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PHYSICS OF SEMICONDUCTOR DEVICES

AlGaAs/GaAs Photovoltaic Cells with an Array of InGaAs QDs

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Abstract—Specific features of the fabrication of AlGaAs/GaAs single-junction photovoltaic cells with an array of quantum dots (QDs) by molecular beam epitaxy have been studied. It was shown for the first time that, in principle, vertically coupled QDs can be incorporated, with no dislocations formed, into the structure of photovoltaic cells without any noticeable deterioration of the structural quality of the *p*–*n* junction. Owing to the additional absorption of the long-wavelength part of the solar spectrum in the QD medium and to the subsequent effective separation of photogenerated carriers, a ~1% increase in the short-circuit current density J_{sc} was demonstrated for the first time in the world for photovoltaic cells with QDs. The maximum efficiency of the photovoltaic cells was 18.3% in conversion of the unconcentrated ground level solar spectrum AM1.5G.

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1. INTRODUCTION

Modern tendencies in the engineering of the world's power have stimulated a substantial increase in the interest in alternative energy sources. Photovoltaic converters (PVC), or solar cells (SCs), are the most promising, ecologically safe candidates for diminishing the petroleum addiction of the world and, in contrast to organic and inorganic power sources, convert solar radiation directly into electric power. The future of solar energetics is now associated with III–V semiconductor heterostructures suggested by Alferov in 1966 [1]. Among the important advantages of PVCs of this kind over silicon photovoltaic cells are the higher efficiency, enhanced radiation hardness and temperature stability, and higher conversion efficiency of concentrated solar radiation. Nevertheless, there exist a number of factors limiting the efficiency of such PVCs [2]. One of the most important and fundamental problems in energy conversion by semiconductor solar cells is the loss through carrier thermalization. On the one hand, the energy gap of a SC should be sufficiently narrow for absorbing as large a part of the solar spectrum as possible; on the other hand, high-energy photons (from the short-wavelength part of the solar spectrum) generate in this case "hot" electron–hole pairs and, as a result, a large part of the photon energy is lost via thermalization.

The most effective and widely used approach partly obviating the problem is based on a series connection of single-junction solar cells with different energy gaps via tunnel diodes into multiple-junction (cascaded) heterostructure PVCs [3]. A decrease in the energy gap of materials of the *p*–*n* junctions away from the photosensitive surface provides effective absorption of photons in a certain energy range by each element of the cascade and, as a result, a higher utilization efficiency of solar radiation is achieved. However, making larger the number of elements of the cascade results in that the PVC design becomes more intricate and the number of heterointerfaces and tunnel diodes grows, which leads to a rise in the internal loss and, in particular, to a higher series resistance of the PVCs. Moreover, high-efficiency multiple-junction solar cells can be fabricated from a limited set of materials that can provide lattice matching. In the end, these problems restrict the maximum number of junctions and the most presently efficient solar cells are GaInP/GaInAs/Ge triple-junction PVCs [4].

There exists a new approach to the solution of this problem, which supplements the concept of multiple-junction heterostructure solar cells. This approach is based on the use of semiconductor structures with self-organized quantum dots (QDs): pseudomorphically grown heterostructures with the limiting case of quantum confinement. Owing to the discrete electronic spectrum of QDs, it becomes possible, in principle, to solve the problem of the thermalization loss [5]. By varying the size and shape of QDs and the composition of the host (layer in which the QDs are embedded), the edge of the absorption band associated with the additional transition in QDs [6] can be modified in a controlled way, which can extend the spectral sensitivity range and raise the photocurrent in pseudomorphically grown QD-based PVCs. A rather interesting approach aimed at minimizing the loss associated with the incomplete absorption of the solar spectrum consists in that the energy levels in QDs can serve as an intermediate band for performing effective photoelectric conversion of photons with energies lower than the energy gap of the matrix [7]. True, such an approach requires that QDs should be doped to provide partial occupation of the intermediated band by carriers, which may lead to a higher probability of radiative recombination and to additional optical loss and thereby can neutralize the positive contribution to the photocurrent from QDs [8].

The present study is devoted to the examination of the photoelectric properties of a medium constituted by InGaAs QDs placed in a *p–n* junction and to the analysis of the physical processes of photoelectric energy conversion in an absorbing medium with an array of QDs.

2. EXPERIMENT

All the samples studied were grown by molecular beam epitaxy in a RIBER49 installation on Si-doped GaAs (001) substrates. In(Ga)As self-organized QDs were formed in a GaAs matrix in the Stranski–Krastanow growth mode [6]. The evolution of the surface morphology in the course of growth was observed in situ by means of the reflection of high-energy electron diffraction.

Epitaxial structures with QDs were characterized by transmission electron microscopy (TEM) on a Philips EM 420 electron microscope at an accelerating voltage of 100 kV. Samples for plane-view and cross-sectional TEM examination were prepared by chemical etching and mechanical grinding–polishing, followed by sputtering with Ar^+ ions in a Gatan DouMill600 installation.

Photoluminescence (PL) in the structures was excited by a YAG:Nd laser operating at the second harmonic in the CW mode (532 nm, 1–5000 W cm^{-2}). The signal was detected using a monochromator and a cooled Ge diode.

The photovoltaic cells under study were fabricated by the photolithographic method. In the process, the bus bars of the upper contact were thickened by electrochemical deposition of gold to a thickness of ~2 μm. The photocells were 3.2 × 8.3 mm in size, with shading of ~8% of the surface area by the contact grid. ZnS/MgF_2 layers served as antireflection coatings.

Spectral dependences of the external quantum yield of the PVCs were studied at wavelengths of 340–1200 nm by comparing the photocurrents in the experimental and reference photodetectors exposed to frequency modulated monochromatic light. The results obtained were used to calculate the photogenerated current density for the standard AM1.5G conditions (1000 W m^{-2}). The load current–voltage (*I–V*) characteristics were measured using a four channel pulsed solar simulator with a spectrum close to AM1.5G [9].

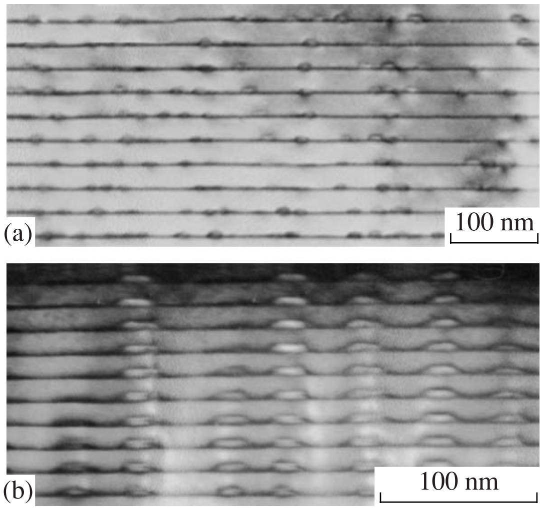


Fig. 1. Cross-sectional TEM image of vertically stacked InAs QDs with a GaAs spacer thickness of (a) 30 and (b) 10 nm.

3. RESULTS AND DISCUSSION

The main difficulty encountered when using self-organized In(Ga)As QDs in PVCs is their low surface density [typically (2–5) × 10^{10} cm^{-2}], which leads to a rather low gain (absorption) in the QD array. The surface density of the QDs can be raised by performing growth on misoriented (100) substrates, but this can be done only within a comparatively narrow range [10]. The most promising way to overcome this difficulty consists in vertical stacking: successive deposition of several sheets of the QDs and spacer layers [6]. Theoretically, such a multilayer stacking should result in a monotonic increase in the QD density with the number of layers, without any tendency toward leveling-off. In actual practice, this is only partly true for the case of comparatively thick (>20 nm) GaAs spacers, with the resulting QD arrays characterized by a wide fluctuation of the QD size (see Fig. 1a). It should be noted that the uniformity of the QDs depends on the deformation energy. Consequently, making the GaAs spacer thinner (< 15 nm) will lead to spreading of the deformation fields of the lower QD sheet into the GaAs layer, which will, in turn, cause vertical alignment (coupling) of the QDs in the sheets (see Fig. 1b). However, the buildup of elastic stresses in the layers causes a steady increase in the average QD size with the number of stacked layers, and, on exceeding the critical QD size, gives rise to misfit dislocations. As a result, to preserve the high structural perfection and optical quality of vertically coupled QDs, it is necessary to diminish either the average indium content of the QDs, or the effective thickness of the InAs layer deposited during QD growth.

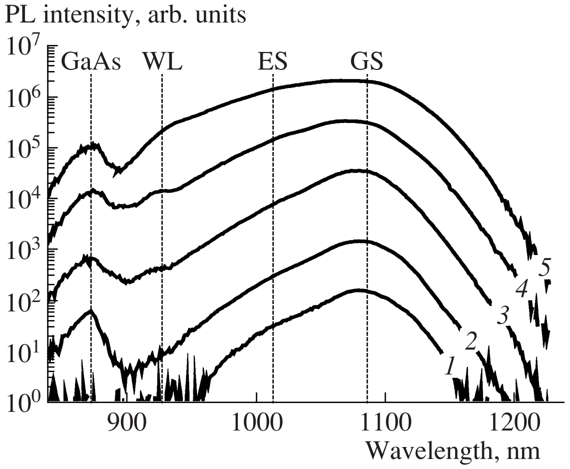


Fig. 2. PL spectra of vertically coupled (ten sheets) InGaAs QDs in a GaAs matrix at room temperature and different optical excitation power densities: (*1*) 1, (*2*) 10, (*3*) 150, (*4*) 1×10^3, and (*5*) 5×10^3 W cm^{-2}. Designations: GS, ground state of a QD; ES, excited state of a QD; WL, wetting layer of a QD; and GaAs, GaAs matrix.

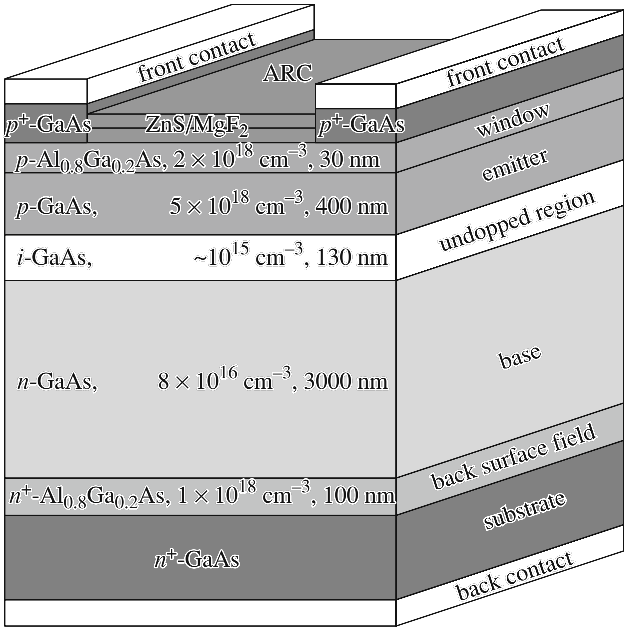


Fig. 3. Schematic of an AlGaAs/GaAs single-junction PVC with an *n*-AlGaAs back potential barrier and thin *p*-AlGaAs wide-gap window.

According to the results of our preliminary studies, the optimal number of sheets of QD arrays deposited (stacked) in the coupling mode without using special growth techniques (successive decrease in the effective thickness of the InAs layer with increasing number of QD sheets or partial relaxation of stresses in the structure via introduction of GaP layers) is 10–15.

Figure 2 shows the room temperature PL spectra of a heterostructure comprising of ten vertically coupled sheets of InGaAs QDs (GaAs spacer thickness 10 nm), embedded in GaAs. The evolution of the PL spectra, observed as the density of the optical pumping power increases, makes it possible to estimate the width of the integrated energy spectrum of states of composite QDs. For example, local peaks corresponding to emission from the excited states of the QDs (ES), In-enriched wetting layer (WL), and GaAs matrix are observed in addition to the line associated with recombination via the ground state (GS). At the same time, a correct estimate of the degree of inhomogeneous broadening of the energy spectrum of the QD array is only possible at low temperatures (commonly below 100 K), when carriers are randomly distributed over QD states (nonequilibrium distribution) and the PL spectrum adequately reflects the energy spectrum of the ground states of the QD array at low excitation densities. As a result, the full width at half-maximum (FWHM) of the GS peak is ~40 nm at 77 K, which points to a high uniformity of the QDs under study. It s noteworthy that, according to TEM data, these multilayer structures with InGaAs QDs have a total QD density of ~5×10^{11} cm^{-2}.

To examine the photoelectric properties of the absorbing QD medium developed in this study and evaluate the efficiency of the approach suggested, we fabricated PVCs as standard AlGaAs/GaAs single-junction solar cells (SCs) with a back *n*-AlGaAs potential barrier and a thin *p*-AlGaAs wide-gap window, similar to previously suggested designs [11, 12]. The SC structures were fabricated in two variants (Fig. 3): with an array (ten sheets) of vertically coupled InGaAs QDs (henceforth QD-SC) and without QDs (henceforth ref-SC) in the *i*-type GaAs region, with the total thickness of this region being the same (130 nm) in both cases. Figure 4 shows the spectral dependences of the external quantum yield of the PVCs under study. The QD-SC has a broader spectral sensitivity range, compared with ref-SC, which extends to as far as 1100 nm. It should be noted that a similar effect has already been observed upon introduction of In(Ga)As QDs into AlGaAs/GaAs PVCs by several teams of researchers [8, 13, 14]. However, a clearly pronounced correlation between the density of states in the QDs and the long-wavelength part of the photosensitivity spectrum of QD-SCs was demonstrated for the first time in this study. Because excited states are degenerate to a greater extent than the ground state of a QD and the wetting layer is actually a quantum well, the efficiency of conversion (absorption) of light increases with the energy of incident photons. Also noteworthy is the good agreement between the sensitivity spectra of both PVCs in the visible range, which not only points to a dislocation-free growth of the array of vertically coupled QDs, but also shows that the high structural quality of the *p–n* junction is preserved [13].

Figure 5 shows load *I–V* characteristics of the PVCs under study for the ground level solar spectrum

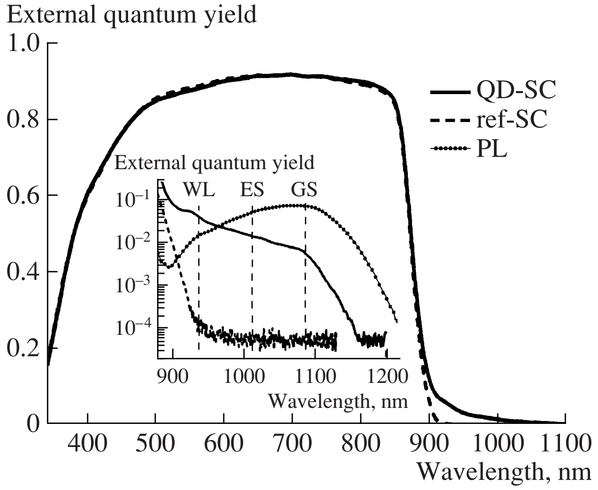
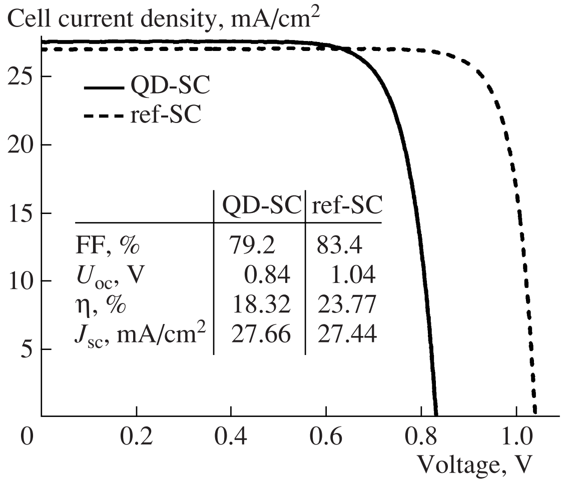


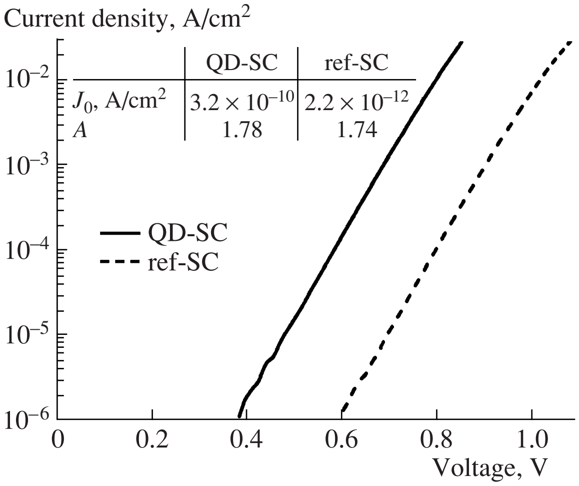
Fig. 4. Spectral dependences of the external quantum yield of AlGaAs/GaAs single-junction solar cells with a QD array (QD-SC) and without QD array in the *i*-type region (ref-SC). Inset: long-wavelength part of the spectrum of the external quantum yield, plotted on the semilog scale, and a PL spectrum (PL, arb. units) at the maximum excitation density. Designations: GS, ground state of a QD; ES, excited state of a QD; and WL, wetting layer of a QD.

AM1.5G. It is noteworthy that there is no degradation of the short circuit current density (J_{sc}) in the QD-SCs under study, which is due to the negligible number of nonradiative recombination centers, whose formation is, in principle, possible in growth of strained QD arrays, as in the case reported in [13, 14]. Moreover, a ~1% gain in the current density J_{sc} is observed for the first time in QD-SCs owing to the absorption of the long-wavelength part of the solar spectrum in the QD medium and to the effective separation of photogenerated carriers because of the formation of minibands in the array of vertically coupled QDs [15]. At the same time, introduction of the QD medium into the photocell leads to a substantial decrease in the open circuit voltage (U_{oc}), which, combined with the somewhat smaller fill factor of the light *I–V* characteristic (FF), limits the maximum efficiency of the QD-SCs to a value of 18.3%. The observed negative effect in QD-SCs is due to the introduction of the narrow-gap material (QD array) into the *i*-type region, with the current transport by the recombination mechanism (diode coefficient, or ideality factor, $A \approx 2$) at a higher (by a factor of 100) reverse saturation current density J_0, compared with the ref-SCs (Fig. 6), which is due to radiative recombination in the narrow-gap material. Detailed studies of dark *I–V* characteristics of the *p–n* junction and of the effect of the ratio of the solar light concentration for both types of PVCs are underway. We believe that this problem can be solved by engineering of the electronic structure of QDs in order to control the type of carrier distribution in QD arrays [16].



	QD-SC	ref-SC
FF, %	79.2	83.4
U_{oc}, V	0.84	1.04
η, %	18.32	23.77
J_{sc}, mA/cm^2	27.66	27.44

Fig. 5. Load *I–V* characteristics of PVCs (area 3.2 × 8.3 mm^2, 8% shading) with a QD array (QD-SC) and without a QD array in the *i*-type region (ref-SC) for the ground-level solar radiation spectrum AM1.5G and solar light concentration ratio $K = 1$. Inset: main working parameters of the PVCs: FF, fill factor; U_{oc}, open-circuit voltage; η, efficiency; and J_{sc}, short-circuit current density.



	QD-SC	ref-SC
J_0, A/cm^2	3.2×10^{-10}	2.2×10^{-12}
A	1.78	1.74

Fig. 6. "Dark" *I–V* characteristics of PVCs with a QD array (QD-SC) and without a QD array in the *i*-region (ref-SC), plotted on a semilog scale. Inset: results of approximation of the curves: A, ideality factor; and J_0, reverse saturation current density.

4. CONCLUSIONS

Thus, specific features of the formation of high-density arrays of quantum dots were analyzed in this study within two promising approaches: vertical stacking of QD sheets and QD growth in the Stranski–Krastanow mode. The method of molecular-beam epitaxy was used to fabricate single junction AlGaAs/GaAs photovoltaic cells with an array of InGaAs QDs in the *i*-region. The dislocation-free growth mode of ten sheets of vertically coupled QDs made it possible to preserve the high structural quality of the *p–n* junction in the QD-SCs under study. A correlation between the density of states in the QDs and the long-wavelength part of the photosensitivity spectrum of QD-SCs was demonstrated for the first time. Owing to the additional absorption of the long-wavelength part of the solar spectrum in the QD-medium and to the effective separation of photogenerated carriers (because of the miniband formation), a ~1% gain in the short-circuit current density J_{sc} was demonstrated for the first time in the world. However, the introduction of a narrow-gap material (QD array) into the *i*-region of the QD-SCs led to a substantial decline in the open-circuit voltage U_{oc} = 0.84 V, which, combined with the decrease in the filling factor of *I–V* characteristics, limited the maximum efficiency to a value of 18.3%.

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