The influence of temperature and arsenic molecular form at crystallization stage on the InAs nanostructure growth during droplet epitaxy

N E Chernenko, S V Balakirev, M M Eremenko and M S Solodovnik

Institute of Nanotechnologies, Electronics and Equipment Engineering, Southern Federal University, Taganrog 347922, Russia

nchernenko@sfedu.ru

Abstract. In this work, experimental studies of the influence of the arsenic molecular form (dimer or tetramer) and substrate temperature on the crystallization of In/GaAs droplet nanostructures during droplet epitaxy have been carried out. We have shown the critical influence of the temperature and arsenic molecular form on the reproducibility of the characteristics of an array of self-organizing InAs nanostructures during crystallization. We also showed that a decrease in the initial In droplet size has a positive effect on the reproducibility of the parameters of the InAs nanostructures arrays. Our work also showed important role of substrate temperature at the crystallization stage.

1. Introduction
Droplet epitaxy is currently one of the most interesting methods of molecular beam epitaxy due to its capabilities in the formation of semiconductor and hybrid nanostructures [1 – 4]. In turn, these structures have great potential for the creation of nanophotonic elements and devices, sources of single and entangled photons, and promising computing platforms on their basis [5 – 7]. Quantum-dimensional structures obtained by the droplet epitaxy technique differ from nanostructures obtained by the Stransky-Krastanov growth method not only in the variety of shapes, but also in functional characteristics, which is due to a number of specific processes underlying the mechanism of droplet nanostructure formation [8 – 12]. At the same time, despite a number of advantages, the use of this technology is still very limited due to its complexity and a huge number of control parameters [4, 13 – 19]. This is especially true of the crystallization stage when metal nanodroplets transform into crystalline semiconductor nanostructures [20 – 23]. It should also be noted separately that the GaAs/AlGaAs system remains the most studied system, while In-containing systems have practically not been studied.

The goal of this work was experimental study the effect of droplet crystallization temperature and arsenic molecular form on the crystallization of indium nanodroplet structures with different initial sizes and their transformation into InAs nanostructures during droplet epitaxy.

2. Experiment
For experimental study, we used GaAs (100) epi-ready wafers. After oxide native removal at substrate temperature of 580°C and growth of buffer layer with thickness of 250 nm we closed all sources. Then substrate temperature was cooled down to droplet deposition temperature. The droplet formation
The sample temperature was 150℃ and 300℃. Effective thickness of indium deposition was 3.0 for all samples to guarantee obtain droplet structures in the entire range of conditions under consideration.

Then we exposed obtained samples under identical conditions in equivalent arsenic fluxes at two different cracking zone temperatures of the valve source, providing arsenic supply in the form of dimers (As₂) or tetramers (As₄) and different substrate temperature during crystallization. Additionally, we also changed the temperature of the substrate at the crystallization stage to establish the relationship between the morphological characteristics of the arrays of droplet and crystalline nanostructures.

After the completion of the nanostructure formation all samples was examination by atomic force and electron microscopy techniques to obtain information about morphology and density of InAs nanostructures.

3. Results and discussion

Our experimental studies have shown that the crystallization temperature has a crucial effect on InAs nanostructure formation. As it can be seen from Figure 1, decreasing of temperature during crystallization stage from 500°C to 400°C leads to suppression of separate InAs quantum dot synthesis and the stage-by-stage formation of the nanodots + ring + diffusion disk and diffusion disk (without any dots) systems at lowest sample temperature. Moreover, it should be noted that a decrease in temperature at the stage of crystallization does not lead to a change in the density of InAs/GaAs structures, only their morphology.

At the same time, in the high-temperature region, there are no diffuse regions around the nanostructures, which may indicate that most of the indium remained in the droplet and transformed into the InAs nanocrystals. In this case, the initial In droplet size is practically irrelevant – the results obtained for various thicknesses of indium deposition correlate well with each other. We believe that this behavior of the system can be due to both thermodynamic and kinetic factors that directly affect the reaction between the metal and arsenic.

**Figure 1.** SEM images of InAs nanostructures, obtained during crystallization of In nanodroplets using As₄ flux at different temperatures: (a) 500°C, (b) 450°C, (c) 400°C.

The study of arsenic molecular form influence has shown that the use of tetramers (As₄) makes it possible to obtain crystal InAs nanostructures which correlate in their parameters (size, density) with their predecessors – an ensemble of In nanodroplets. This is true over the entire range of temperatures under consideration.

It is important to note that with a decrease in the initial size of In droplet nanostructures, the degree of their correlation with the final size of InAs crystal nanostructures increases, and their morphology also improves. As it can be seen from comparative analysis of images shown in the Figure 2a and Figure 3b InAs structures obtained at low temperature and having a small initial size have a pyramidal shape with clear edges, which is characteristic of quantum dots. Whereas large metal nanodroplet obtained at high temperature transform to flower-like nanostructures during crystallization stage. It is important to note that this result is very similar to the results obtained in the previous step. Therefore, apparently, we can say that the droplet crystallization process is largely limited precisely by kinetic factors.
Figure 2. SEM images of InAs nanostructures obtained by crystallization of In droplets in a fluxes of arsenic tetramers (a) and dimers (b) after deposition of 3.0 ML at growth temperature of 300°C.

In the case of dimers, the situation is completely different. On the one hand, the use of a flux of arsenic dimers leads to the formation of structures with a diameter of 20 – 50 nm in the entire range of considered conditions (Figure 2b and Figure 3b).

At the same time, the correlation between the parameters of the ensemble of metal nanodroplets and the final crystal structures is practically not observed either in density or in size – regardless of the initial density and the initial size of the structures after crystallization, approximately the same picture is observed. The difference between InAs crystal structures obtained using different arsenic forms increases with increasing growth temperature. As it can be seen from SEM images in Figure 2 and Figure 3, for low-temperature samples (small initial droplet size), the indium structures are not very different in size and density for the crystal structures obtained using tetramers (Figure 3a). Although they have a wide variation in size and shapes.

Figure 2. SEM images of InAs nanostructures obtained by crystallization of In droplets in a fluxes of arsenic tetramers (a) and dimers (b) after deposition of 3.0 ML at growth temperature of 150°C.

At the same time, high-temperature samples are characterized by a more uniform size distribution with a much larger discrepancy between the droplet and crystal structure sizes. This effect of the molecular form of arsenic may be due to the different kinetics of the reactions occurring during the crystallization process using di- and tetramers.
4. Conclusion
Thus, we have shown that the crystallization temperature is extremely important for the controlled and reproducible production of crystalline InAs/GaAs nanostructures in droplet epitaxy. It is shown that an increase in crystallization temperature leads to an improvement in the correlation of parameters between the arrays of droplet and crystalline nanostructures. It was also shown that the use of dimers significantly alters the crystallization processes, in contrast to tetramers. This leads to the fact that during crystallization in the case of using arsenic dimer fluxes, there is no correlation in size and density between droplets and crystal nanostructures. Therefore, the use of arsenic tetramers at the crystallization stage seems to be preferable in InAs droplet epitaxy.

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