Advances in Science and Technology Vol. 74 (2010) pp 231-236
© (2010) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AST.74.231

AlGaAs/GaAs photovoltaic cells with InGaAs quantum dots

V.M.Lantratov[1,a], S.A.Mintairov[1,b] S.A.Blokhin[1,2], N.A.Kalyuzhnyy[1],
N.N.Ledentsov[1], M.V.Maximov[1,2], A.M.Nadtochiy[1,2], A.S.Pauysov[2],
A.V.Sakharov[1], M.Z.Shvarts[1]

[1] Ioffe Physical Technical Institute of RAS, Russian Academy of Sciences, 26 Polytekhnicheskaya, St.Petersburg, 194021, Russia
[2]St.Petersburg Academic University Nanotechnology Research and Education, Russian Academy of Sciences, Khlopina 8-3, St. Petersburg, 195220, Russia

[a]lantr@scell.ioffe.ru, [b]mintairov@scell.ioffe.ru

Keywords: solar cells, quantum dots, Bragg reflector.

Abstract. We studied the different carrier kinetic mechanisms involved into the interband absorption of quantum dots (QDs) by photocurrent spectroscopy. It was shown that in vertically coupled InGaAs QDs an effective carrier emission, collection and separation take place due to minizone formation. The possibility for the incorporation of vertically-coupled QDs into solar cells (SC) without any deterioration of structural quality of the *p-i-n*-junction has been shown. Due to the additional absorption of solar spectrum in QD media and the subsequent effective separation of photogenerated carriers, an increase (~1%) in short-circuit current density (J_{sc}) for the QD SC-devices has been demonstrated. However the insertion of QDs into intrinsic region reduced the open circuit voltage (V_{oc}) of such devices. Moving the QD array in the base layer as well as including the Bragg reflector (BR) centered on 920 nm resulted in increase of the V_{oc}. Moreover an improved absorption in the QD media for SC with BR led to further increase of J_{sc} (~1%). The efficiency for QD SCs at the level of 25% (30 suns AM1.5D) has been demonstrated.

Introduction

Photovoltaic (PV) devices, so called solar cells, are promising alternatives to traditional fuel resources. However, the low power conversion efficiency caused by the non-zero contribution of different loss mechanisms prevents widespread application of solar cell technology [1]. The common approach to improve the efficiency of PV devices is based on stacking layers with different band gap together in multiple heterojunction cells [2]. However, the need in the lattice matching and tunnel junctions significantly limit the maximum achievable conversion efficiency (up-to-date 41%) [3]. Recently, self-assembled quantum dots were proposed for using in solar cells, providing an approach complementary to the multi-junction solar cells [4-6].

In this paper we report on detailed study of physical processes of energy conversion in In(Ga)As QD media and the critical issues related to optimization of QD structures for effective photovoltaic conversion.

Experimental Procedure

The use of QDs provides much more freedom in absorption band and strain engineering as compared to the case of bulk material. The spectral characteristics of In(Ga)As QDs and the carrier localization in QD arrays can be precisely controlled by changing the QD size and shape. Quite low absorption level in QDs can be overcome by vertical staking technique. However, the real QD density (especially for case of vertical coupling technique) is limited by the critical QD size at which the misfit dislocation nucleates. Our additional investigations showed that the average In composition of the QDs should be decreased to achieve reasonable optical quality of high-dense vertically coupled In(Ga)As QDs without use of any strain reduce technology. Thus, we focused on

InGaAs QDs grown in submonolayer deposition mode. Two *p*-*i*-*n*-PV structures based on InGaAs QDs with the ten stacked QD sheets with the GaAs spacer thickness of 30 nm (sample A) and 10 nm (sample B) has been grown. To estimate the future perspectives of the QD media in photovoltaic, single-junction AlGaAs/GaAs solar cells with back surface field (BSF) *n*-AlGaAs layer and thin wide band gap *p*-AlGaAs window were used (see Fig. 1). The QD media consisted of ten vertically coupled sheets of InGaAs QDs with 10 nm-thick GaAs spacer. The SC structures have been grown in four configurations: with the QD media in the middle of the *i*-GaAs region (i-QD-SC); with the same structure but using the BR centered on 920 nm instead of BSF AlGaAs layer (BR-QD-SC); with the QD media between *i*-GaAs region and *n*-GaAs base (base-QD-SC) and in a conventional design (without QDs) keeping the *i*-region width of 130 nm (conv.-SC). The details of SC design and fabrication have been described elsewhere [7]. All SC devices were made with face contact grid shadowing of 6%.

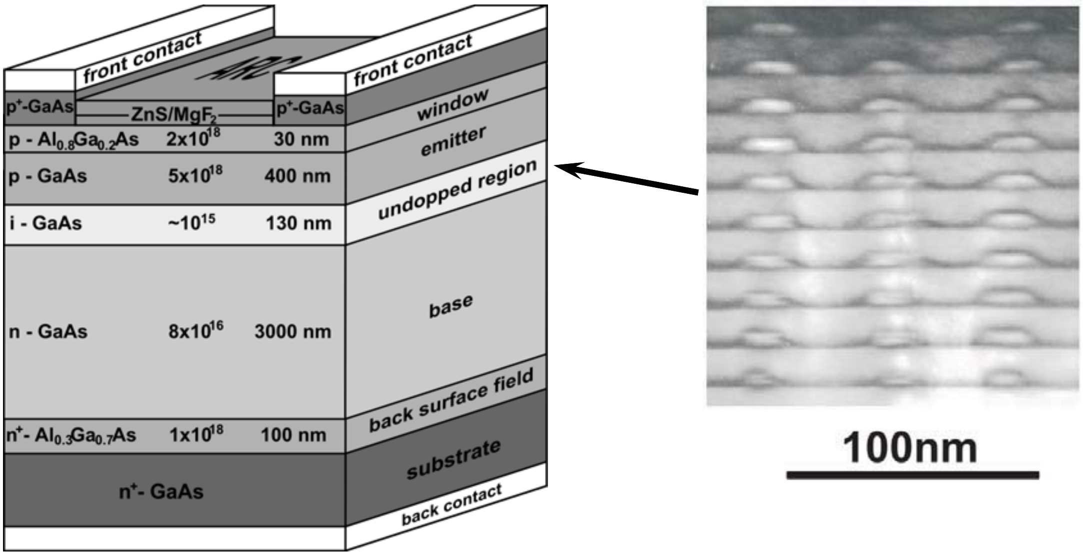

Figure 1: The design of the AlGaAs/GaAs single-junction solar cells with QD arrays (on the left) and TEM image of the ten vertically coupled QD sheets (on the right).

Results and Discussion

QDs approach. Fig.2 depicts the results of photocurrent spectroscopy over a wide temperature range for two *p*-*i*-*n*-PV samples based on the ten stacked InGaAs QD sheets with different GaAs spacer thickness. The spectra represent clearly peaks corresponded to ground state (GS), excited state (ES), wetting layer (WL) and GaAs matrix of vertically stacked QDs. For uncoupled QDs (sample A) the decrease in temperature leads not only to the shift of absorption, but also to sequential disappearing of contribution from GS, ES and even from WL (see Fig.2.a). While in case of vertically coupled QDs, the high level of light absorption and carrier emission were surprisingly observed even at helium temperatures, as shown in Fig.2.b. Moreover the contribution to total current for sample B was slightly higher then that for sample A even at room temperature.

Such behavior could be explained by the following phenomenological model of the *p*-*i*-*n*-structure with one QD sheet (fig.3.a). Electron-hole pairs generated due to interband absorption with a rate g can escape from a QD in the matrix during τ_{esc} or disappear due to radiative or non-radiative recombination during τ_{rec}. Since only the process of carriers' emission from QDs give a contribution in the photocurrent the competition between these processes determines total photocurrent of QD array [8]:

$$I_{PC} \sim \frac{g}{\left(1+\tau_{rec}/\tau_{esc}\right)}. \tag{1}$$

There are two basic mechanism of carriers' emission form QDs: thermal activation and tunneling through the potential barrier [9]. In the first case carriers get additional activation energy ΔE necessary to overcome the potential barrier from the lattice thermal oscillations and emission rate is described by the following equation [10]:

$$\tau_a^{-1} \sim \exp\left(-\Delta E / k_B T\right), \tag{2}$$

where T – temperature, k_B – Boltzmann constant. It is clear that increasing temperature results in increase of carriers' emission rate. At the low temperature probability of the thermal activation for the carriers localized in QDs is very low and tunneling through the potential barrier becomes the only possible mechanism of the emission. In this case the emission rate depends only on the height of the barrier (E_B), electric field (F) and effective mass (m^*) of the carriers [11]:

$$\tau_{tun}^{-1} \sim \exp\left(-\sqrt{m^* \cdot E_B^3} / F\right) / m^* . \tag{3}$$

Appling a bias voltage leads to a change of zones bending at the interfaces of the *p*- and *n*- layers with the active area and change of the barrier transparency. Thus thermal activation of the photogenerated carriers is the dominating mechanism of the carriers' emission for the sample A.

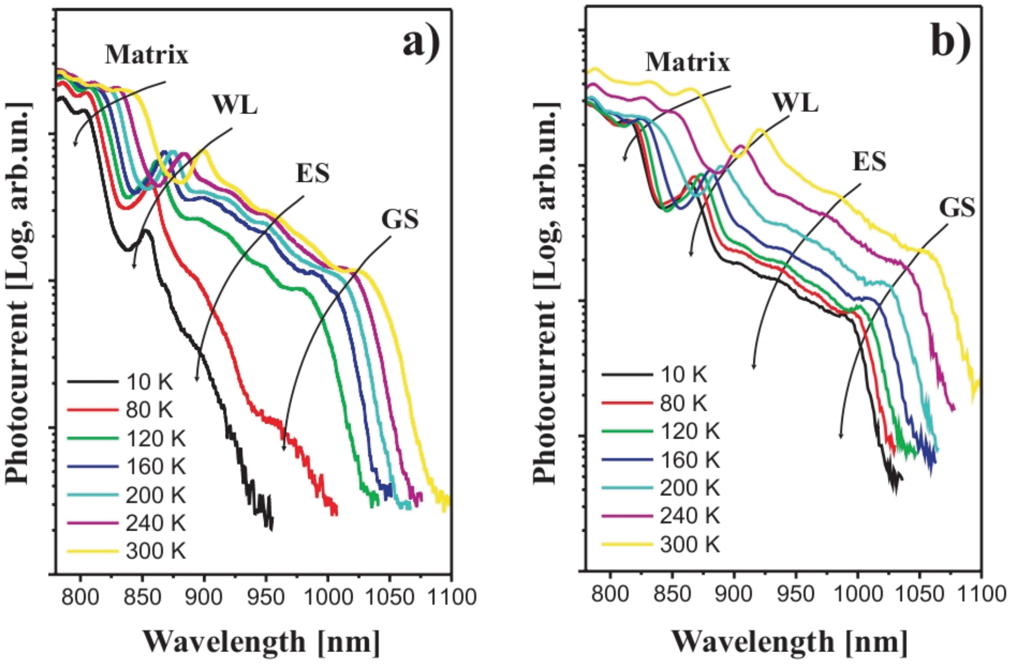

Figure 2: Temperature evolution of photocurrent spectra for *p-i-n*-PV-structures based on stacked InGaAs QDs with the spacer thickness of 30 nm (a, sample A) and 10 nm (b, sample B).

For explaining the observed behavior of the sample B it is necessary to consider the effect of QD vertical coupling. In case of vertical stacking of QDs the deformation fields of the bottom QD sheet penetrate in the GaAs spacer and make essential impact on the formation of upper QD sheet when the thickness of the spacer is lower than 20 nm. Finally this leads to the vertical arrangement (coupling) of the QD sheets in columns. In according with theoretical calculations of Ref. [12], decreasing the spacer thickness down to the size of QDs (less than 5 nm) results in the hybridizations of electron levels, which leads to a minizone formation (so called electron coupling) providing an effective resonance tunneling of the carriers from the QD array to the emitter and base. Hence when the thickness of the spacer is about 10 nm one can assume that within the bounds of one column of the vertically coupled QDs a non-resonance tunneling from one QD to another is possible (fig.3.b). If the rate of this process is higher then that for carrier's recombination in QDs the photogenerated carriers can be spatially separated within the column of vertically coupled QDs. In this case photocurrent doesn't depend on temperature and bias voltage.

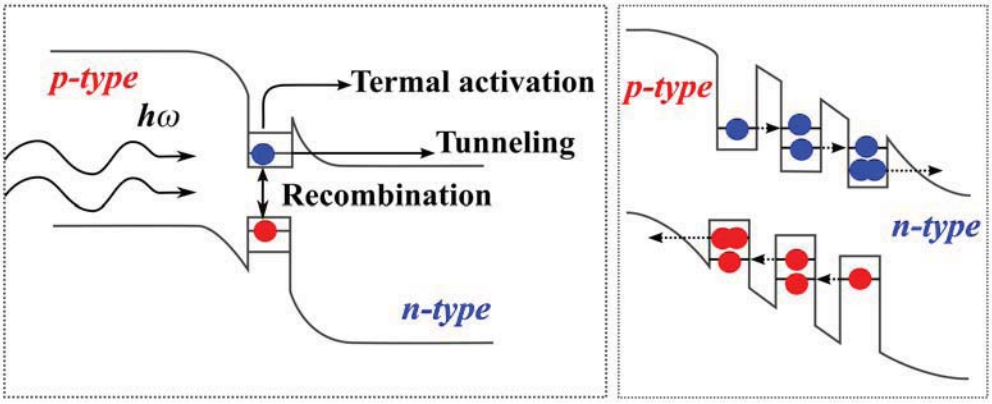

Figure 3: The model of the photogenerated carriers' separation in the *p-i-n*-PV structures with one QD sheet (on the left) and vertically coupled QD array (on the left).

SC results. Fig.4 shows spectral dependencies of the external quantum efficiencies for investigated solar cells. All QD-SC devices demonstrate a wider absorbing spectral range up to 1100 nm as compared to that for conv.-SC device. The matching of photosensitivity spectra for i-QD-SC, BR-QD-SC and reference SC in the visible and IR spectral range (340-800 nm) is an evidence of dislocation-free growth of vertically coupled QDs as well as of high structural quality of the *p-n* junctions.

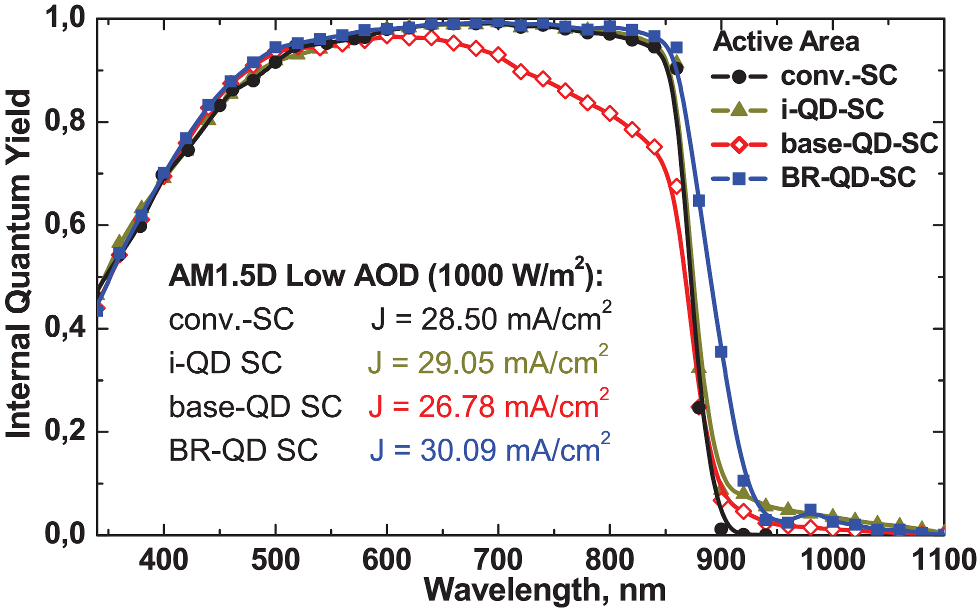

Figure 4: External quantum efficiency for conv.-SC, i-QD-SC, Base-QD-SC and BR-QD-SC.

The i-QD-SC demonstrated ~1% increase in J_{sc} in comparison with conv.-SC owing to QD absorption in the long-wavelength range of solar spectrum under effective separation of photogenerated charge carriers. However, the insertion of QD-media results in noticeable reduction of V_{oc} (see. Fig. 5) which limits the maximum achievable efficiency (η) at the level of ~21.6% (30 suns, AM1.5D) for developed i-QD-SC cells in comparison with conv.-SC (η=25.8, 10 suns, AM1.5D).

To understand the origins of this effect, the dark current measurements were carried out. In conv.-SC devices, the mixed current flow mechanism takes place with the domination of recombination process (diode factor, A~1.81) under low exposure level and with the domination of diffusion processes (A~1.56) under concentrated solar exposure. The insertion of QD array into the *i*-region of SC-device results in domination of recombination mechanism (A~1.86 and A~1.76 under low and high exposure level, correspondingly) with sufficiently higher reverse saturation current density (100-fold) as compared to that for conv.-SC devices. Thus, the drop of open-circuit voltage and efficiency in QD-SC is associated with the radiative recombination in narrow-band gap material of InGaAs QDs.

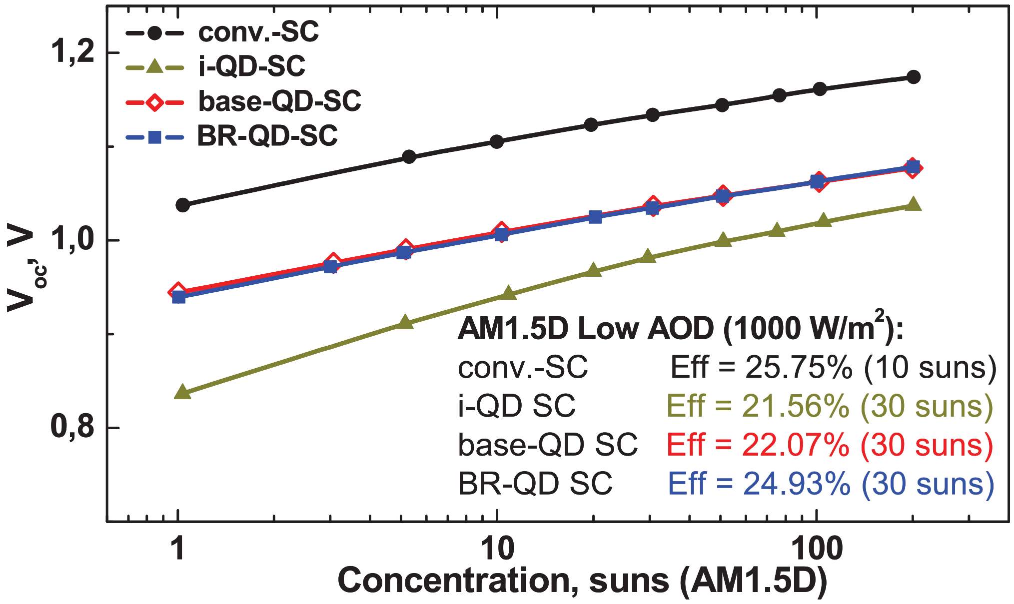

Figure 5: The dependencies of open circuit voltage on concentration of incident solar spectrum for i-QD-SC, i-QD-SC, Base-QD-SC and BR-QD-SC.

Moving the QD array from the *i*-region of a *p-n* junction decreases the reverse saturation current density and increases the V_{oc} (Fig.5), thus an occupation of the QDs by photogenerated carriers occurs at higher voltage. However the Base-QD-SC (Fig. 4) demonstrates drop in long-wavelength sensitivity caused by worse carriers' collection from the base region which can be explain by capturing the photogenerated holes from the base layer in the QDs and their further recombination. Lower electrical field in the QD region also results in less photosensitivity in the range of 900-1100 nm for the Base-QD-SC. In spite of worse carriers collection the Base-QD-SC demonstrates an efficiency of 22.1% (30 suns, AM1.5D) which exceeded the efficiency of i-QD-SC.

Using the BR also results in an increase of the V_{oc} most probably due to more effective collection of the carriers from the base layer. Moreover insertion of the BR results in significant increase of the photosensitivity within the range of 900-950 nm and thus in photocurrent rising up to 30.1 mA/cm^2 (AM1.5 low AOD). Together with the highest value of photocurrent this allowed to active efficiency at the level of ~25% (30 suns, AM1.5D).

For further increasing efficiency the optimum position of the QD array in a *p-n* junction has to be found providing a compromise between increasing the V_{oc} and decreasing the J_{sc}. It is also possible to improve the absorption of long-wavelength photons by using a BR centered at ~1000 nm instead of developed one.

Conclusion

The photovoltaic devices with self-assembled In(Ga)As QDs have been fabricated and studied. It was observed that the vertically coupled InGaAs QDs are the most promising medium for solar cells as compared to other types of self-organized QDs. For the first time QD-based solar cells demonstrated ~2% increase in short circuit current due to QD absorption in the long-wavelength optical region of solar spectrum and effective separation of photogenerated carriers through minizones. The radiative recombination in narrow-band gap material of InGaAs QDs is responsible for the drop of open-circuit voltage and efficiency in QD-SC cells. It was shown that shifting the QDs to the base layer results in an increase of the V_{oc} and the potential of efficiency improvement for QD-SCs was considered. Using the BR centered on 920 nm allowed to increase V_{oc} simultaneously with an increase of J_{sc}, which resulted in achieving the efficiency of about 25% (AM1.5D) for QD-SC devices.

Acknowledgments

The work was supported by Purpose-oriented program of Russian Federal Agency of education "Scientific and educational personal of innovation Russia" And the Russian Foundation on Basic Research (grants № 09-08-00954-a).

References

[1] V.M.Andreev, V.A.Grilikhes, V.D.Rumyantsev, Photovoltaic Conversion of Concentrated Sunlight (John Willey & Sons Ltd., 1997)
[2] C.H.Henry, J. Appl. Phys., 51, 4494 (1980)
[3] Dimroth F et. al. Appl. Phys. Lett. **94** 223504 (2009).
[4] V.Aroutiounian et al., J. Appl. Phys., 89, 2268 (2001)
[5] A.Luque et al., J. Appl. Phys., 99, 094503 (2006)
[6] S.M.Hubbard et al., Appl. Phys. Lett. 92, 123512 (2008)
[7] S.A.Blokhin et al., Fizika i Tekhnika Poluprovodnikov, 43, 537 (2009)
[8] S.C. McFarlane, J. Barnes, K.W.J. Barham, E.S.M. Tsui, C. Button, J.S. Roberts. J. Appl. Phys., 86, 5109 (1999).
[9] P.W. Fry, I.E. Itskevich, S.R. Parnell, J.J. Finley, L.R. Wilson, K.L. Schumacher, D.J. Mowbray, M.S. Skolnick, M. Al-Khafaji, A.G. Cullis, M. Hopkinson, J.C. Clark, G. Hill. Phys. Rev. B, 62, 16784 (2000).
[10] D.V. Lang. J. Appl. Phys., 45, 3023 (1974).
[11] G. Vincent, A. Chantre, D. Bois, J. Appl. Phys., 50, 5484 (1979).
[12] N.N. Ledentsov, V.A. Shchukin, M. Grundmann, N. Kirstaedtler, J. Bohrer, O. Schmidt, D. Bimberg, V.M. Ustinov, A.Yu. Egorov, A.E. Zhukov, P.S. Kop`ev, S.V. Zaitsev, N.Yu. Gordeev, Zh.I. Alferov. Phys. Rev. B, 54, 8743 (1996).