Effect of arsenic pressure during overgrowth of InAs quantum dots with a thin low-temperature GaAs layer on their optical properties

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This paper presents the results of the experimental studies of InAs quantum dot overgrowth by a low-temperature GaAs layer at different arsenic vapor pressures. We reveal that a threefold decrease in the arsenic pressure at a fixed deposition rate of the capping layer leads to a change in the shape of the photoluminescence spectrum of quantum dots with one maximum at the level of 1.19 eV to the shape of the spectrum with two low-energy contributions at the levels of 1.08 and 1.15 eV. Based on the analysis of the power dependences of the photoluminescence spectra, we conclude that the low-energy contributions of the photoluminescence of quantum dots overgrown at a low arsenic pressure correspond to the ground-state emission of two groups of quantum dots with different average sizes formed during mass transfer in the „quantum dot—wetting layer—matrix" system.

Keywords: quantum dots, InAs/GaAs, Stranski—Krastanov mechanism, molecular beam epitaxy, arsenic pressure.

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1. Introduction

Despite the undying interest in research on the epitaxial growth of $A^{III}B^{V}$ semiconductor quantum dots (QDs) due to their unique optical properties [1,2], the functional performance of devices based on them is still far from the theoretically predicted limits. Thus, InAs QD lasers, despite their low threshold current density [3,4] and high internal quantum efficiency [5,6], have relatively low output power and small modulation bandwidth [7]. In addition, due to the rapid development of quantum technologies, there is an increasing need for more and more precise control of the geometrical parameters of individual QDs, directly affecting the performance of high-performance photonic devices [8]. Meanwhile, special attention is paid to the study of morphological properties of QDs (shape, size, and density) and their change in the process of overgrowth with a layer of wide-band matrix, as they ultimately determine the electronic and optical properties of nanostructures and functional characteristics of devices based on them. The results of transmission electron microscopy and cross-sectional scanning tunneling microscopy studies show that during QD overgrowth, there is an intensive transfer and mutual mixing of material, leading to QD „erosion", as well as changes in their chemical composition [7,9–12]. Capping of an array of InAs QDs with only 1 monolayer (ML) of GaAs can lead to a significant change in their size and surface density, as well as a change in the size distribution from unimodal to bimodal [13]. According to previous transmission electron microscopic studies, capping InAs QDs with a 2 nm thick GaAs layer changes their average height from 10 to 1.5 nm [10]. Such significant changes in the QD overgrowth process are explained by the need to minimize the elastic energy of the system, which increases due to the formation of a hetero-boundary between strongly mismatched materials, under conditions of non-uniform relaxation of the QD lattice and the corresponding stress distribution around it [14].

The technological regimes used during the growth of the cover layer have a significant impact on the parameters of the overgrown QDs. Thus, lowering the temperature of InAs QD capping with GaAs layer to 300°C preserves the original pyramidal shape of the QDs and sharp hetero-boundaries with the matrix layer [9]. However, despite the preservation of the initial parameters of the QDs, it is known that a decrease in the overgrowth temperature even by 30°C relative to the growth temperature of the QDs themselves leads to a deterioration of their optical properties [7]. On the contrary, nucleation of QDs at elevated temperatures or reduced growth rates favors the enhancement of mass transfer processes with a corresponding decrease in QD height [11]. A similar effect on the QD characteristics is exerted by the interruption of growth during the overgrowth stage, which promotes mixing of the QD material and the surrounding matrix in order to achieve an equilibrium state of the system with minimum energy [9]. Nevertheless, despite the large number of papers devoted to the study of the influence of regimes of overgrowth on the processes of mass transfer and changes in the shape and properties of quantum dots, the question of the influence of the arsenic flux value at the stage of the cover layer formation (overgrowth) remains poorly studied. Meanwhile, this technological parameter can have a significant effect on the photoluminescence (PL) spectra of the structure with QD, which is due to the increasing sensitivity of the epitaxial system to the magnitude of the arsenic flux with decreasing growth temperature, when the mobility of adatoms decreases and the probability of capture of excess As atoms and formation of defects of stoichiometric character increases [15].

This paper presents the results of the study of the effect of arsenic pressure during the overgrowth of InAs QDs with a low-temperature GaAs layer on their PL properties.

2. Experiment procedure

Samples were grown on GaAs (001) substrates in a SemiTEq STE 35 molecular-beam epitaxy setup with solid-state sources. In first step, a standard oxide removal procedure was performed, after which a GaAs buffer layer of 250 nm thickness was grown at 580°C temperature. In the next step, an $Al_{0.33}Ga_{0.67}As$ layer with a thickness of 100 nm and a GaAs layer with a thickness of 50 nm were formed. The sample temperature was then reduced to 500°C and 2.5 ML InAs was deposited at a rate of 0.05 MS/s at an arsenic pressure (in the form of tetramers) of $1 \cdot 10^{-5}$ Pa (P_0). The formation of QDs by the Stranski–Krastanov mechanism was registered by the change of the diffraction pattern of reflected high-energy electrons from linear to point-like. After a 30-second growth interruption in the arsenic flux, the QDs were overgrown with a low-temperature GaAs layer of 10 nm thickness at 500°C at different arsenic pressures: (1) $P_{\mathrm{As}} = P_0$, (2) $P_{\mathrm{As}} = 3P_0$. Then the layer growth was stopped, the arsenic pressure was set to $4P_0$, and the substrate temperature was raised to 580°C to grow the high-temperature part of the heterostructure consisting of a 90 nm thick GaAs layer, a 50 nm thick $Al_{0.33}Ga_{0.67}As$ barrier, and a 10 nm thick GaAs cover layer. After completion of the structure growth, annealing was carried out at 610°C in a arsenic flux.

To evaluate the initial parameters of the QDs, InAs QDs were grown on the GaAs surface under similar conditions without subsequent overgrowth. Morphology was monitored using an FEI Nova Nanolab 600 scanning-electron microscope (SEM) and an NT-MDT Ntegra atomic-force microscope.

For PL studies, the samples were placed in a Janis ST-500 flow-type cryostat providing measurements in the temperature range 77–300 K. PL excitation was performed using a $YLF:Nd^{+3}$ laser operating in continuous mode ($\lambda = 527$ nm). The laser power was varied in the range 0.08–35.7 mW. Laser light was focused onto the sample surface using a Mitutoyo lens $\times 5$ to a spot with a diameter of 20 μm. The PL signal was detected with a SOL Instruments MS 5204i monochromator and an InGaAs single-channel detector using synchronous detection (SRS 830 Stanford Research Systems).

3. Results and discussion

Fig. 1, *a* shows the SEM image of an array of uncapped InAs QDs characterized by the presence of two groups of structures: the most representative QDs with an average diameter of 22 nm and a surface density of $4 \cdot 10^{10}$ cm^{-2}, as well as coalesced QDs with a surface density of $3 \cdot 10^{8}$ cm $^{-2}$ and an average diameter of 40 nm. The size distribution of QDs is described by a normal Gaussian curve with a distribution half-width of 9 nm (Fig. 1, *b*).

Fig. 2 shows the PL spectra of QDs overgrown with a 10 nm thick GaAs layer at different arsenic pressures. In spectra obtained at room temperature (Fig. 2, *a*), the position of the maximum intensity of the GaAs line is at 1.42 eV for the spectra of both samples in which the QDs were overgrown at both low and high arsenic pressures. At the same time, in the low-energy area of the spectra containing the peaks corresponding to the wetting layer and QD, significant variations are observed depending on the arsenic pressure used during QD overgrowth.

The position of the maximum of the PL intensity of the wetting layer at 300 K shifts from 1.33 to 1.31 eV in the transition from the pressure $P_{\mathrm{As}} = P_0$ to $3P_0$ (Fig. 2, *a*), which may be related to the suppression of mass transfer processes leading to changes in the thickness and /or composition of the wetting layer. In contrast, the PL QD peak undergoes a short-wavelength shift, which corresponds to the effect observed when the amount of deposited QD material decreases [16,17]. It is known that when QDs are overgrown with a layer of wide-band matrix, significant changes occur in the system leading to modification of both geometrical characteristics of QDs (shape, size and density in the array) and their chemical composition due to mixing of QD and matrix materials. At the same time, as a rule, QDs tend to decrease their height, changing their shape from initially relatively high aspect ratio, pyramidal, to a flatter one, which makes it possible to reduce the lattice mismatch with the matrix material by reducing the degree of relaxation of the QD material [10]. The effect of QD transformation is enhanced when the temperature increases or the growth rate decreases during the overgrowth stage, which is due to the intensification of diffusion processes in the system „QD–wetting layer–matrix“ [7,11,12,18]. Fig. 2, *a* shows that decreasing the arsenic pressure during overgrowth has a similar effect on the spectrum of the PL QD as increasing the growth rate at the overgrowth stage or decreasing the substrate temperature — the position of the PL maximum shifts to the long-wavelength area, which is characteristic of oversized QDs. This pattern may be related to the significant difference in material transfer mechanisms during the overgrowth process at low and high arsenic pressures. At high pressure, the system is more inherent in the preservation of the original uncapped QD array, due to which the PL spectrum shows a unimodal Gaussian distribution of the PL intensity with a maximum at level 1.19 eV. At the same time, the low arsenic pressure

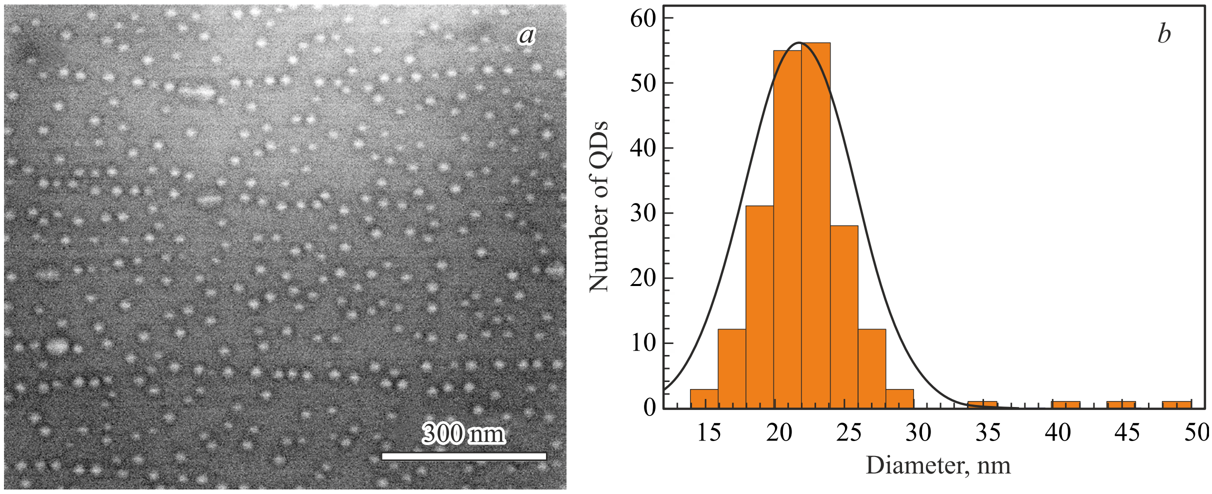

Figure 1. SEM image (a) and size distribution (b) of an array of uncapped InAs/GaAs QDs.

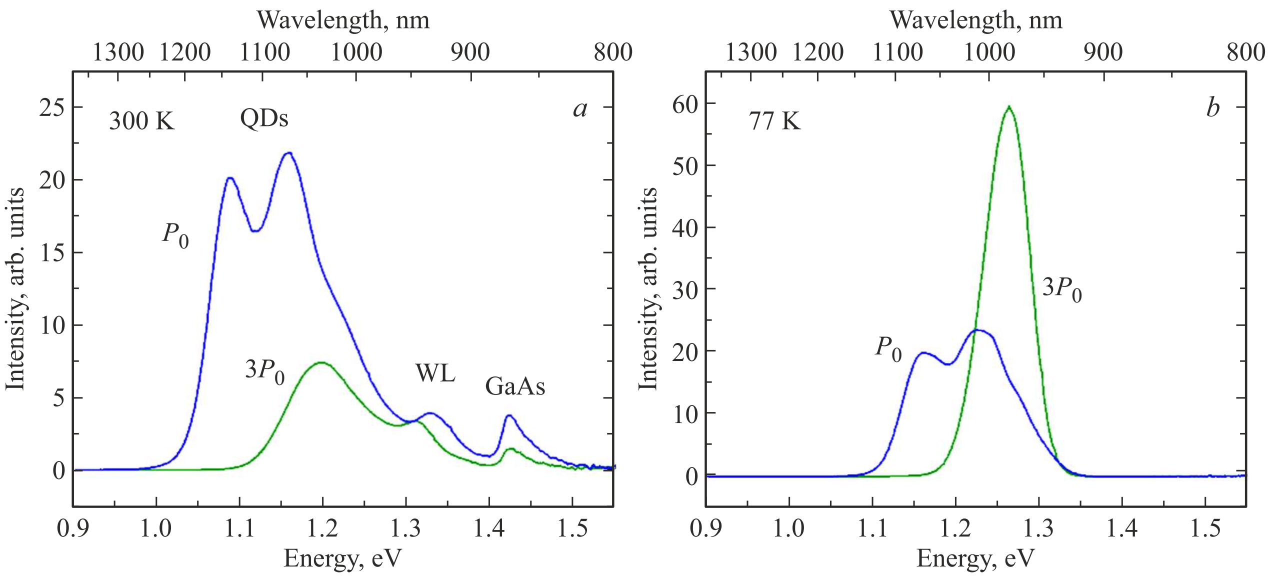

Figure 2. PL spectra at 300 (a) and 77 K (b) of samples with QDs overgrown at different arsenic pressures (optical pump power $W = 35.7$ mW).

favors an increase in the intensity of atomic diffusion during overgrowth, resulting in enhanced mass transfer and an increase in the size of the QDs. Two most representative fractions of QDs of different sizes emerge, which contribute to the PL spectrum at 1.08 and 1.15 eV levels.

It should be noted that the correlation of the PL contribution of larger-sized QDs with the presence of coalesced QDs is unlikely, since their surface density is 2 orders of magnitude lower than that of basic QDs. In addition, the emission of InAs/GaAs QDs with an average diameter of 40 nm is expected at room temperature to be ~ 1400 nm (~ 0.9 eV) [19], which is not observed in the spectra in this paper.

The integrated PL intensity from QDs nucleated at low and high arsenic pressures differs almost 5 times in favor of low arsenic pressure in the case of room temperature PL measurements. However, at a temperature of 77 K (Fig. 2, b), the integral intensities almost do not differ in value, which may indicate the high defectivity of the material structure of the cover layer formed at high arsenic pressure. During the low-temperature overgrowth, excess arsenic does not have time to desorb from the surface and is incorporated into the layer composition, forming stoichiometric defects that act as centers for non-radiative recombination of charge carriers and lead to a decrease in the PL intensity on the spectrum. At the same time, the shape of the spectra remains practically unchanged when the temperature of the QD PL measurement is lowered to 77 K (Fig. 2, b): in the high-pressure case, one maximum of the PL intensity at the level of 1.26 eV is

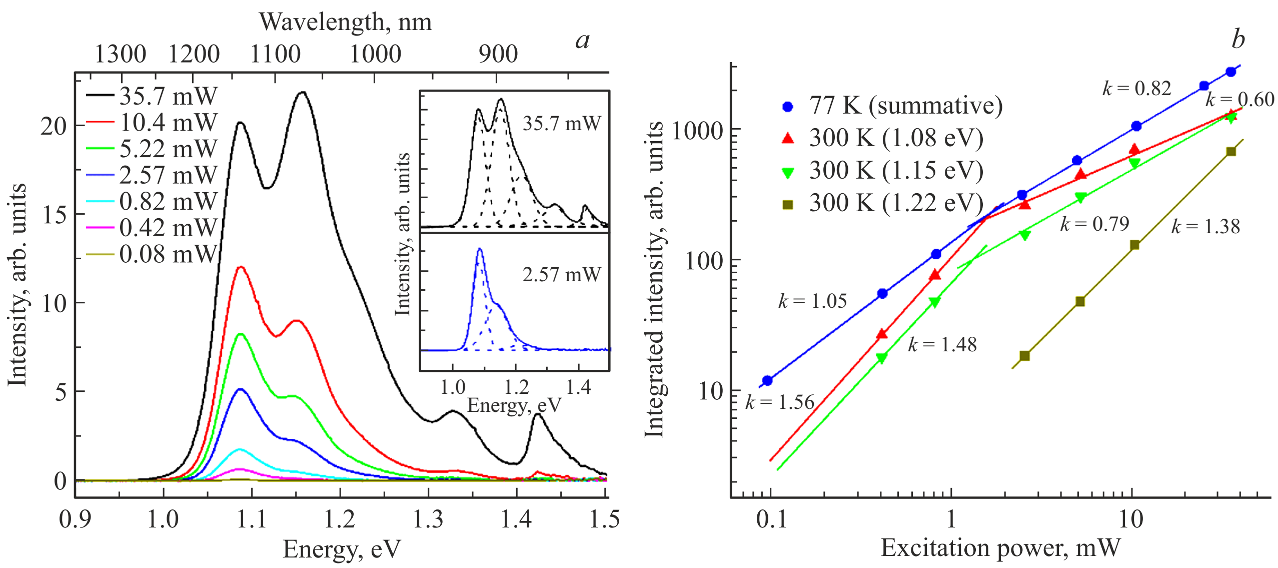

Figure 3. PL spectra obtained at room temperature of the sample with QDs overgrown at low arsenic pressure under different optical pumping power (a) and the dependence of the integral intensity of the Gaussian functions obtained by approximation of the PL spectra of QDs obtained at room temperature and the integral intensity of the PL spectra obtained at 77 K (b). In the inserts in Fig. 3, a, the dashed lines indicate Gaussian lines approximating the PL spectra for pump powers of 35.7 and 2.57 mW. (A color version of the figure is provided in the online version of the paper).

observed; in the low-pressure case, two peaks at the levels of 1.16 and 1.23 eV are observed.

To analyze in more detail the PL line on the spectra of QDs overgrown at low arsenic pressure and to verify the assumption of the presence of QD fractions of different size, the dependence of the PL on the optical pumping power was investigated (Fig. 3).

In the PL spectra (300 K) of the structure with the QDs overgrown at low arsenic pressure, at the optical pumping power > 2 mW, in addition to two pronounced peaks at the energy levels of 1.08 and 1.15 eV, a short-wavelength shoulder approaching the level of the wetting layer is observed (Fig. 3, a). The deconvolution performed in different variants indeed shows the best agreement when three Gaussian contributions to the area of the PL spectrum related to the QD emission are taken into account (dashed lines in the inserts Fig. 3, a). Decreasing the excitation radiation power leads to a regular attenuation of each of the PL contributions, but the high-energy contribution at 1.22 eV (brown line in 3, b) undergoes the largest change. It is known that the analysis of the dependences of the integrated intensity of PL I on the optical pumping power W plotted on a logarithmic scale allows to identify the charge carrier recombination mechanisms by the slope coefficients k of the straight line approximating the experimental points and described by the expression $I \propto W^k$ [20–22].In Fig. 3, b the power dependences of the integrated intensity of each of the lines of the low-pressure arsenic overgrown PL QD spectra measured at temperature 300, and as well as the integrated intensity of the PL spectra measured at temperature 77 K, are presented. Analysis of the dependence on the graph shows that when the excitation power reaches 2.57 mW, the dependence for 77 K (blue line in Fig. 3, b) changes its character from super-linear to sublinear, i.e. changing the slope of the straight line from $k > 1$ (1.05) to $k < 1$ (0.82). Similar changes occur in the PL power dependences for the low-energy contributions when measured at 300 K: the line slope for the peak at 1.08 eV decreases from $k = 1.56$ to $k = 0.6$, for the peak at 1.15 eV — from $k = 1.48$ to $k = 0.79$. The characteristic change in the slope coefficients of the straight line for each of the presented cases is due to the saturation of low-energy quantum states of QDs with increasing pumping power, which is associated with limiting the number of recombination transitions of charge carriers and increasing the probability of excitation of levels with higher energies [20,23]. As can be seen in Fig. 3, a, the two characteristic PL peaks persist even when the laser excitation power is reduced by 2 orders of magnitude, which may indicate the presence of a bimodal size distribution QD in the system. However, the high-energy contribution at 1.22 eV disappears when the excitation level is reduced to 2.57 mW, which correlates with the dependencies presented in Fig. 3, b. The sharpest change in the slope of the line is observed for the low-energy contribution at 1.08 eV, which corresponds to the largest-sized QDs (red line in Fig. 3, b). At a lower rate, the contribution saturates at 1.15 eV, which corresponds to a family of smaller QDs (green line in drawing 3, b) because they have a higher ground-state quantum state energy. Nevertheless, the sublinear character of the PL power dependence still indicates saturation of the QD ground state confirmed by the appearance of excited state contributions at the same pump power level of 2.57 mW are described by a straight line with an $k = 1.38$ slope (brown line in

Fig. 3, *b*). Thus, the analysis confirms the assumption made at the beginning of the paper that the bimodal character of the spectrum of PL QDs overgrown at low arsenic pressure is due to the emission of QDs of different sizes, and the short-wavelength shoulder observed at the energy level of 1.22 eV describes the emission transition from the excited level of QDs (presumably of larger size).

4. Conclusion

Thus, the experimental studies have shown that the arsenic vapor pressure during the process of overgrowth of InAs QDs with a low-temperature GaAs layer has a significant effect on the optical properties of the formed structures. At elevated arsenic pressure, a single QD peak at an energy level of 1.19 eV is observed on the PL spectrum measured at 300 K. Decreasing the arsenic pressure by 3 times at unchanged growth rate and substrate temperature leads to a shift in the position of the QD PL maximum to 1.15 eV, as well as the appearance of an additional low-energy line at 1.08 eV and a high-energy (short-wavelength) shoulder at 1.22 eV on the PL spectra. Analysis of the power dependences of the PL spectra of the structures with QDs overgrown at low arsenic pressure shows that the QD array has a bimodal size distribution due to the redistribution of material during the overgrowth process. In this case, the short-wavelength shoulder (1.22 eV) on the spectra appears as a result of radiative recombination of charge carriers thrown to the excited level of QDs at high levels of optical pumping power.

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Conflict of interest

The authors declare that they have no conflict of interest.

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