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Inter-level carrier dynamics and photocurrent generation in large band gap quantum dot solar cell by multistep growth

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ABSTRACT

In this work we present a solar cell structure where the concept of intermediate band is exploited by a high energy barrier AlGaAs material with embedded InAs-based quantum dots via a multistep growth approach. In this way the intrinsic issues related to different surface kinetics of involved species (Ga, In and Al adatoms) and affecting crystal quality are successfully overcome. With respect to energy band engineering of the cell, this growth approach introduces a two-dimensional quaternary layer and consequently an additional energy band, between the host junction and the dot energy levels. This band results strongly related to the quantum dot states by thermal transferring and inter-level filling processes. Moreover, low temperature (up to 100 K) photocurrent generation via additional infrared absorption is promoted by the employed band engineering, thus representing an effective method to extend intermediate band solar cell design flexibility.

1. Introduction

Intermediate Band Solar Cells (IBSCs) are an innovative concept of photovoltaic system [1] with a theoretically predicted increased efficiency with respect to the Schockley-Queisser limit of single junction solar cell [2]. The working principle for these devices is founded on the insertion of one or multiple [3] energy levels available for the photogenerated carriers within the matrix semiconductor energy gap. Practical applications are limited by the materials which can be effectively employed to satisfy the intermediate band theory, for which both, a high photo-voltage and a high photo-current (PC), should be achieved with the introduction of an intermediate band in the host junction. The most studied system so far consists of InAs Quantum Dots (QDs), self-organized in a GaAs matrix, widely employed in the last decades for demonstrating high performance optoelectronic devices such as telecom lasers [4] or semiconductor optical amplifiers [5]. Indeed, this material system has been a successful case-study to identify some crucial features for intermediate band operation in solar cells: high solar concentration and low temperature operation two photon experiments [6,7] even at the single QD level [8], influence of continuum background and related cross transitions [9], to name a few.

However, the extensive recent research carried out on this field clearly highlighted, both theoretically and experimentally [6,9–12], that the InAs/GaAs system is not the ideal one for the IBSC model for several reasons. Firstly, the related energy band profiling intrinsically leads to the dominance of carrier thermal escape at room temperature [13,14]. Secondly, the InAs/GaAs QD system is negatively affected by unavoidable wetting layer (WL) energy states and by its interaction with the continuum of states [9,15–17]. Therefore, the need for further search on the material side for a more effective exploitation of this promising photovoltaic concept is evident.

The IBSC potentialities are based on a proper engineering of the host material energy gap (E_G) and of the device energy bands. In the widely studied GaAs/InGaAs QD system, the host GaAs bandgap energy, E_G, is equal to 1.42 eV, while the insertion of QDs within the matrix generates a band of energy levels available for confined electrons (ranging from the ground state E_0, usually found at around 1.1–1.2 eV, depending on the employed QD growth conditions, to the excited states, E_n, with $n = 1, 2, 3$). Energy splitting of holes levels is generally excluded by this evaluation, because of their larger effective masses [1].

Ideally, significantly improved efficiency from IBSCs is theoretically expected for E_G values as large as 1.95 eV [1], which ensure sufficiently

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wide separation from the intermediate band and the bulk continuum. By the addition of Al in the GaAs barrier, larger values of E_G can be straightforward achieved. Ref.s [18,19] have actually demonstrated an enlarged absorption spectral range by integrating quaternary AlGaInAs QDs in AlGaAs barrier, whereas Ramiro and coworkers [20] reported on InAs/AlGaAs QD-IBSCs where high activation energy can reduce thermal carrier escape. Recently, suppression of carrier thermal escape has been shown up to Room Temperature (RT) in a dot-in-well structure where InAs QDs are embedded in a GaAs quantum well (QW) within a higher AlGaAs barrier, with improved confinement of carriers within the QD states [21]. Most importantly, increasing the host band gap resulted strategic for the latest demonstration of some basic principles of the concept [22].

However, when Stranski-Krastanov InAs QDs are directly inserted in an AlGaAs matrix, despite the similar lattice mismatch of the InAs/GaAs and InAs/AlGaAs systems, relevant differences in chemical species features and mobility influence the related island density, size, and growth mode [23]. Moreover, self-assembling growth of nanostructured ternary and/or quaternary compounds generally results in an intricate chemical composition [24] which in turn leads to quite rich and elaborate energy level diagram, thus opening new different scenarios for the photo-generated electron/hole dynamics and requiring a detailed investigation to assess their role in the device energy conversion efficiency. Actually, nanoscale engineering has been also recently proposed for IBSC [25] and demonstrated to be an effective tool to ensure photovoltage recovery.

In this work we propose an IBSC growth scheme for InAs-based QDs within an AlGaAs barrier, consisting of a multistep procedure aimed at limiting the strain field propagation and promoting adatom surface migration as assessed by high resolution structural analysis. With respect to IBSC operation, this material design leads to a quaternary wetting layer acting as a band of two-dimensional quantum confined energy states, and strongly interacting with the 0D QD-related energy levels. Moreover, with respect to the InAs/GaAs systems, the presented growth approach allowed increasing the QD carrier confinement, widening the energy range for sub-bandgap absorption. At the same time, the presence of 2D states band is supposed to be effective in suppressing the QD radiative recombination processes, thus providing a strong increment of PC via two step two photon(TS-TP) absorption in the related spectral region, up to 100 K.

2. Experimental methods

The solar cell heterostructures were grown by Molecular Beam Epitaxy for III-V's compounds, using a Riber Compact 21 system. Samples were characterized by Atomic Force Microscopy (AFM) and Scanning/Transmission Electron Microscopy (STEM). STEM analyses were carried out by using a JEM-ARM200F TEM/STEM instrument, operating at 200 kV, with a resolution of 78 p.m. Energy dispersive x-ray spectroscopy (EDS) was used to obtain chemical information from different areas of the sample.

Various cells were realized with dimensions ranging from 2 × 2 to 4 × 4 mm^2 defined by 800 nm height mesas realized by standard optical lithography and wet chemical etching, in order to isolate cells from each other. The thermally evaporated and annealed (at 410 °C) metal contacts were: Ti(60 nm)/Au(260 nm) for the p-type, and GeAu (75 nm)/Ni(35 nm)/Au(200 nm) for the n-type. A metallic finger grid on the top side of devices was realized by optical lithography, metal deposition and lift-off. The heavily doped p-type GaAs cap layer was removed by wet chemical etching and no anti reflection coating was used. The device key figures, measured at standard AM 1.5 conditions are: short circuit current $J_{sc} = 10\ mA/cm^2$, open circuit voltage $V_{oc} = 0.78$ V, efficiency $\eta = 5\%$ and fill factor FF = 61%.

The cells were analyzed in details by combining photoreflectance (PR) measurements at RT with photoluminescence (PL) spectroscopy and external quantum efficiency (EQE) measurements, from 10 K to 300 K. For PR measurements, the light beam of a Quartz-Tungsten-Halogen lamp (150 W), passed through a JY Triax 320 monochromator (0.32 m of focal length), was focused on the sample surface, where a superimposed laser beam (632 nm, chopped at 233 Hz) provided the modulated perturbation. The reflected light was then focused on a photodiode (Si or InGaAs) and the current signal (pre-amplified and converted in voltage signal) was feeding a dual phase SR830 Stanford Research Lock-in amplifier. The relative change in reflectance is given by: $\Delta R(\lambda)/R(\lambda)$, where $\Delta R(\lambda)$ and $R(\lambda)$ are, respectively, the ac modulated and the dc average signal. PL signal was excited by Ar+ laser (514 nm), dispersed by a JY iHR320 monochromator and detected by a cooled NIR-photo-multiplier (Hamamatsu) operating in single photon counting mode. In the EQE measurements the cell was illuminated by a light beam (primary excitation source) delivered by a JY Triax 320 monochromator equipped with a 150 W Quartz-Tungsten-Halogen lamp. The cell was connected to a trans-impedance low-noise preamplifier that biased it at 0 V (short-circuit configuration) and the resulting PC signal I_{SC} (converted in voltage signal) was measured by a lock-in amplifier.

The EQE spectra at different temperatures were also taken in reverse bias configuration, varying the voltage value from 0 V to −3V, and under a secondary light beam in the IR spectral range, supplied by a 150 W Xe lamp through a long wavelength pass filter ($\lambda > 1200$ nm).

3. Results and discussion

The solar cell structure, grown on n^+-type GaAs substrate, is shown in Fig. 1(a) and detailed in Table 1. It consists of 200 nm n-type (doped to $1 \times 10^{18} cm^{-3}$ with Si) $Al_{0.17}Ga_{0.83}As$ layer, followed by a 480 nm $Al_{0.17}Ga_{0.83}As$ intrinsic region, 200 nm p-type (doped to $2 \times 10^{17} cm^{-3}$ with Be) $Al_{0.17}Ga_{0.83}As$, 30 nm p-type $Al_{0.6}Ga_{0.4}As$ (window layer, $2 \times 10^{17} cm^{-3}$), and by 200 nm highly doped p^+-GaAs with $1.5 \times 10^{18}\ cm^{-3}$ doping contact layer. Three widely spaced (40 nm) and electronically uncoupled quantum dot layers were stacked in the centre of the intrinsic AlGaAs region. The AlGaAs spacer was grown as for QD lasers [4] with the first 5 nm immediately grown at the same temperature as the QDs (530 °C), and the remaining 35 nm grown at higher temperature (620 °C).

The advantages of using such a temperature profile in the present experiment, with QDs embedded in an AlGaAs barriers, are multiple. First, the low temperature fast overgrowth of QDs with 5 nm of AlGaAs allows to freeze the intermixing effects associated with QD overgrowth [26]. Secondly, the substrate heating for completing spacer growth is particularly important for high quality Al-containing compounds, since Al has a higher bond strength to As with respect to Ga, resulting in a lower adatom mobility. For each QD layer growth, the substrate temperature was lowered down to 530 °C. The deposition of the QDs consists of a single cycle procedure performing a gradual change from a quaternary to ternary and finally binary compound, as shown in Fig. 1(b). First Al, Ga and In cells were opened simultaneously under As overpressure, in order to form a virtual quaternary submonolayer (0.9 ML of $Al_{0.22}In_{0.09}Ga_{0.69}As$) acting as a nucleation layer for QDs. Afterwards, Al cell was closed and a deposition of 1.4 ML of $In_{0.12}Ga_{0.88}As$ followed. The multistack was completed with 2.9 ML of InAs. The 2D to 3D transition is observed by reflection high energy electron diffraction (RHEED) pattern change at the very end of the stack, after deposition of 2.9 MLs of InAs. As opposed to a similar quaternary QD growth [27], our approach is based on a single cycle deposition, where each layer allows to get a vertical gradient in the planar lattice parameter (a). As shown in Fig. 1(b), a gradually evolves from 5.65 Å in the barrier, to 6.06 Å in the final InAs, thus reducing the overall strain associated to the QD formation. The other effect is the presence of both Al and In species in the first meta-layer which provides a higher level of control for species mobility. Since one of the key points required for the operation of QD-IBSCs is to increase the energy level of conduction band, this can be accomplished only by increasing Al