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The investigation of InGaAs quantum dot growth peculiarities for GaAs intermediate band solar cells

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Abstract. In this work the growth peculiarities of InGaAs quantum dots (QDs) on GaAs surface have been investigated by metal-organic vapor-phase epitaxy (MOVPE). The influence of the main structural parameters, such as the amount of deposited InGaAs material and the thickness of the GaAs cap layer, on the optical properties of QDs has been considered. For these parameters the optimal values at which achieved the best photoluminescence intensity of QDs embedded into the matrix of the GaAs-based light-emitting structure have been established. The possibility of using several layers of QDs with the preservation of the optical properties of the investigated structures has been demonstrated. The design of solar cell (SC) based on GaAs with QD arrays in the active area has been proposed. It was shown that 20 layers of QDs embedded into the proposed SC structure contribute to the photogenerated current up to 0.97 mA/cm² for AM0 spectra and up to 0.77 mA/cm² for AM1.5D spectra, while maintaining the high quality of the p-n junction.

1. Introduction
Solar cells (SC) based on A3B5 semiconductor heterostructures are the most effective solutions among renewable energy sources. However in this field of photovoltaics there are still a lot of unresolved issues, such as fundamental losses, which impedes approaching the efficiency to the theoretical limit [1]. Currently, one of the most successful approaches which allow reducing the fundamental losses are multi-junction (cascade) solar cells (MJSC) [1, 2], in particular based on the lattice-matched InGaP/GaAs/Ge material system.

Today there is an alternative approach to reduce the fundamental losses aimed, in particular, at incomplete absorption in SC structure based on a single p-n junction. In the past two decades theoretical models which describe SC with an intermediate band (IBSC) have been actively developing. In these models the spectral sensitivity (and thus the efficiency) increases due to multiphoton absorption processes in semiconductor structures based on a single p-n junction [3, 4]. IBSC is proposed as an approach that allows transforming an additional part of the solar radiation spectrum by capturing photons with energy below the band gap of the matrix, to generate current while maintaining a high output voltage. As a candidate to practical realization of such approach the quantum dot arrays (QDs) are proposing [5]. The bulk layers containing QDs embedded in the SC matrix creates additional energy levels for the absorption of low-energy photons (so-called subbandgap photons), thus extend the spectral sensitivity of the device and increasing the photogenerated current.
Currently, QDs widely used in active area of lasers and allow increasing the radiation wavelength, improving thermal stability and reducing the threshold current, compared with traditional devices. However, first successful results of the application QDs in photovoltaic began publishing only recently and demonstrate the expansion of spectral sensitivity of the SC via photoelectric effect in InAs/GaAs QD [6-8]. In these works a noticeable but small contribution of QDs to the internal quantum efficiency of single-junction SC has been obtained. Wherein, one of the main problems in the practical realization of the approach are the structural stresses caused by a large number of QD layers in a bulk SC material that lead to the quality degradation of the p-n junction and decrease in the quantum yield in the short-wave part of the spectrum.

In this paper we propose introducing a small amount of Ga (~ 20%) into the composition of InAs QDs in order to reduce the difference between the lattice parameters of the QDs and the GaAs SC matrix and, thus, reduce the stresses in the structure of the device. This will preserve the structural quality of the p-n junction in SC without introducing technologically complex layers that compensate the stresses in the structure. In the paper, technological features of In$_{0.8}$Ga$_{0.2}$As QD grown in the GaAs matrix are discussed in detail. SCs with QDs in active area which demonstrate the high quality of the p-n junction in the GaAs absorption region have been obtained.

2. Experimental procedure

All structures have been grown using the MOVPE technique by means of R&D installation with a horizontal reactor at low pressure (100mbar). Metal-organic compounds were used as sources of Group III elements (trimethylgallium (TMGa), trimethylaluminum (TMAI) and trimethylindium (TMIn)). Arsine (AsH$_3$) and phosphine (PH$_3$) were used as a source of the Group V elements (As and P). Experiments were carried out on (100) GaAs substrates misoriented to the (111) direction by 6º. InAs QDs with a density of up to 1∙10$^{10}$ cm$^{-2}$ were obtained for misoriented substrates [9].

In the study two series of light-emitting structures based on GaAs with InGaAs QD in the active area were grown to estimate their optical parameters by the photoluminescence (PL) method. In the first structure the active area included a single In$_{0.8}$Ga$_{0.2}$As QD layer placed in the center of a 500 nm GaAs waveguide surrounded by wide-gap Al$_{0.3}$Ga$_{0.7}$As barriers to prevent carrier leakage to the surface or substrate (Fig. 1a).

The growth was carried out according to the following technological process: after growing 250 nm Al$_{0.3}$Ga$_{0.7}$As and 250 nm GaAs at 700°C the reactor cooled down to the growth temperature of QDs (520°C). Then the In$_{0.8}$Ga$_{0.2}$As material was deposited for the nucleation and formation of QDs by Stranski-Krastanov mode [10]. After that the QDs were covered with a layer of GaAs at the same temperature in order to protect them from degradation during the subsequent reactor heating. Then the rest of the GaAs waveguide and wide-band Al$_{0.3}$Ga$_{0.7}$As were grown at 600 °C.

![Figure 1](image_url)
In the second type of experimental structures (Fig. 1b) the absorption was increased due to 1, 5, 10 and 20 layers of QDs grown through the GaAs spacers with a thickness 35 nm. The spacers grew at elevated temperature 600°C which was also necessary for preparing a planar surface for each subsequent layer of QD [8]. These structures were designed to investigate the possibility of embedding several layers of QDs into the active region of GaAs SC.

In both types of structures the main technological parameter that varied depending on the experiment was the amount of In$_{0.3}$Ga$_{0.7}$As deposited material. The amount of InGaAs material was varied from 1 to 4 monolayers (ML). The thickness of GaAs cap layer was chosen based on the known lateral sizes of QDs [7, 8] and was 5 nm for all experimental structures. Nevertheless, an additional experiment was performed to evaluate the effect of this parameter on the PL spectrum in which the thickness of GaAs cap layer was 7 nm with the amount of InGaAs material of 2 ML. The bulk of the light-emitting structure was grown at growth rates of 1.5 μm/h while the GaAs cap layers grew at a reduced growth rate 0.75 μm/h since in [7] the authors showed a positive effect of decrease the GaAs cap layer growth rate on the optical properties of the obtained QDs. The deposition of InGaAs in all structures occurred at the constant growth rate 0.167 ML/s and temperature of 520°C. To obtain the PL spectra a 532nm YAG:Nd laser of 350mW power was used. All measurements were carried out by means of a cooled Ge photodetector using a standard lock-in amplifier. The multifunctional installation has been used for measuring the external quantum efficiency (EQE) of the SCs. The measuring hardware included an unblocked ultra-violet halogen light source, a grating monochromator with 2 nm/mm dispersion within 300–1200 nm wavelength scanning range, and an optical chopper of 90 Hz and high sensitivity lock-in electronics. The EQE measurement was controlled by a laptop. The lock-in technique allows weak output signals at the QD sensitivity range to be detected confidently.

3. Results and discussion

3.1. A growth peculiarities of InGaAs QDs on GaAs surface

Optical properties of single-layer structures (Fig. 1 a) were studied by PL method to determine optimal growth parameters for QDs. This method allows estimating the physical parameters of QDs in terms of position, intensity and number of PL peaks. In this case, the criterion for optimality of growth parameters was the highest PL intensity of QDs. Fig. 2 shows PL spectra at the different amount of InGaAs material. The PL intensity in the absorption region of QDs (950-1300 nm) was estimated and it was shown that with the deposition 2 ML InGaAs and 5 nm GaAs cap layer QDs with the highest PL intensity are formed compared with samples grown with a larger amount of InGaAs material. It can be seen that the deposition of 1 ML InGaAs is not enough to start the formation of coherent islands since the obtained spectrum has a shape close to the quantum well one with two apparent peaks: 870 nm from the GaAs matrix and 900 nm from the wetting layer of the QD. The resulting optimum thickness of 2 ML exceeds the critical thickness for the formation of InAs QDs on the GaAs surface, which is 1.7 ML like it has been shown in [8]. In fact, In$_{0.3}$Ga$_{0.7}$As has a smaller difference in the parameters of the crystal lattices with GaAs so when the QD growth in the Stranski-Krastanov mode the more material is required to begin the formation of the islands.

The spectra obtained have the same shape and consist of two apparent peaks that are red-shifting after deposition of more than 3 ML of InGaAs. This indicates the formation of QDs of two different types with differing lateral sizes. In Fig. 2 they are highlighted as QD1 and QD2 for small and large QDs respectively. With increasing the quantity of MLs QD sizes also increase proportionally which leads to the red-shift of the PL peaks (in Fig. 2 it is shown by arrows). The PL intensity significantly drops with increasing the quantity of MLs which is the result of an increase the population of defective QDs that were formed after reaching the critical thickness of InGaAs due to coalescence processes (after QDs formation the migration of In atoms along the uncapped surface proceeds towards energetically favorable QDs with large lateral sizes). Also, QDs of high altitude after capping with 5nm of GaAs layer became not completely covered and dissolve during further growth.
Figure 2. The PL spectra at room temperature of single QD layers at the different amount of In$_{0.8}$Ga$_{0.2}$As material with 5 nm GaAs cap layer at laser pump of 30W/cm$^2$ (a) and 1kW/cm$^2$ (b).

In Fig. 2 the red dotted line shows the PL spectrum for QDs covered with 7 nm of GaAs cap layer. It can be seen that it is red-shifted compared with QDs which are covered with 5-nm GaAs cap. PL from QD1 is suppressed in this case which is apparently due to the poor quality of thicker low-temperature GaAs cap. Wherein, the appearance of an apparent long-wave shoulder indicates an increase the contribution of large QDs which before were partially dissolved after thin capping. Based on the single-layer structure a series of experiments with 5 layers of QDs was carried out in order to increase the absorption in the further SC structure. A wide range quantity of MLs from 1.75 to 3 ML was investigated. Figure 3 shows how the shape of the PL spectrum changes with increasing the amount of InGaAs material at 5 nm GaAs cap layer.

Figure 3. PL spectra at room temperature for 5 layers of QDs depending on the amount of In$_{0.8}$Ga$_{0.2}$As material with 5 nm GaAs cap layer at laser pump of 30W/cm$^2$ (a) and 1kW/cm$^2$ (b).

After growing several layers of QDs the evolution of the spectra still unchanged which is indicated by the position of the PL peaks and by the half-width of the spectral lines. With increasing the number of QD layers a red-shift of the entire spectrum is also observed, accompanied by a decreasing of the PL intensity comparable with single-layer QD-structures. This shows that the optimum amount of InGaAs material still the same after transition from single-layer technology to the technology of QDs arrays and for the solid solution In$_{0.8}$Ga$_{0.2}$As this value is 2 ML. Wherein, the optimum thickness for GaAs cap layer is 5 nm for QD arrays. These growth parameters were used for embedding QD arrays into the active area of GaAs SC.
3.2. Embedding InGaAs QDs in active area of GaAs SC

The heterostructure of the GaAs SC (Fig. 4 a) was grown with an increased i-region for embedding the QD arrays. This structure was used as a reference in the study of the spectral characteristics of SC with QD. The arrays containing 1, 5, 10 and 20 In_{0.8}Ga_{0.2}As QD layers were embedded into four SC heterostructures in the middle of the i-region (Fig. 4 b).

![Figure 4](image)

Figure 4. Experimental structures of reference GaAs SC(a) and SC with QDs in active area (b).

The total thicknesses of the base, emitter and i-region layers for all SC structure were the same to ensure comparable charge carrier collection. Experimental SC samples were created by forming the front and rear solid Ni contacts and etching out the contact layer of p+-GaAs from the surface free from the front contact (without using antireflection coating).

![Figure 5](image)

Figure 5. Spectral characteristics of the internal quantum yield of GaAs SC with embedded InGaAs QD arrays in comparison with the reference GaAs SC without QD: a - the whole absorption spectrum, b - the absorption range of QD.

Figure 5 a shows the spectral characteristics of the internal quantum yield of the obtained SC in comparison with the reference GaAs SC without QD arrays. In the long-wave part of the spectrum (880-1100 nm) beyond the GaAs absorption limit the extended spectral sensitivity was observed caused by photocurrent generated in the QD by absorbing subbandgap photons. The greatest contribution to the spectral sensitivity have been demonstrated by wetting layer at wavelength of ~ 940 nm (marked as WL) and an excited state of QDs with small lateral sizes at wavelength of 980 nm (marked as ES).

For QD array of 20 layers the values of 0.97 mA/cm² for AM0 and 0.77 mA/cm² photogenerated current are achieved. This corresponds to 0.05 mA/cm² and 0.04 mA/cm² after recalculated per 1 QD layer. Such increase in the photogenerated current does not definitely insure an increase of SC efficiency, however the technology of QD arrays can be used for current balance in MJSC. It is important to note that as a result of the embedding QD arrays (up to 10 layers) the quality of the p-n
junction is still comparable with the reference GaAs SC as evidenced by the absence of a critical drop in the spectral sensitivity in the GaAs absorption range. A small drop in the short-wavelength spectral sensitivity is observed for a SC with 20 layers of QDs.

4. Conclusions

Thus, in this work an experimental analysis of InGaAs QD arrays formation in a GaAs matrix by the MOVPE method in the Stranski-Krastanov mode was carried out. In the framework of single QD layer technology the optimal growth parameters at which the high PL intensity of test light-emitting structures was observed have been found. With the deposition 2 ML of In$_{0.8}$Ga$_{0.2}$As covered with 5 nm thick GaAs cap layer QDs with maximum PL intensity were formed. As in the case of the InAs/GaAs system the bimodal distribution of QDs by size after In$_{0.8}$Ga$_{0.2}$As deposition on the GaAs surface by the MOVPE method was observed. The position of the peaks and the bimodal nature of the PL spectra still the same for QD arrays.

The developed technology was used for embedding QD arrays in the active area of GaAs SC. The maximum calculated contribution of QDs in the range from 880 to 1100 nm for a sample with 20 layers was 0.97 mA/cm$^2$ for space spectrum (AM0), and 0.77 mA/cm$^2$ for terrestrial spectrum (AM1.5D). Wherein, critical drop in the spectral sensitivity was not observed in the absorption region of GaAs which indicates the quality of the p-n junction comparable to the reference GaAs SC.

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