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LOW-DIMENSIONAL SYSTEMS

Control over the Parameters of InAs–GaAs Quantum Dot Arrays in the Stranski–Krastanow Growth Mode

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Abstract—The effect of the growth temperature on the density, lateral size, and height of InAs–GaAs quantum dots (QD) has been studied by transmission electron microscopy. With the growth temperature increasing from 450 to 520°C, the density and height of QDs decrease, whereas their lateral size increases; i.e., the QDs are flattened. The blue shift of the photoluminescence line indicates decreasing QD volume. The observed behavior is in agreement with the thermodynamic model of QD formation. The effect of lowering the substrate temperature immediately after the formation of QDs on the QD parameters has been studied. On lowering the temperature, the lateral size of QDs decreases and their density increases; i.e., the parameters of QD arrays tend to acquire the equilibrium parameters corresponding at the temperature to which the cooling is done. The QD height rapidly increases with cooling and may exceed the equilibrium value for a finite time of cooling, which enables fabrication of QD arrays with a prescribed ratio between height and lateral size by choosing the time of cooling. *© 2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

The prevalence of structures with unidimensional localization of carriers, i.e., quantum wells (QW), in modern semiconductor electronics is largely connected with the simplicity of their 2D bandgap engineering, which allows varying the width and composition of QWs and the bandgap of a matrix. Quantum-cascade lasers—very complex devices demanding a strictly defined band structure—have been proposed and designed. As further progress in semiconductor electronics will be associated with the wide application of structures with 3D localization of carriers, i.e., quantum dots (QD), the development of the bandgap engineering for these structures is an important fundamental and applied problem.

A recent breakthrough in the technology, physics, and device applications of QDs is associated with the use of self-organization processes in the course of epitaxial growth. It was shown experimentally and in theory that an array of elastically strained islands ordered in shape and size can be formed on the surface during the heteroepitaxial growth of strained layers [1]. Currently, the InAs-GaAs system, in which QDs are formed via Stranski–Krastanow growth mechanism, is the best studied and the most important for device applications. In spite of the fact that the self-ordering represents a decisive factor which enables the use of QDs as an active region in semiconductor devices, this effect imposes serious limitations on the possibility to control the shape and size of islands and, correspondingly, their band diagram. To overcome these limitations, a variety of techniques have been proposed, such as the formation of vertically-coupled QDs [2], the deposition of an initial layer of stressors [3], and the activated decomposition of a solid solution [4]. These technological approaches allowed for substantial progress in controlling the parameters of QD arrays. It is necessary to note that in all of the above-listed methods a layer of initial dots is formed at the first stage and subsequent growth is determined by the elastic field induced by this layer. Thus, control over the shape, size, and density of QDs in the Stranski–Krastanow growth mode can offer additional versatility in the application of more sophisticated technologies. In the present study, we have investigated the impact of temperature conditions on the height, lateral size, and density of InAs–GaAs QD arrays, and demonstrated that changing the temperature after the deposition of QDs allows the tuning of their parameters to be controlled.

2. EXPERIMENT

The structures were MBE-grown on semi-insulating (100)GaAs substrates. After removing the oxide from the substrate, a GaAs buffer layer was grown at the substrate temperature T_s = 600°C. To prevent the diffusion of nonequilibrium carriers into the substrate, a six-period GaAs/$Al_{0.25}Ga_{0.75}As$ (20 Å/20 Å) superlattice was grown on the buffer-layer surface. Further, a

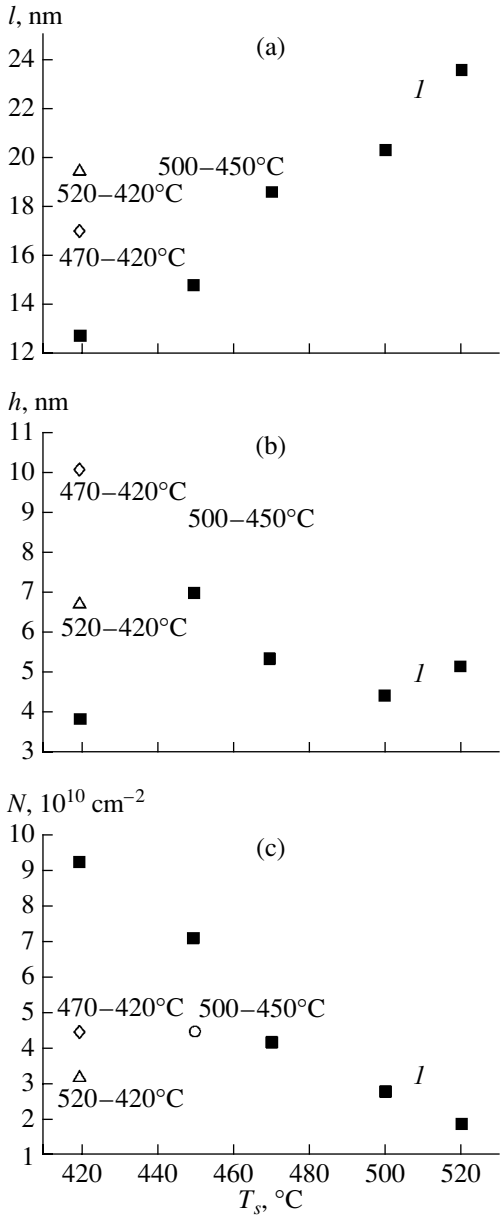

Fig. 1. Average (a) lateral size *l*, (b) height *h*, and (c) density *N* of QDs vs. the substrate temperature T_s. (*1*) Structures grown at fixed T_s; for structures grown with T_s lowered immediately after QD deposition, the growth temperatures and the final temperature of cooling are indicated.

0.1 μm-thick GaAs layer was grown, and then the substrate was cooled to the temperature of the QD deposition. Next, three InAs monolayers (ML) were deposited at temperatures of 520, 500, 470, 450, or 420°C. The formation of islands began at approximately 1.7 ML InAs. The formed QD layer was overgrown with a 100-Å-thick GaAs layer at the temperature of InAs deposition after a 10-s-interruption of growth. The 10-s interruption was necessary to improve the size uniformity of the island arrays [5]. Further, the substrate temperature was raised to T_s = 600°C, and a 400-Å-thick

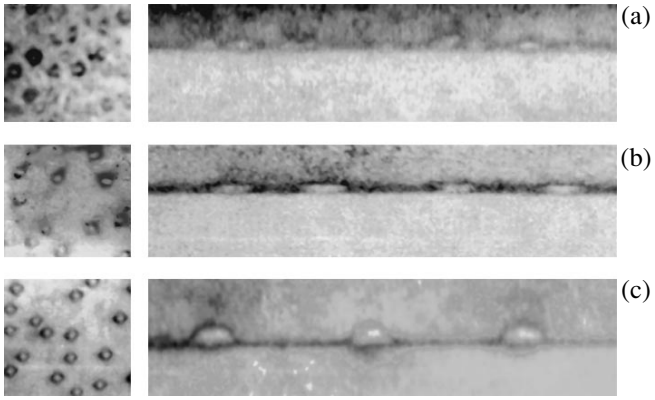

Fig. 2. TEM images of structures grown at (a) 450°C and (b) 500°C, and (c) cooled from 500 to 450°C for 120 s. Left: plan view images obtained under multiple-beam conditions along (001) zone axis; right: cross-sectional (010) images obtained under double-beam conditions with (200) reflection excited.

GaAs layer, a superlattice similar to the lower one, and a capping GaAs layer were grown in series. Another batch of samples was grown with the substrate temperature lowered after the deposition of QDs. In the modes used, the substrate was cooled for 120 s: from 520 to 420, 500 to 450, or 470 to 420°C. The QDs were overgrown with a GaAs layer at the final temperature.

The PL was excited by an argon-ion laser (λ = 514.5 nm, the excitation density 500 W cm^{-2}) and recorded using an MDR-23 monochromator and a North Coast E0/817R Ge *p–i–n* photodiode. A Philips EM 420 microscope with 100 kV acceleration voltage was used for transmission electron microscopy (TEM). The samples in planar (001) and transverse (110) and (010) configuration were prepared by standard thinning technology, i.e., grinding, polishing, and final sputtering of the material with Ar^+ ions at grazing angles to the sample surface.

3. THE EFFECT OF GROWTH TEMPERATURE ON THE PARAMETERS OF QD ARRAYS

Figures 1a, 1b, and 1c show, respectively, average values of the QD lateral size *l*, height *h*, and density *N* as functions of the substrate temperature. These dependences were obtained from an analysis of TEM images; typical images are shown in Fig. 2. As seen in Fig. 1, raising the substrate temperature from 420 to 520°C results in an increase in lateral size of QDs and a decrease in their density. The dependence of the QD height on T_s is more complicated: it is 4 nm for T_s = 420°C, decreases from 7 to 4.5 nm in the range 450–500°C, and at 500°C it is 6 nm. It is noteworthy that the values of the lateral size and height of an island determined from TEM images are very sensitive to the conditions of image recording, as well as the film thickness. Thus, the data shown in Fig. 1 indicate only a general tendency under similar conditions of image

recording. It should also be noted that the density and average lateral size were estimated based on the analysis of planar images containing several hundred QDs, whereas the height was determined from several cross-sectional images with the number of QDs an order of magnitude smaller. Therefore, the density and lateral size were determined with higher precision than the height.

To analyze the temperature dependence of the average QD volume, we can use the position of the PL spectral peak, i.e., the localization energy of the electron-hole pairs, E_{exc}. The localization energy depends on the QD volume and shape. The effect of the QD shape on the optical transition energy was calculated in [6]. It was shown that, for a fixed-volume InAs QD in a GaAs matrix, the change in its shape from a pyramid to a flat island results in a red shift of about 30 meV. Figure 3 shows the PL spectra of QDs grown at different temperatures. The temperature increase in the range from 450 to 520°C results in a blue shift of the PL spectrum, which indicates decreasing QD volume. Taking into account the increasing QD lateral size with rising substrate temperature (Fig. 1), we can conclude that the blue shift related to the decreasing QD volume and the red shift associated with decreasing QD height cancel one another.

It is evident that the experimentally observed decrease in the volume of islands contradicts the kinetic models of self-limited growth in the Stranski–Krastanow mode [7–9], which predict increasing island volume with rising temperature, due to a high coefficient of surface diffusion of adatoms and a weaker effect of the diffusion barriers at higher temperatures.

According to thermodynamic theories [10–13], arrays of 3D islands ordered in shape, size, and relative positions are a new class of equilibrium surface structures. According to the thermodynamic model, the effects of entropy make a smaller volume of islands more favorable at elevated temperatures [14]. For flat 2D islands of fixed height and different lateral sizes, the theory yields an approximate dependence of the island volume V on temperature T_s in the following form:

$$V(T_s) \approx V(0)\left[1 - \frac{T_s}{2T_{s\,\mathrm{ch}}}\right], \qquad (1)$$

where the characteristic temperature $T_{s\,\mathrm{ch}}$ depends on the island volume and has a value >800 K (530°C) for islands containing more than 1000 atoms. The observed decrease in the average volume of islands with rising temperature emphasizes the role of effects related to entropy, therefore being, in agreement with the thermodynamic model of island formation. Notwithstanding the fact that a real system of 3D islands with different shapes requires more sophisticated theoretical treatment than the one in [14], the general tendencies are the same because the effects of entropy in an equilibrium array of islands are responsible for a smaller volume at higher temperatures.

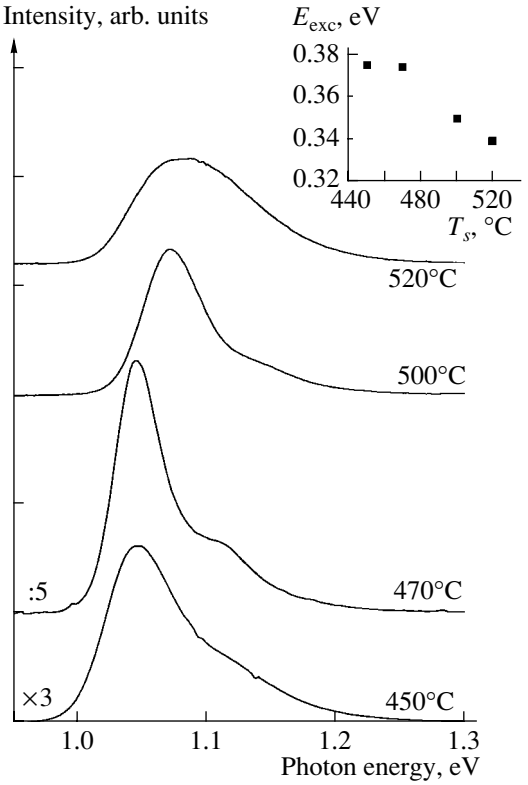

Fig. 3. PL spectra of QDs grown at different temperatures. Inset: the exciton localization energy in a QD, E_{exc}, with respect to the GaAs matrix. The spectra were recorded at T = 300 K.

It is necessary to note that the attainment of an equilibrium QD volume at low temperatures is possible only with prolonged interruptions in growth, because the exchange reactions at the surface are hindered. The small volume of the QDs grown at 420°C is due to the fact that, in our case, the same short-term interruption was made during the growth of all of the structures after InAs deposition. The increasing QD height at 520°C, which was observed in TEM images, can be attributed to broadening of the composition profile at high growth temperatures [18], which is confirmed by the blue shift of the PL line.

4. THE EFFECT OF DECREASING THE TEMPERATURE AFTER InAs DEPOSITION ON THE PARAMETERS OF QD ARRAYS

We have studied the behavior of an array of islands in the case of prolonged interruption of growth, and also in the case of lowering the temperature immediately after the deposition of InAs (prior to overgrowing with GaAs). The interruption of growth for 10 s improves the size uniformity of QDs [5]. Raising the period interruption to ~120 s at a fixed temperature does not modify the size and density of QDs, but results in the formation of large, randomly arranged clusters. With the interruption time made even longer, the den-

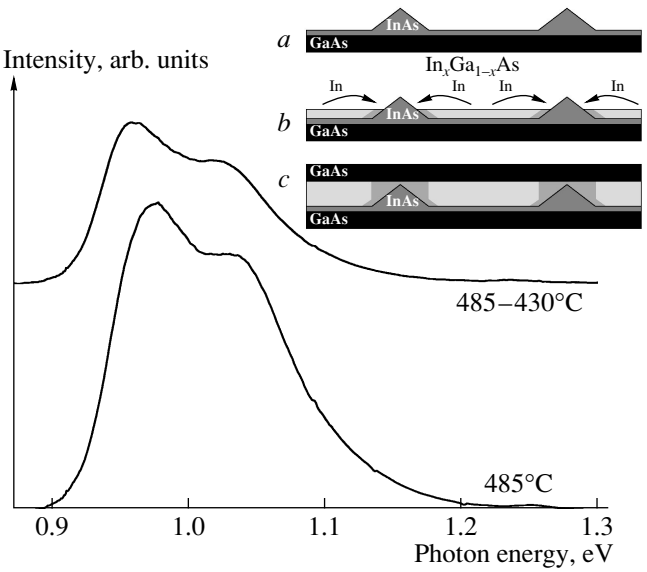

Fig. 4. PL spectra of QDs grown by activated decomposition of InGaAs solid solution at a fixed substrate temperature T_S = 485°C with the substrate cooled from 485 to 430°C after QD formation. Inset: the scheme of activated decomposition. The spectra were recorded at T = 300 K.

sity of large islands increases and that of coherent islands decreases [14, 5]. This effect can be accounted for as follows: according to the thermodynamic model, there exists a probabilistic size distribution of QDs. Though the probability of formation of large dots is low, a certain number of these exists on the surface. If the volume of an island exceeds some critical value, dislocations can develop within it. Such islands can be formed also due to nonideality of the substrate, i.e., the presence of defects and dislocations. The islands with dislocations attract In from small coherent islands located nearby. It is interesting to note that, even upon prolonged interruptions of growth, the size and shape of coherent QDs undergo only small changes, and no islands of intermediate size are observed. Thus, despite the fact that the applicability of the thermodynamic approach is, strictly speaking, limited by the presence of islands with dislocations, it appears to be valid for the subsystem of coherent QDs in this case as well.

Now we will discuss the effect of lowering the temperature after QD formation on the density, lateral size, and height of QDs. As seen from Figs. 1 and 2, cooling induces a decrease in the lateral size of QDs and a significant rise in their density. These trends are in qualitative agreement with the thermodynamic model, because, on lowering the temperature from T_{s_1} to T_{s_2}, the parameters of an array of islands tend towards the values corresponding to T_{s_2}. Owing to the finite time of cooling, the lateral size and density of dots do not have enough time to reach their equilibrium values corresponding to the final temperature. It is noteworthy that the average heights of QDs in structures grown with cooling significantly exceeds the heights of dots grown either at the initial or at the final temperature. This effect, which is presumably associated with the specific kinetics of attaining the equilibrium size by QDs, invites further study. The increase in the QD volume during cooling is confirmed by a strong red shift of the PL in the structures grown with the substrate temperature lowered in the course of deposition (Fig. 4).

Cooling the QD array immediately after InAs deposition offers new ways to control the density, lateral size, and height of QDs. For example, the density and lateral size of QDs grown at 500°C and cooled to 450°C nearly coincide with those for dots grown at 470°C, but the former are nearly two times higher. We believe that, with proper choice of the cooling rate and time, the parameters of QD arrays can be varied within certain limits.

We have also studied the effect of cooling on the properties of QDs produced by more sophisticated technology, specifically, the stimulated decomposition of InGaAs solid solution [4]. In this growth process, the initial InAs–GaAs points obtained by depositing a D_{IS} InAs ML are overgrown with $In_xGa_{1-x}As$ with an average thickness H (usually, D_{IS} = 1.7–3.5 ML InAs, x = 0–0.3, H = 0–6 nm). In the course of overgrowth with InGaAs, it is more energetically favorable for In atoms to diffuse toward QDs, in which the lattice constant is closer to that of InAs, and for Ga atoms to diffuse to inter-QD regions, in which the lattice constant is closer to that in GaAs. This process entails an effective increase in size of the initial QDs, with a corresponding red shift of the PL line. The inset to Fig. 4 schematically shows the activated decomposition of a solid solution. The fact that QDs are buried under the InGaAs layer provides an additional contribution to the red shift of the PL line because of a decrease in the band gap of the matrix and a redistribution of strain fields within QDs. The existence of several parameters of growth (D_{IS}, x, H) opens the way to efficiently control the parameters of QD arrays, in particular, to obtain an emission wavelength of 1.3 μm, while maintaining the high structural and optical quality of the samples.

Figure 4 shows the PL spectrum of a structure with QDs grown by activated decomposition of a solid solution at 485°C. In this case, the initial InAs islands obtained by depositing 2.4 MLs were overgrown with $In_xGa_{1-x}As$ (x = 0.15) with an average thickness of 6 nm. Cooling the structure to 430°C (after the formation of dots) resulted in a red shift of the PL line by ~30 meV. Thus, the general trends which are valid for the Stranski–Krastanow growth mode are also observed for QDs produced by more complicated technology—the activated decomposition of a solid solution.

5. CONCLUSION

The effect of substrate temperature on the parameters of QD arrays (density, lateral size, height) and on

the position of the PL spectral peak has been studied. As the temperature rises from 420 to 520°C, the lateral size of QDs increases from 13 to 23.5 nm and their density decreases from 9.2×10^{10} to 1.9×10^{10} cm^{-2}. The blue shift of the PL line, which is observed as the temperature rises from 450 to 520°C, is indicative of a decrease in the QD volume with rising temperature. The increasing lateral size with decreasing volume means that the dot height decreases, i.e., dots become flatter. The conclusion on decreasing QD height is confirmed by the TEM data (a slight increase in the height at 520°C observed in TEM images can be attributed to the broadening of the composition profile at higher growth temperatures). Decreasing QD volume with rising substrate temperature is in agreement with the predictions of the thermodynamic model for the Stranski–Krastanow growth mode, which predicts the existence of an equilibrium shape, volume, and density of QDs for a given substrate temperature. The small height of QDs at 420°C is accounted for by the low rate of exchange reactions at the surface, which results in a long time being required for QDs to reach the equilibrium size.

When the temperature is lowered immediately after the formation of QDs, their density, lateral size, and height tend to the equilibrium values, which correspond to the temperature at which cooling is done. In our experiments the time of cooling was limited (120 s), so the density and lateral size of QDs reached values intermediate between the equilibrium parameters for the initial and final temperatures. At the same time, the height of QDs increased very rapidly and exceeded the equilibrium value corresponding to the final temperature. Thus, the appropriate choice of the rate and time of cooling allows fabrication of QD arrays with the prescribed ratio between the height and lateral size of QDs. The choice of the growth temperature and the use of cooling immediately after the formation of QDs provides the opportunity to control the QD parameters in the Stranski–Krastanow growth mode, and also in the case of more complex technologies such as the formation of vertically coupled QDs [2], growth in the strain field of the initial layer of stressors [3], and activated decomposition of a solid solution [4].

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