Role of the wetting layer in the crystallization stage during droplet epitaxy of InAs/GaAs nanostructures

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Abstract. In this paper, we present the results of experimental study of the role of the wetting layer in the crystallization stage of droplet nanostructures in the lattice-mismatched InAs/GaAs material system. We demonstrate that the thickness of the wetting layer can significantly affect the characteristics of nanostructures formed during crystallization in the arsenic flux. While the surface density of InAs nanostructures does not increase relatively to the initial droplet density obtained at 300 °C, a significant increase of the nanostructure density is observed after crystallization of droplets obtained at 200 °C. This behaviour is attributed to the additional stress-driven Stranski-Krastanov quantum dot formation and confirmed by the 2D-3D transformation of indium layer obtained at 100 °C.

1. Introduction
Droplet epitaxy is a promising technology that has many advantages over other molecular beam epitaxy (MBE) techniques, including those based on the Stranski-Krastanov growth mode [1-9]. The technique allows obtaining a wide variety of nanostructures: quantum dots [7,10-11], single and multiple quantum rings [12,13], nanoscale disks [14], hybrid nanostructures with metal clusters and complexes based on them [15-17]. At the same time, unlike the Stranski-Krastanov growth mode, droplet epitaxy does not require lattice mismatch to produce quantum dots, which makes it possible to use it for the quantum dot formation in almost any material system of AIIIBy group which is remarkable for its unique electronic, optical and technological properties [18-25]. However, the influence of processes occurring in the wetting layer of lattice-mismatched systems during the crystallization stage has not yet been studied. This is especially important due to the presence of a pronounced temperature dependence of the wetting layer thickness [26].

The purpose of this work is to study the effect of the wetting layer thickness on the characteristics of InAs/GaAs quantum-size structure arrays during the stage of crystallization in the arsenic flux.

2. Experimental procedure
The samples were grown on GaAs(001) epi-ready substrates in a SemiTEq STE 35 MBE system with solid-state sources of arsenic and group III elements. The growth procedure was monitored by an in situ reflection high-energy electron diffraction (RHEED) system. After removal of a native surface oxide and annealing of the substrate under an excessive As flux, a flat GaAs surface was formed by
growing a 250 nm thick buffer layer at a substrate temperature \( T \) of 580 °C and a nominal growth rate \( v \) of 1 ML/s which is typical for MBE growth of a GaAs buffer layer [27-30]. Then, the substrate temperature was gradually decreased to 520 °C and the valved As cell was closed to discontinue the supply of \( \text{As}_4 \).

After the background pressure was reduced to \( \sim 1 \cdot 10^{-7} \text{ Pa} \), the substrate temperature was decreased to a temperature of In deposition measured by thermocouple. The RHEED pattern showed a characteristic \((2\times4)\) surface reconstruction over the entire cooling period. Then, In atoms were deposited at a nominal growth rate of 0.25 ML/s (preliminarily calibrated by the growth of InGaAs ternary compounds) during 6, 10 and 12 s at deposition temperatures of 300, 200 and 100 °C, respectively, which yielded an amount of indium material corresponding to 1.5, 2.5 and 3.0 monolayers (ML) of InAs. Then, the samples were quenched and transferred out of the chamber for the scanning electron microscopy (SEM) and atomic force microscopy (AFM) characterization.

In order to study the influence of the wetting layer on the crystallization processes, we exposed the metallic layers under As flux equivalent to that used for the growth of GaAs buffer layer and annealed them during 10 min at \( T = 400 \) °C. Then, the samples were re-examined by SEM and AFM methods.

3. Results and discussion

Deposition of 1.5 ML of In at \( T = 300\)°C leads to the formation of droplets with an average diameter of 80 nm and surface density of \(9.1 \cdot 10^7\) cm\(^{-2}\) (Figure 1a). As demonstrated in our previous study [26], critical thickness of droplet formation at an increment of the deposition thickness equal to 0.25 ML is 0.75 ML, i.e. droplets do not form until at least 1 ML of indium is deposited. Therefore, we can conclude that approximately 0.75 ML of material is consumed to form droplets while 0.75 ML remains on the surface as a wetting layer.

![Figure 1(a, b). Morphology of the InAs/GaAs(001) droplet epitaxial system after (a) deposition of 1.5 ML of In at \( T = 300\)°C; (b) subsequent crystallization of metallic droplets in the As flux.](image)

After crystallization of this system in the arsenic flux, a slight increase in the nanostructure size up to 90 nm is observed (Figure 1b). This increase is not unexpected since droplets absorb As atoms in an approximate ratio 1:1 to a number of In atoms in a droplet. However, droplets do not increase twice in size because an average interatomic distance in In crystal is larger than in InAs crystal. A similar size increase of InAs nanostructures in comparison with In droplets was observed elsewhere [11].

Arsenic crystallization of In droplets obtained at \( T = 300\)°C does not increase the surface density of nanostructures. Moreover, it leads to a decrease of their surface density from \(9.1 \cdot 10^7\) to \(4.5 \cdot 10^7\) cm\(^{-2}\) (Figure 1b). Although this phenomenon can be a result of an accidental error during droplet array formation, the difference in values can also be due to the diffusion decay of droplets under the As flux.
It was previously shown in many studies that In atoms migrate outwards from droplet when exposed by a low-value arsenic flux or at a high crystallization temperature [31-33].

At a lower temperature (200°C) a deposition thickness of 1.5 ML is not sufficient to form droplets [26], therefore 2.5 ML of indium was deposited with subsequent formation of metallic droplets (Figure 2a). Crystallization of this system in the arsenic flux led to a sudden change in the density of InAs/GaAs nanostructures by an order of magnitude – from 2,2·10⁸ to 1,1·10⁹ см⁻² (Figure 2). Due to the introduction of an additional component into the composition of droplet nanostructures, their average size also increases from 60 to 80 nm.

![Figure 2(a, b). Morphology of the InAs/GaAs(001) droplet epitaxial system after (a) deposition of 2.5 ML of In at T = 200°C; (b) subsequent crystallization of metallic droplets in the As flux.](image)

We suppose that the increase in the surface density is due to the fact that under these conditions the thickness of the wetting layer is about 2.0 ML. This value significantly exceeds the critical thickness for the Stranski-Krastanov growth mode. Therefore, under high temperature conditions, an additional contribution to the InAs nanostructure formation is observed, due to the transformation of an overstressed two-dimensional wetting layer into three-dimensional crystalline islands.

![Figure 3(a, b). Morphology of the InAs/GaAs(001) droplet epitaxial system after (a) deposition of 3.0 ML of In at T = 100°C; (b) subsequent crystallization of metallic layer in the As flux.](image)
In order to confirm the phenomenon of Straski-Krastanov nanostructure formation, we decreased the deposition temperature down to 100°C and deposit larger amount of material so that droplet did not form. A deposition thickness of 3 ML was sufficient to observe a continuous two-dimensional layer on the surface with no droplets formed (Figure 3a). Then, we crystallized the overheated indium layer in the arsenic flux at a high temperature of 500°C. As a result of this process, the formation of InAs/GaAs nanostructures with a high surface density of $2 \times 10^{10} \text{cm}^{-2}$ was observed on the surface (Figure 3b).

The most probable reason of this phenomena is the strain-induced transformation of the wetting layer by the Stranski-Krastanov growth mechanism [34]. Formation of InAs nanostructures when no droplets were formed after deposition of indium was previously shown elsewhere [35]. Whereas indium two-dimensional layer is defective and presumably has an amorphous structure, InAs layer formed as a result of arsenic incorporation has a relatively similar lattice constant as compared to GaAs crystal. This leads to the emergence of stresses which are a driving force for the 2D-3D-transition of the wetting layer [36]. As a result, an array of InAs quantum dots is formed on the surface but it should be born in mind that the wetting layer may still exist on the surface.

Thus, the arsenic crystallization of In/GaAs systems obtained by droplet epitaxy may lead to both a decrease and an increase in the surface density of nanostructures depending on the wetting layer thickness. Furthermore, the formation of InAs nanostructures after crystallization of the two-dimensional layer is possible. Besides these phenomena must be taken into account when the crystallization of In nanostructures with specified parameters is carried out, they may be used intentionally to control the geometrical parameters of nanostructures.

4. Conclusions
In order to achieve maximum correspondence between the parameters of In droplet arrays in the first and of InAs crystalline nanostructure in second stages during droplet epitaxy, crystallization should be carried out under conditions under which the wetting layer thickness does not exceed 1.5 ML. Crystallization of an indium layer obtained at a low temperature and a large deposition thickness may lead to a formation of additional nanostructures which are not crystallized metallic droplets but nanostructures emerged from the stressed wetting layer.

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