The effect of post-growth interruption on the formation of InGaAs/GaAs quantum dots obtained by MOVPE

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Abstract. In this work, the study of formation regimes of In₀.₈Ga₀.₂As quantum dots on GaAs surface by metallorganic vapour-phase epitaxy has been carried out. The influence of post-growth interruption after the quantum dots deposition on the optical and physical properties of the formed objects has been investigated. It has been established that the interruption time of 2-5 seconds is optimal for the In₀.₈Ga₀.₂As/GaAs material system and growth conditions. For the chosen interruption time, the quality of formed quantum dots and their physical sizes were estimated using transmission electron microscopy: lateral size is 10–20 nm, height is not exceeding 5 nm and concentration is ~9.8∙10¹⁰ cm⁻².

1. Introduction
Quantum-sized heterostructures, such as quantum wells (QWs) and quantum dots (QDs), are now widely used in semiconductor optoelectronics. Laser diodes with a QW and QD-based active area allow achieving an emission wavelength in excess of 1300 nm, which gives a significant advantage over traditional devices [1]. The field of semiconductor solar cells (SCs) with an intermediate band (intermediate band solar cells - IBSC) based on QDs is now being actively developed. The main task of such devices is reducing fundamental losses by increasing the spectral sensitivity and efficiency of the device through multiphoton absorption processes [2, 3].

Today, InAs/GaAs is the most demanded material system for forming QDs in III-V based devices. The epitaxial growth of such QDs in the Stransky-Krastanov mode has been widely studied in the framework of molecular beam epitaxy technique. However, in the case of QDs for SCs, it is necessary to develop metallorganic vapour-phase epitaxy (MOVPE) technology for their growth, since MOVPE is only technique for photovoltaic device production. At present, a number of issues related to the formation of InₓGa₁₋ₓAs/GaAs QDs by MOVPE have been discussing in the literature. In particular, the critical material thickness for forming QDs with high photoluminescence intensity (PL) was determined for both InAs [4, 5] and InₓGa₁₋ₓAs with different “x” values [6–8]. It was shown that during the QD self-assembled growth the critical thickness is influenced by the vapor pressure of the V group elements [9]. The effect of GaAs cap layer thickness on optical properties of QDs, which is necessary to protect the islands from dissolving during the temperature ramping steps in MOVPE reactors [10], was investigated. Also, conditions were found, at which InGaAs QDs are formed with a bimodal size distribution [11, 12]. Also, the important parameters affecting the optical properties of QDs are their size distribution uniformity, the quality, which is determined by the number of defective islands formed during self-assembled growth, and the probability of formation a large clusters, which is a result of coalescence of closely spaced QDs. The authors [13] showed that for the formation of defect-free coherent InGaAs islands, it is necessary to include in the epitaxial process an interruption step after QD deposition and their following thermal annealing. The post growth interruption step is
necessary to allow the atoms diffusing freely along the growth surface and participating in QD self-assembled growth. The interruption step parameters dramatically affect the surface morphology with InGaAs QDs and, mainly, their size. In [14] it was concluded that a corresponding time of the post-growth interruption step should be determined for each material system and specific growth conditions.

Previously [7], we already showed the advantage of using In$_{0.8}$Ga$_{0.2}$As QD arrays to create GaAs SC in comparison with InAs QDs. Key parameters, such as the optimal In$_{0.8}$Ga$_{0.2}$As thickness and the structural parameters of the GaAs cap layer were found. The aim of this work is to determine the optimal time of post-growth interruption for forming defect-free In$_{0.8}$Ga$_{0.2}$As/GaAs QDs with high PL intensity.

2. Experimental procedure

All structures were grown using the MOVPE technique by means of R&D installation with a horizontal reactor at low pressure (100 mbar). A series of heterostructures optimized for photoluminescence (PL) measurements were grown (figure 1). The active area of the test structures included a single In$_{0.8}$Ga$_{0.2}$As QD layer placed in the center of a 500 nm GaAs waveguide was surrounded by wide-gap Al$_{0.3}$Ga$_{0.7}$As barriers to prevent carrier leakage to the surface or substrate. 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 was 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 the Stranski-Krastanov mode. The In$_{0.8}$Ga$_{0.2}$As material amount for the QDs formation was chosen according to the previous study, which was devoted to determination of the maximum PL intensity of In$_{0.8}$Ga$_{0.2}$As/GaAs heterostructures and was 2 ML (~6 Å) [7].

![Figure 1. In$_{0.8}$Ga$_{0.2}$As/GaAs QDs experimental structure for PL.](image)

Then the epitaxial growth was stopped for a post-growth interruption step. At this step, after depositing an In$_{0.8}$Ga$_{0.2}$As layer (needed for the QD nucleation), the structure was kept during several seconds at stabilized temperature equal to the QD growth temperature. The test structures in the series differed by the time of the post-growth interruption step. In the study, five structures were grown, in which the interruption times were 0, 2, 5, 15 and 30 seconds. After that the QDs were covered with a GaAs cap layer at the same temperature in order to protect them from degradation during the subsequent reactor heating. The rest of the GaAs waveguide and wide-band Al$_{0.3}$Ga$_{0.7}$As layer were grown at 600 °C.

The structures were studied by the PL method, which is a fast and convenient tool for characterizing the optical properties of QDs, and also can be used to estimate roughly their physical parameters. To obtain the PL spectra, a 532 nm YAG:Nd laser of 350 mW power was used. All measurements were carried out by means of a cooled Ge photodetector using a standard lock-in amplifier. A multifunctional installation was 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 cross-section and plan view of the investigated QD layers was examined by transmission electron microscopy (TEM). The samples were prepared for the TEM study using the conventional procedure of preliminary mechanical thinning followed by final ion beam milling (3.5 keV Ar+ ions). The TEM study was carried out with a JEOL JEM 2100F microscope at 200 kV accelerating voltage.

3. Results and discussion

For each structure, PL spectra were recorded under various conditions. The measurements were carried out at room temperature, liquid nitrogen temperature and at various laser pumping levels of 30 W/cm² and 1 kW/cm² (figure 2).

![PL spectra](image)

**Figure 2.** PL spectra of the experimental structures: a, b – at laser pumping of 30 W/cm² for temperatures of 300 and 77 K, respectively; c, d – at laser pumping of 1 kW/cm² for temperatures of 300 and 77 K, respectively.

The sample for which the interruption step was excluded has demonstrated the lowest total PL intensity at room temperature. The wide PL spectrum of this sample indicates a large size distribution of QDs due to insufficient time for atoms to migrate over the surface. In the lack of post-growth interruption, the size of small islands is not increase by attaching adatoms migrating over the surface. Therefore, instead of large QDs, three-dimensional islands with misfit dislocations are formed [13]. Thus, the lack of post-growth interruption does not allow obtaining high-quality QDs with high PL intensity and size uniformity.

In the case of samples with the post-growth interruption step the following similar evolution of the PL spectra was observed for all measurement conditions. The long wavelength shift of the whole spectral dependence occurred with an increase of the interruption time. This is due to the high sensitivity of the QD size distribution to the post-growth interruption time that was already noted earlier.
InGaAs/GaAs QDs as well as for other material systems [8, 15]. During interruption step, QDs are formed by Stranski-Krastanov mode and having large lateral size act as energetically favorable places for the attachment of adatoms, which are diffused freely over the surface. This leads to QD size redistribution, and the contribution of small QDs to the PL intensity decreases due to the decrease of their concentration. As a result, the PL spectrum is a significant widening and the FWHM changes from 48 meV for a 2 seconds interruption to 116 and 126 meV for 5 and 30 seconds interruption, respectively (the data on figure 2 b at laser pumping of 30 W/cm² and temperature of 77 K). This effect is well illustrated in figure 2 c, in which four distinct PL peaks can be distinguished. A peak at 870 nm corresponds to a GaAs matrix; a peak at 940 nm is a wetting layer; a wide spectral peak at ~ 1060 nm is the small QD contribution; and a long-wavelength shoulder at ~ 1200 nm corresponds to the large QD contribution.

For the obtained spectra, the dependence of the PL integral quantum efficiency on the interruption time was calculated (figure 3), which is necessary for a general illustration of the QD layer quality. The samples with an interruption time of 15 and 30 seconds demonstrated an equally low intensity and almost identical shape of the PL spectra (figure 2 - the orange curve is presented for the sample with an interruption time of 30 seconds). Since the concentration of large islands in these samples has increased significantly, an increase of the intensity of the long-wavelength PL shoulder and its shift to a longer wavelength region is observed. At high excitation density, the multimodality of QD in size has a greater effect on the PL spectrum, since enough carriers are created to fill the energy levels of both large and small QDs (figure 2 c and d - orange curve). Such increase in the interruption time leads to an increase in the QD size, as well as to the probability of the formation of coalesced defective QDs (strained clusters), which create nonradiative recombination centers. This explains the overall drop in the PL intensity for the samples with an interruption time of 15 and 30 seconds.

![Figure 3. PL integral quantum efficiency versus the interruption time.](image)

The value of the optimal interruption time is in the range of 2-5 seconds (figure 3). Such interruption step is enough to QDs are finally formed self-assembled and the interruption makes a positive effect on QD size uniformity and their quality. On the other hand, a longer interruption leads to degradation of the QD optical properties due to a significant increase in their size during the coalescence processes.

To evaluate the physical parameters of QDs grown with using the investigated growth modes, TEM images in two projections were obtained for experimental structures with an interruption time of 5 seconds: the cross section (figure 4) and plan-view (figure 5) of a QD layer. Figure 4 a shows the high structural quality of the matrix material after QD growth. The height of the obtained objects does not exceed 5 nm which is a typical result for the amount of the material being used [4]. This allows
concluding that a 5 nm thick GaAs cap layer is enough for complete QDs covering. Otherwise, the tops of the formed coherent islands would remain uncovered during prolonged temperature ramping that could lead to their dissolving and creating defects on the growth surface.

The lateral sizes of QDs grown with an optimal interruption time of 5 seconds were evaluated. The minimum size of the obtained objects is ~10 nm and does not exceed 20 nm. Using TEM plan-view images the concentration of the obtained objects was statistically estimated as $9.8 \times 10^{10} \text{ cm}^{-2}$.

Conclusions

In this work, we studied the technological regimes for forming $\text{In}_{0.8}\text{Ga}_{0.2}\text{As}$ QDs on the GaAs surface by the MOVPE technique. After PL study of samples with different interruption time (from 0 to 30 seconds) it was established that the post-growth interruption step is necessary for the final formation of self-assembled QDs, since it significantly improves their size distribution uniformity and quality. The maximum PL intensity was achieved for structures with a post-growth interruption time in the range of 2–5 seconds. The analysis of TEM images revealed the physical parameters of the formed QDs: the distribution of lateral sizes is from 10 to 20 nm, the height is not exceeding 2–5 nm, the concentration of QDs is $\sim 9.8 \times 10^{10} \text{ cm}^{-2}$. The quality of the QD layers and the parameters of the obtained objects indicate the suitability of the technological regimes found in the work for their further use in the epitaxial growth of semiconductor devices with QDs in the active area.

Acknowledgements
The work has been supported by the Russian Foundation for Basic Research (grant No. 18-08-01281).

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