GaInAs Quantum Dots (QD) grown by Liquid Phase Epitaxy (LPE)

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Abstract. The majority of the semiconductor structures with QD today are grown by MBE and MOCVD. It is known that the best material quality can be achieved by LPE because, in contrast to MBE and MOCVD, this method is realized at near-equilibrium conditions. To develop QD LPE technology first of all it is necessary to find a growth technique allowing the crystallization of epitaxial materials with very small volume. This can be done by means of different techniques. In this work we apply a low temperature short-time growth method, which allows the production not only of single, but also of multilayer heterostructures. We have grown GaₓIn₁₋ₓAs QD on GaAs (100) substrates at 450 C. The details of the QD formation, depending on composition of the GaₓIn₁₋ₓAs solid solutions, have been studied by atom-force microscopy. The photoluminescence spectra of investigated samples show, in addition to a short-wave GaAs related peak, a longer wavelength line, which disappears after removal of the grown GaInAs material using an etching solution. This fact, together with atom-force microscopy results can be interpreted as a proof that QD heterostructures were grown successfully by LPE.

1. Introduction
Starting from the 1970’s, liquid phase epitaxy (LPE) became the main method of the production of different multilayer structures. In nowadays semiconductor’s technology the overwhelming majority of devices based on multilayer structures, including QD’s, are grown by means of molecular beam epitaxy (MBE) and gas phase epitaxy, especially metal-organic chemical vapor deposition (MOCVD). This happened because the LPE has several shortcomings in comparison with MBE and MOCVD. But in spite of the advantages of MBE and MOCVD, the LPE technique is still an important technological method for growing various epitaxial films and multilayer structures. First of all the quality of materials grown by this method is excellent. For example, the internal quantum efficiency of radiative recombination for lightly doped direct-bandgap III-V binary compound and solid solutions grown by LPE is close to 100% [1,2]. This phenomenon can be explained because the crystallization process in LPE is carried out at conditions not far from equilibrium. So the purpose of the work was to develop the LPE growth technology and to investigate the QD structures on the base of GaInAs/GaAs system. To solve this problem first of all it is necessary to find a LPE growth method of epitaxial layers with very small thickness (in another words a very small volume of the growing materials). In the present work we have used low growth temperature and a short time of contact between

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substrate and liquid phase. It is known, that in the MBE and MOCVD technologies, when there is a lattice mismatch between the substrate and epitaxial layer, QD can be grown due to a self organizing mechanism [3]. In the present work we have used LPE and studied the influence of the lattice mismatch between GaAs substrate and Ga\textsubscript{x}In\textsubscript{1-x}As epitaxial layers on the process of QD crystallization. In other words we have investigated the growth peculiarities of very thin Ga\textsubscript{x}In\textsubscript{1-x}As epitaxial films as a function of composition (x). By ”epitaxial films” we mean not only complete epitaxial layers but also separated islands (including the QDs), growing on the substrate’s surface during an epitaxial process due to the lattice mismatch between substrate and growing material. Previous reports on the growth of QD’s by LPE include the growth of InAsSbP [4] and InAs [5] QD’s on GaAs substrates, InSb QD’s on InAs [6,7] and GaAs [6] substrates and PbSe [8] on GaSb substrates. In works [4,6,8] the growth experiments were done using very short times of contact, of the order of ms, between the liquid solution and the substrate. To achieve such short times the contact was done trough a narrow slit (1 mm wide) and using electric motors to obtain high slider speeds. In Ref. [5] a special pulsed cooling method was applied to a supersaturated liquid phase at 400 C. There are several reviews [9-11] about the growth by LPE of quantum structures, such as quantum wells and QD’s.

2. Experimental

The usual routine employed to prepare the growth experiments is described in Ref [12]. All samples were grown at a temperature of 444 C (note that the usual and typical growth temperatures in the LPE of Ga - In - As system are in the interval 550-650 C). Growth time in the most cases was 15 seconds, but for some samples it was near 1 second. Prior to the crystallization of the GaInAs solid solutions or pure InAs, a buffer GaAs layer with thickness of a few microns were grown on the surfaces of the GaAs substrates. The morphology of the grown samples was studied by means of atom force microscope (AFM). The photoluminescence spectra of the structures were recorded using a 100 mW Ar laser with a wavelength of 514 nm and a 0.5 m spectrometer. An InGaAs photodetector was used for detection in conjunction with conventional lock-in techniques.

3. Results and discussion

First of all, to estimate the composition of GaInAs (and accordingly the lattice mismatch between substrates and epitaxial layers), the phase diagram of the Ga-In-As system at the used growth temperature has been calculated by means of usual procedure, applied for the different III-V systems [13].

![AFM Image of the structure grown from the In-As liquid phase at 444 °C during 15 s. The density of nano-islands is about 2.6x10\textsuperscript{10} cm\textsuperscript{-2}. The average diameter and height are ~ 16 nm and 4 nm, accordingly.](image)

When the growth experiments were done at 444 C, complete epitaxial Ga\textsubscript{x}In\textsubscript{1-x}As layers could be obtained in the composition range 1 \leq x \leq 0.75. In contrast, at a growth temperature of 550 C, this composition range was reduced to 1 \leq x \leq 0.93 as usual for this system. This
can be explained by the big difference between the thicknesses of the epitaxial layers grown at high and low temperatures due to the solubility differences of As in a solution of Ga and In as can predicted from the phase diagram.

Table 1. The data of the Ga$_x$In$_{1-x}$As epitaxial layers obtained at 444 C.

| Growth Time | $X_{In}/X_{Ga}$ | Kind of Structure | Density $QD/cm^2$ | Calculated Composition $Ga_xIn_{1-x}As$ |
|-------------|-----------------|-------------------|------------------|--------------------------------------|
| 15 s        | 15              | O                 | 0.95             |                                      |
| 15 s        | 20              | O                 | 0.87             |                                      |
| 15 s        | 25              | O                 | 0.8              |                                      |
| 15 s        | 30              | X                 | $\approx 8.8\cdot10^8$ | 0.7                                  |
| 15 s        | 40              | X                 | $\approx 2.3\cdot10^9$ | 0.35                                |
| 15 s        | 50              | X                 | $\approx 3.0\cdot10^9$ | 0.2                                  |
| 15 s        | Pure In         | X                 | $\approx 2.6\cdot10^{10}$ | 0                                   |
| ~1 s        | Pure In         | X                 | $\approx 1.3\cdot10^{10}$ | 0                                   |

![Figure 2](image-url)  

Figure 2. The dependence of the magnitude of A as function of the composition of the solid phase.

If the composition $x$ of the Ga$_x$In$_{1-x}$As solid solutions decreases from $x = 1$ to $x \leq 0.75$, the quality of epitaxial films becomes worse as evidenced by an increase of the full widths at half maximum and a decrease of the intensity of the photoluminescence spectra. With our crystallization regime, complete epitaxial Ga$_x$In$_{1-x}$As films cannot be grown on the GaAs surface if their composition is $x < 0.75$. In these cases the ternary solid solutions are crystallized as separated islands. To study the morphology of such islands, AFM images of the structures with different compositions of the Ga$_x$In$_{1-x}$As solid solutions have been investigated. These images were processed to estimate the density of grown QD’s. As an example, the image corresponding to pure InAs is shown in Fig. 1. All these data are assembled in Table 1. The column titled "Kind of Structure" indicates with an "X" the cases when separated Islands were observed and with an "O" the growth of complete layers.

It is possible to see from this table that the QDs density increases with the In concentration in the solid phase. This is likely related to the increase of lattice mismatch. The highest density of the QD is achieved in the case of InAs/GaAs structures.
Figure 3. The PL spectra at 22 K and different levels of excitations (Ar laser power: 10, 30 and 70 mW) of the InAs/GaAs nano-islands structure.

Figure 4. The PL spectra at 22 K of the GaAs substrate, the GaAs substrate with buffer layer, the structure with InAs QDs and the structure with removed InAs QDs.

As an indication of the total volume or weight of material forming the QDs, a quantity $A$ was defined as the product of the average height, diameter, and density. The dependence of the magnitude of $A$, as function of the composition of the solid phase is shown in Fig. 2. It is possible to see that its dependence looks like the corresponding liquidus isotherm in the Ga-In-As system.

The photoluminescence spectra (PL) at 22 K and different levels of excitations of the InAs/GaAs nano-islands structure are shown on the Fig. 3. The first line on these spectra with a peak at 814 nm is associated with the GaAs buffer layer and the second one with a peak at 1030 nm could be related to the emission from the InAs QD’s since its position does not change with excitation level. To further test this assumption we have used a chemical etching where the InAs nano-islands have been removed from the GaAs surface. The PL spectra of structure before and after etching are shown on Fig. 4. It is possible to see from this figure that
the second line disappears after the InAs nano-islands have been removed, which proves that QDs were grown successfully in our LPE experiments.

4. Conclusions
Using a short-time, low-temperature LPE growth technique it is possible to obtain InAs/GaAs nano-islands or QDs. The existence of these nano-islands has been proved by means of atom force microscope images and photoluminescence spectra. The highest density of such nano-islands (in the case of InAs/GaAs structures) was $2.6 \cdot 10^{10} \text{ cm}^{-2}$.

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6. References
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