Quantum Dots obtained by LPE from under-saturated In-As liquid phases on GaAs substrates

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Abstract. In this work we inform about quantum dots (QD) obtained by Liquid Phase Epitaxy (LPE) on GaAs substrates from under-saturated In-As liquid phases. In our processes, we have prepared saturated In-rich liquid phases by dissolving an InAs wafer at one of the temperatures interval from 450 to 414 °C for 60 minutes. The contact between In-As liquid phase and the GaAs substrate was always done at a constant temperature of 444 °C for 5 seconds. Thus, the growth temperature for most of the samples was higher than the liquidus temperature. We think that the growth driving force is related to a transient process that occurs when the system is trying to reach equilibrium. Under the atom force microscope (AFM) we have observed nano-islands on the surfaces of the samples obtained from under-saturated liquid phases prepared at 438, 432 and 426 °C. The 25 K photoluminescence spectrum shows a peak at a 1.33 eV, in addition to the GaAs related line.

1. Introduction
The growth of quantum structures as a mean to improve the characteristics of optical devices is normally done using modern expitaxial techniques such as MBE and MOCVD [1-4]. However it is well known that high quality material can be grown at low cost using Liquid Phase Epitaxy (LPE) but it has serious disadvantages for the growth of very small structures due to the high initial growth speed and the large interface transition layers. In a previous work it was shown that it is possible to grow Ga_xIn_{1-x}As Quantum Dots (QD) on GaAs substrates by LPE [5]. Normally in this technique the crystallization is driven by the supercooling of the liquid phase. New experimental results show that Ga_xIn_{1-x}As QD’s can be grown from under-saturated liquid phases. This is a very unusual effect in LPE that deserves wider studies to fully understand the phenomena involved in the crystallization process. The growth conditions of the QD’s and a possible explanation for its formation is given in this work.

2. Experimental
The graphite boat used had a typical structure containing two parts. One part is a fixed body with cells for the liquid phases. Another part is a sliding rule to make contact between the substrate and the liquid phase [6]. The growth was done in a horizontal semitransparent furnace under a 30 cm³/min flow of high purity H₂. The GaAs substrates had n-type conductivity, Si doped with a free carrier concentration of 10¹⁶ cm⁻³ and with (100) orientation. The InAs used to prepare the liquid solutions...
was non-intentionally doped with free electron concentration near $10^{17}$ cm$^{-3}$. 6N In was used as solvent. Prior to the growth experiments the GaAs substrates were chemically etched in the well known mixture of $1$ H$_2$O$_2$: $5$ H$_2$SO$_4$: $1$ H$_2$O. The InAs crystals were etched with HCl only.

The experiments were carried out in two stages. During the first stage, different As saturated In solutions were prepared in contact with an InAs “substrate” for 60 minutes at different temperatures from 414 to 450 °C. The InAs “substrate” weight losses allowed us to calculate the composition of the liquid phases.

In the second stage, the reactor was opened to remove the InAs used as source for saturation and it was replaced by a GaAs substrate. The growth temperature for all experiments was fixed at 444 °C and the growth time was 5 s. In this way the degree of under-saturation of the In-As solution was exactly known.

The morphology of the prepared samples was studied by Atom Force Microscope (AFM). The photoluminescence spectra were measured at 24 K in a closed cycle refrigerator using a 50 mW Ar laser tuned at 514 nm for excitation and collecting the emission with a 50 cm spectrometer. A Ge photodiode and a conventional lock-in amplifier were used for detection.

3. Results and discussion

Some results and the associated growth conditions are shown in table 1. In this table the amount of As in liquid phase was determined from the measurements of the weight losses of the InAs “substrate” as described above.

| Sample | Saturation Temperature (°C) | ΔT (°C) | $X_{As}^L$ (10$^{-3}$ mol) | Surface |
|--------|-----------------------------|---------|--------------------------|---------|
| fe102  | 450                         | + 6     | 6.618                    | No QDs  |
| fe104  | 438                         | - 6     | 5.413                    | QDs     |
| fe105  | 432                         | - 12    | 4.704                    | QDs     |
| fe106  | 426                         | - 18    | 3.990                    | QDs     |
| fe107  | 414                         | - 30    | 3.525                    | No QDs  |

As it can be seen the QDs are formed only inside some limited range of under-saturation degree ($ΔT$). The AFM images of some samples are shown in figure 1. The highest density of QDs was achieved in the sample with -18 degrees of under-cooling in its liquid phase.

![AFM images of samples](image-url)

**Figure 1.** Surfaces from different samples grown from under-saturated liquid phases. a) Sample fe104, shows a low density of QDs; $ΔT$= -6 °C. b) Sample fe105, after grown from a liquid phase with 12 °C under-saturation. c) Fe106 presents the highest density (7.2x10$^9$ QD/cm$^2$).

We also measured photoluminescence spectra for all samples. In samples where the AFM image show the presence of QDs, the emission spectra have two peaks, one corresponds to the emission of the substrate (1.48eV) and the other one shows a peak whose energy (1.33eV) can be related to QDs luminescence as reported in literature[7-9]. The highest intensity of this second peak was observed in the sample with the highest density of QDs as shown in figure 2.
The same peak is observed in the other samples but due to its low intensity we do not show it here. This small intensity is connected to the low density of QDs observed under the AFM.

![Figure 2. Photoluminescence spectra of sample fe104, taken at 25 K showing the substrate (1.48 eV) and QDs (1.34 eV) emissions.](image)

It is well known that the driving force for crystallization is the super-saturation of the nutrient phase. However in our case, in spite that the liquid phase was under-saturated, it was possible to deposit some material on the GaAs substrate. Since the volume of the crystallized material is very small and the lattice mismatch is large enough, the formation of QD’s is possible in our experiments.

A possible explanation could be based in the transient processes that take place between liquid and solid phases which are not in equilibrium. In the first moment of contact GaAs dissolves into the under-saturated In-As liquid solution. From In-Ga-As liquidus isotherm it is possible to see that the solubility of As in the melt decreases when Ga is added to the liquid phase [10-13] it is reasonable to suppose that near the substrate surface the dissolved GaAs turns the solution to supersaturated inducing a transitory crystallization. These crystallizations are observed in the AFM images as islands whose size and density depend on the experimental conditions.

3. Conclusions
It is shown experimentally that structures with QDs can be grown by LPE under very unusual conditions, i.e. from non-saturated liquid phases.

A possible explanation for these effects is suggested and is based on a transient phenomena occurring in a non-equilibrium system.

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