of Physics, Queens College of CUNY, Queens, NY 11367, USA
[b] The Graduate Center of CUNY, New York, NY 10016, USA
[c] Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA
[d] Department of Chemistry, City College of CUNY, New York, NY 10031, USA

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ABSTRACT

Intermediate band solar cells can potentially have an efficiency of ~63% under full solar concentration, but the material systems investigated until now are far from optimum and are fraught with growth related issues such as low quantum dot densities, presence of wetting layers, and strain driven dislocations. Also, incorporation of type-I quantum dots increases carrier recombination rates, resulting in inferior performance. Here, we show that a novel material system with stacked type-II ZnTe-rich submonolayer QDs embedded in ZnCdSe has close to the optimal material parameters required for an intermediate band material system. We have grown structures comprising of as many as 150 layers of QDs that are formed without wetting layers and that have a valence band offset of ~0.8 eV relative to the host with a bandgap of ~2.1 eV. We demonstrate the possibility of intermediate band formation and subsequent absorption of below bandgap photons. Additionally, these structures are expected to have longer radiative lifetimes and to suppress Auger recombinations owing to their type-II nature.

1. Introduction

The intermediate band (IB) solar cell (SC) concept proposed by Luque and Martí in 1997 [1] provides a new insight into the conversion efficiencies of SCs, and offers a potential way to increase the limiting efficiency of an ideal single-gap SCs from 40.7% [2,3] to 63.2% [1,4,5] under full concentration. IB-SCs rely on multi-photon absorption with assistance of an IB lying in the mid-gap of an active material forming a SC [1,4,5]. Such an IB allows harvesting of photons with energy below the bandgap via transitions from the host semiconductor valence band (VB) to the IB and from the IB to the conduction band (CB) in addition to the conventional VB to CB transitions. The absorption of the additional IB assisted photons increases the photocurrent, while preserving the open circuit voltage, thus improving the external efficiency of the cell [1,4,5]. The formation of an IB by means of quantum dots (QDs) is considered to be the most practical and attractive approach to fabricate an efficient IB-SC [4,5].

In the QD based IB-SCs, either electron or hole confinement levels within the QDs give rise to an IB [4,5] depending on the bandgaps and band-offsets of the constituent materials. The proof of concept has been successfully demonstrated in the type-I InAs/GaAs QDs [6,7] with the IB engineered out of electron confinement levels; moreover, the efficiencies obtained show significant improvements as compared to the reference GaAs cell when QDs are appropriately doped [8]. However, the main constraints that limit the performance of such IB-SCs are [4,5]: (i) the bandgaps of the proto-type InAs/GaAs QD SCs are far from the theoretically calculated optimal values for host bandgap (~1.95 eV) and the IB (~0.71 eV) [1,4,5], though some modifications have been proposed for the purpose of optimization [9,10]; (ii) an insufficient increase in the short circuit current because of relatively low absorption due to the small number of QD layers; relatively a few layers of QDs can be grown via the Stranski–Krastanov growth mode due to accumulation of strain and subsequent formation of dislocations [11]; (iii) a reduction of the open circuit voltage due to the existence of the wetting layers formed as a consequence of the Stranski–Krastanov growth; the presence of a wetting layers prevents the QDs to form well-separated confined states for electrons (or holes), resulting in a continuum of states following strong thermal escape, reducing the open circuit voltage; (iv) type-I QDs have both types of carriers spatially confined in the same volume, enhancing the probability of electron–hole scattering and recombination [12,13]. Here, we propose submonolayer type-II ZnTe-rich QDs embedded in a $Zn_xCd_{1-x}Se$ ($x \sim 0.51$) matrix as an IB

* Corresponding author at: Department of Physics, Queens College of CUNY, Queens, NY 11367, USA. Tel.: +1 718 997 3370.
E-mail address: sdhomkar@qc.cuny.edu (S. Dhomkar).
[1] Both these authors contributed equally to this work.

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material and show the feasibility of such a system to address the above mentioned deficiencies of the proto-type QD based IB-SCs. The proposed structure is believed to possess the material parameters with the best possible match to those of an ideal IB-SC.

The $Zn_xCd_{1-x}Se$ alloy has a band gap of about 2.1 eV at room temperature [14], when grown lattice matched to InP, hence it can be used as a host material with a bandgap close to the ideal one. Also, ZnTe QDs having a VB offset of about 0.8 eV [15–17] relative to the $Zn_{0.51}Cd_{0.49}Se$ can be used to engineer an optimum IB out of the hole confinement levels. To verify this assumption, we thus have grown submonolayer ZnTe/ZnCdSe multilayer QDs with as many as 150 periods by means of migration enhanced epitaxy (MEE). The submonolayer nature of these QDs and their growth mechanism allow them to form without the formation of the wetting layers. The multilayer nature of the vertically correlated ZnTe/ZnCdSe QDs is shown to manifest via the IB related absorption. Hence, incorporation of ZnTe/ZnCdSe submonolayer QDs in a practical device is expected to increase the short circuit current, while the formation of QDs without the wetting layer is expected to preserve the open circuit voltage. Moreover, the type-II nature of these heterostructures is also expected to suppress the non-radiative Auger [18] recombination as well as to improve the process of charge extraction [19]. In subsequent sections, we show that such a system indeed possesses 'close-to-ideal' material and physical properties and thus could lead to a practical efficient IB-SC.

2. Experimental

2.1. Growth

Three samples (referred hereon as A, B, and C) were grown epitaxially on (001) semi-insulating InP substrates with increasing Te content in a RIBER 2300P molecular beam epitaxy system. After the growth of the InGaAs and ZnCdSe buffer layers, multilayered structure of ZnTe-rich QDs within a ZnCdSe matrix was grown via MEE, by exposing the growing surface to alternate elements using a specific shutter sequence shown in Fig. 1(a). A ZnCdSe barrier (nominally 8 monolayers) was first grown, followed by the three identical cycles of sequential depositions of Zn and Te separated by 5 s of growth interruptions. The whole sequence of the growth of the ZnCdSe barrier and the ZnTe QDs was then repeated 150 times to achieve a multilayered structure as illustrated in Fig. 1(b). Details of the growth technique have been reported elsewhere [20]. The Te source temperatures for samples A, B, and C were 236 °C, 241 °C, and 250 °C respectively, which correspond to beam equivalent pressures of 0.38×10^{-7} Torr, 0.63×10^{-7} Torr, and 1.2×10^{-7} Torr respectively.

3. Characterization

Low temperature PL measurements were performed using a Janis Research closed cycle refrigerating system. The 351 nm emission line from an Ar^+ laser was used as an excitation source and the excitation intensity was varied by over four orders of magnitude using neutral density filters. The PL was dispersed through a third stage of a TriVista SP2 500i triple monochromator and was detected by a thermoelectrically cooled charge coupled device camera. The HRXRD measurements were carried out at Beamline X20A at the National Synchrotron Light Source at the Brookhaven National Laboratory. All measurements were performed using monochromatic synchrotron radiation at 8 keV, with a double-crystal Ge (111) monochromator. To enhance the angular resolution, a Si (111) analyzer was placed in front of the detector. The absorption measurements were done in an ARC closed cycle refrigerating system from 10 K to room temperature. A broad spectrum halogen lamp was used as a light source and the signal was collected using an Ocean Optics VIS–NIR spectrometer.

4. Results and discussion

The special epitaxial technique described in Section 2.1 enables sequential deposition of the elements in submonolayer quantities, which, combined with the short interruptions, gives rise to enhanced surface migration. The submonolayer ZnTe QDs are formed by continuous enlargement of Te isoelectronic centers via Volmer–Weber growth mode without the formation of a wetting layer, analogous to ZnTe/ZnSe QDs reported previously [21,22]. Hundreds of layers containing QDs can be grown by this technique, potentially giving a large number of QDs, all without wetting layers. An additional advantage of such a growth mechanism is that the dopants, for instance Nitrogen for p-type doping in this case, can be easily incorporated preferentially into the QDs [22,23], in order to create a 'half-filled' IB as required for the optimal performance of an IB-SC [7,8].

Low temperature PL was employed to investigate the type-II nature of these QD structures. Fig. 1(c) and inset of Fig. 1(c) show the PL spectra for all the three samples for maximum excitation intensity and three orders of magnitude of lower excitation intensity, respectively at 10 K. Fig. 1(d) shows the dependence of the PL peak positions on excitation intensity with the peak positions showing strong blue shifts with increasing excitation intensity for all samples. Such a strong shift is a characteristic feature of type-II band alignment [21,24,25], and it is caused by band bending [24] that effectively changes the overlap of wavefunctions of the photo-generated electrons and holes. The PL peak positions were also found to approximately follow the cube root dependence on the excitation intensities as shown by the dotted lines in Fig. 1(d) for the three samples, in agreement with the prediction for large type-II nanostructures [24,26]. The PL spectra shown in Fig. 1(c) also demonstrate that there is a significant red shift in the PL peak position in case of samples B and C, which have higher Te concentrations as compared to that of sample A. This red-shift in PL emission energy with increasing Te concentration can be attributed to the increase in size of QDs due to higher Te content. Since Te concentration directly relates to Te source temperature (or Te flux), one gets an effective way to control the IB position by varying Te flux during the growth.

To investigate the "below bandgap" absorption occurring due to the possible ZnTe QD-based IB, we performed optical absorption measurements with results shown in Fig. 2. The below bandgap absorption was found to manifest itself via small peaks as indicated by arrows in the absorption spectra shown in Fig. 2. The energy of the below bandgap absorption peaks nominally corresponds to the PL peaks of the spatially indirect excitons in this type-II material system (see Fig. 1(c)). The observation of below bandgap peaks in the absorption spectra in spite of their spatially indirect nature indicates formation of the IB made out of the hole energy levels (detailed discussion on the IB formation is presented below). Due to smaller thicknesses of the disc-like submonolayer ZnTe QDs, the hole confinement energy lies close to the ZnCdSe VB as indicated by the position of absorption peaks in Fig. 2. It also needs to be stressed that the below bandgap absorption was only moderately enhanced with the inclusion of ZnTe QDs because of the undoped nature of these samples. The below bandgap absorption can further be improved by creating a half-filled IB by introducing p-type dopant during MEE cycles [22,23] within the QDs. The absorption measurements also enabled us to calculate the modified band gaps of the ZnCdSe