Effect of the ultra-low arsenic flux on characteristics of In(As) nanostructures formed during droplet epitaxy

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Abstract. In this paper, we present the results of an experimental study of the influence of the ultra-low arsenic flux on the parameters of In nanodroplets obtained by droplet epitaxy on the GaAs substrate. We demonstrate that the arsenic flux can be used to alter the size of droplets without changing their surface density. An increase in the arsenic flux leads to a reduction of the nanostructure size or their complete decay. However, we demonstrate that certain growth conditions allow providing saturation of the size of nanostructures (~30 nm) which ensures good reproducibility of the process. The mechanism of ring and hole formation at various arsenic fluxes is also discussed.

1. Introduction

One of the most significant challenges in modern electronic and photonic devices is a possibility to control characteristics of single nanostructures [1-6]. Applications of quantum communication and computing require operation with single quantum dots with defined parameters [7-9]. Traditional methods of quantum dot formation suffer from an inter-dependence of quantum dot size and surface density which makes it difficult to fabricate small-size nanostructures sufficiently distant from each other [10-13].

Droplet epitaxy is a method of A3B5 nanostructure growth which allows two-stage formation of nanostructures, namely deposition of metal and its further crystallization in the group-V flux [7-9,14-21]. Due to the possibility to control nanostructure parameters at both stages, this method allows formation of low-density droplet arrays with the subsequent altering of their size before the crystallization process. However, a value of the arsenic flux is important to prevent premature fixation of the nanostructure size or their spreading over the surface.

In this paper, we carry out an experimental study of the ultra-low arsenic flux effect on the characteristics of indium droplets formed on the GaAs(001) surface.

2. Experiment

For experimental study, we first prepared GaAs(001) epi-ready substrates by standard oxide removal and further 400-nm buffer layer growth. Then we closed the arsenic valve and cooled down the substrate to a deposition temperature of 300°C. After the background pressure reduced to a value below 1·10⁻⁷ Pa (P₀), we formed droplet arrays on GaAs(001) substrates by deposition of 3.0 and 1.5
equivalent monolayers (ML) of indium. Then we exposed the samples to arsenic fluxes of various ultra-low values.

A clear (2 × 4) reconstruction was observed on the surface by the reflection high-energy electron diffraction (RHEED) prior to the indium deposition. After the indium deposition, a RHEED pattern became hazy and spotty indicating the appearance of metal on the surface [22,23]. No significant changes in the RHEED pattern were observed with further exposure of indium droplets to the ultra-low arsenic flux.

After shutting the arsenic valve, we additionally held the samples in the growth chamber during 5 minutes while cooling down. Then, we transferred the substrates out of the growth chamber and sent them to a scanning electron microscope (SEM) Nova NanoLab 600 and atomic force microscope (AFM) NTEGRA to measure the geometrical parameters of nanostructures.

3. Results and discussion

As we observed previously [24,25], deposition of 3.0 ML and 1.5 ML of indium on the GaAs(001) surface at a temperature of 300°C leads to the formation of arrays of droplets with an average diameter of about 150 nm and 100 nm, respectively, and a surface density at a level of 7 · 10^7 cm⁻² in both cases. Exposure of In droplets to the arsenic flux is normally used to crystallize them into InAs nanostructures requiring further capping for the quantum dot formation. However, we used arsenic fluxes of ultra-low values in order to alter the droplet size without their transformation into InAs nanodots, nanorings or nanoholes.

![SEM images of nanostructures obtained after deposition of 3 ML of indium and further exposure to the ultra-low arsenic flux: (a) P/P₀ = 4; (b) P/P₀ = 6; (c) P/P₀ = 8.1. The 250 × 250 nm² insets demonstrate scaled-up nanostructures.](image)

We demonstrate that an increase in the As pressure ratio leads first to a simple reduction of the average droplet size (Figure 1a). With further increasing arsenic flux, the formation of a ring is observed along the droplet initial perimeter while the droplet is still decreasing in size (Figure 1b,c). It is commonly known that droplet parameters change as a result of the arsenic irradiation and successfully used for the formation of nanorings [26,27] and nanoholes [28,29]. However, we observe that the droplet size can be altered before the final crystallization into InAs nanostructure.

Figure 2 demonstrates As flux dependences of the average diameter of droplets, rings and holes after deposition of 3.0 ML and 1.5 ML of In. While arsenic flux increases, droplets tend to decrease in size. Droplets obtained after deposition of 3.0 ML and 1.5 ML transform into droplet-ring complexes at P/P₀ = 6 and 1.4, respectively, so that the ring diameter is approximately equal to the initial droplet size. The ring forms at the interface of three phases due to an increase in the As concentration and, hence, In to InAs crystallization intensity.

It is worth noting that a reduction of droplets without the formation of rings and holes is possible with increasing arsenic flux (Figure 2, 3.0 ML, P/P₀ from 1 to 6). Furthermore, the droplet size is saturated and becomes equal to approximately 30 nm after reaching a certain arsenic flux value.
This behavior of the growth system enables a controllable reduction of the droplet size and good reproducibility of this process.

Figure 2. Arsenic pressure ratio dependences of the average diameter of droplets obtained after deposition of 1.5 and 3 ML of indium and their further exposure to ultra-low arsenic flux. The caps represent standard deviations of the diameter of nanostructures.

Despite the fact that the study of droplets obtained after deposition of 3 ML of indium demonstrates a clear picture of what occurs on the surface during their exposure to the ultra-low arsenic flux, this amount of deposited material leads to the formation of large droplets which are difficult to transform into optically efficient quantum dots. Therefore, we also exposed droplets formed after the deposition of 1.5 ML (critical thickness for droplet formation at a temperature of 300°C [24]) of indium to the arsenic flux. The surface density of droplets was found to be at the level of $7 \times 10^7$ cm$^{-2}$ as in the case of 3.0 ML. An increase in the arsenic flux also led to the shrinkage of droplets (Figure 2). However, droplets obtained at 1.5 ML are initially smaller in size and less stable, as a result of which the droplet reduction was more abrupt and an arsenic pressure at which droplet-ring complexes formed was shifted to the left (to $P/P_0 = 1.4$).

Although the substrate temperature in a series of experiments remained unchanged (300°C), in the case of exposure of 1.5-ML droplets to the arsenic flux, the hole formation was observed (Figure 2). Whereas the ring diameter was still equal to the initial droplet diameter, the diameter of holes tended to saturate as well as droplets in the case of 3.0-ML droplets to a value of about 30 nm (Figure 2). A typical ring-hole complex formed after exposure of droplets obtained at 1.5 ML to the arsenic flux of value above $P/P_0 = 4$ is presented in Figure 3.

The observation of etching phenomena during the arsenic irradiation of droplets is associated with a significant influence of arsenic flux on the chemical composition of a droplet. As a result of the diffusion of arsenic into the droplet, the equilibrium concentration of atoms in the droplet changes. In order to restore the initial volume atom ratio, compensation of deficient atoms of metal is needed. Because In atoms diffused out of the droplet spreading over the surface, their places are occupied by the nearest Ga atoms belonging to the substrate [30]. Thus, Ga atoms migrate from the substrate leading to the formation of the hole at the place of the droplet (Figure 3).

4. Conclusion

Thus, an independent control of the size of nanostructures can be achieved by using an exposure of droplets to the ultra-low As flux. In order to obtain droplets of a small size to further crystallize them into optically efficient InAs quantum dots, a minimum value of the ultra-low As flux and long exposure times should be used. Otherwise, the formation of rings and holes is possible which can in turn be useful for some specific applications.
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