Droplet epitaxy of GaAs nanostructures on the As-stabilized GaAs(001) surface

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Abstract. The paper presents the results of experimental studies of the formation of self-assembled Ga and GaAs nanostructures on the As-stabilized GaAs(001) surface by droplet epitaxy. The results of investigations of the influence of the effective deposition thickness and surface temperature on the characteristics of arrays of formed structures are presented. The possibility of forming superdense arrays of GaAs nanostructures with a density of up to $4 \cdot 10^{11}$ cm$^{-2}$ is shown. Using a combination of in-situ removal of GaAs oxide and deposition with interruption, regular arrays of GaAs quantum dots of $78 \pm 6$ nm in size and a density of $4.6 \cdot 10^8$ cm$^{-2}$ are obtained at temperatures above 500°C on the GaAs(001) surface structured by local anodic oxidation technique.

1. Introduction

The analysis of instrumental applications of arrays of self-organizing nanostructures (quantum dots, nanowires, nanoclusters, etc.) shows the need for precise control of the resulting structures characteristics: size, density, mutual arrangement, etc [1–8]. The existing methods for the formation of quantum dots using the technology of molecular beam epitaxy are based on the Stransky-Krastanov mechanism – the elastic relaxation of mechanical stresses in lattice mismatched systems. In this technique the growth is achieved by the simultaneous deposition of components of III and V groups. The disadvantages of this approach are the need for the mismatch of crystal lattices and the interdependence between the density and the size of quantum dots formed by such a mechanism [9, 10], which sharply narrows the range of combinations of materials and limits the scope of their application. The weakening of the negative correlation can be achieved through the use of various technological methods (structured surfaces, submonolayer epitaxy, etc.), but obtaining arrays of quantum dots with ultra-low density is still very difficult [11–13].

At the same time, droplet epitaxy, based on separate and sequential deposition of the components of groups III and V, allows not only independently to control the density and size of quantum dots, but also to form quantum dots in any $A^3B^5$ systems [14–16]. Moreover, the method is promising for the integration of low-dimensional $A^3B^5$ systems with silicon technology, as well as for creating hybrid metal/semiconductor systems of great interest for optoelectronics and THz devices due to the appearance of plasmon effects. The use of multi-stage droplet epitaxy techniques makes it possible to effectively minimize the influence of negative factors associated with pre-surface treatment of the surface in the case of using modified substrates, which also advantageously distinguishes this method from other $A^3B^5$ quantum dot synthesis techniques.
The purpose of this work is to experimentally study the formation of various types of GaAs nanostructures on an As-stabilized GaAs(001) surface by droplet epitaxy.

2. Description of the model

Experimental studies were carried out on a molecular-beam epitaxy system SemiTEq STE 35, equipped with solid-state sources of group III components and a valve arsenic source. A GaAs(001) epi-ready wafers were used as growth substrates. In-situ growth control was carried out by observation of RHEED pattern. The temperature $T$ in the 450-600°C range was monitored by a pyrometer, and below 450°C it was controlled by a thermocouple, previously calibrated according to the procedure [17]. After standard procedure of native oxide thermal desorption at 580°C with subsequent surface smoothing by annealing in As$_4$ flux, GaAs buffer layer 500 nm thick was grown at 590°C and growth rate 1 ML/s. Then the source Ga was closed and the substrate cooled to a growth temperature. The source of As$_4$ was closed at 550°C to provide As-surface stabilized conditions and surface reconstruction (2×4).

In the first part of study, the effect of droplet epitaxy parameters – effective deposition thickness and substrate temperature – on the sizes and density of Ga droplets was studied.

The substrate temperature was varied from 150°C to 450°C. The thickness of Ga deposition $H$ was calibrated by the oscillations in the intensity of the RHEED pattern and was varied in the 3-4 MLs range. The effective growth rate $V$ for all samples was 0.5 ML/s. The reconstruction (2×4) was maintained during the cooling, which indicates that there is no accumulation of additional excess arsenic on the surface. After the substrate was cooled to a predetermined temperature, a Ga source was opened and Ga droplets were formed. At the same time, the surface reconstruction in the low-temperature region (up to 300°C) changed from (2×4) to 1×, and at temperatures above 300°C it was changed by 2×.

In the second part of the experiment, after the formation of the GaAs buffer layer, the substrates were removed from the growth chamber, subjected to structuring by local anodic oxidation (LAO), and then used to study growth on modified surfaces. To increase the growth selectivity deposition of Ga was carried out at 500°C with interruptions of 60 s after each 1 ML, which on the one hand made it possible to provide relatively high surface mobility of Ga adatoms, and on the other, to eliminate desorption and rearrangement of the modified regions of the substrate. With the same purpose, the Ga deposition rate was reduced to 0.25 ML/s. After Ga deposition and droplet formation, the samples were exposed in an As$_4$ flux during 15 min at the same temperature, after which the substrate was cooled to room temperature. For comparison, the growth was carried out on flat and modified substrates. After growth, all samples were investigated by AFM and SEM.

3. Results and discussion

As was mentioned in section 2, in the first part of the experiment, the influence of the growth temperature and deposition thickness in the process of droplet MBE on the density and dimensions of the Ga nanostructures formed, without the crystallization stage, was studied. Figure 1 shows SEM images of Ga droplets obtained at an effective deposition thickness of 4 ML and a growth rate of 4 ML/s and different substrate temperatures. It is seen that as the growth temperature increases, the average droplet size increases, and their density, on the contrary, is expected to decrease, which is caused by an increase in the surface mobility of Ga adatoms. Thus, at $T = 150°C$, the density of the structures is $3.6 \times 10^{11} \text{cm}^{-2}$ with an average diameter of $4.54 \pm 3.53 \text{nm}$ (according to AFM measurements). With an increase in temperature to 450°C, the droplet density decreases by an order of magnitude to $3.36 \times 10^{10} \text{cm}^{-2}$, and the diameter increases to $17.65 \pm 9.8 \text{nm}$. The size dispersion thus decreases from 78% to 55%, respectively, which is also related to the growth of the diffusion length of adatoms Ga and the intensification of the exchange processes between droplets of various sizes.
Figure 1. SEM images of GaAs(001) surface after Ga deposition at $H = 4$ ML and different growth temperature: a) $T = 200^\circ$C, b) $T = 300^\circ$C, c) $T = 400^\circ$C. The scale bar is 100 nm.

Figure 2 shows the approximation of the AFM data for the dependence of the density and diameters of Ga droplets on the growth temperature at different effective thicknesses of deposition. It can be seen that a decrease in the thickness of deposition from 4 to 3 ML practically does not affect the density of the formed droplets. The discrepancy between the values is in the range of 4-6%, which is significantly lower than the measurement error. At the same time, the diameter of the Ga droplets decreases, on average, by 24% over the entire temperature range: from $4.54 \pm 3.53$ nm to $3.67 \pm 2.54$ nm at $T = 150^\circ$C and from $17.65 \pm 9.8$ nm to $14.12 \pm 9.4$ nm at $T = 450^\circ$C.

Figure 2. Temperature dependencies of Ga droplet density (a) and diameter (b) at different effective thicknesses: $H = 4$ ML (red) and $H = 3$ ML (blue). Dots – experimental data, line – approximation.

In the second part of the work, we investigated the processes of droplet epitaxy on LAO-modified substrates. After the epitaxial layer surface was structured by the LAO method, a GaAs oxide film was formed on the samples. Therefore, an in-situ removal of the oxide was first carried out according to the procedure [17–19]. We have experimentally determined that to completely remove the oxide layer at a temperature of 500$^\circ$C, it is necessary to deposit about 6 ML of Ga. Then part of the structured samples was extracted, and the relief studies were performed by the AFM technique. It was found that with selected LAO regimes, pits with a depth of $6 \pm 1$ nm and a diameter of $182 \pm 29$ nm were formed on the surface with a rms surface roughness of 0.1 nm.
Thus, taking into account the sacrificial Ga layer with a thickness of 6 ML and an effective deposition thickness of 4 ML, the total thickness of the Ga deposition on the structured substrates was 10 ML.

The density of Ga droplets on the flat areas of all the samples was $2 \cdot 10^8 \text{cm}^{-2}$ with an average droplet diameter of $255 \pm 78 \text{ nm}$ and a height of $31 \pm 3 \text{ nm}$ (Fig. 3a). Such a rapid increase in droplet sizes and a decrease in density with a slight (at 50°C) increase in temperature in comparison with the results obtained in the first stage of the study is primarily due to a decrease in the growth rate to 0.25 ML/s.

![Figure 3](image3.png)

**Figure 3.** AFM images of GaAs(001) surface after Ga deposition by droplet MBE: a) Ga droplets before annealing under As$_4$ flux, b) GaAs nanostructures after annealing under As$_4$ flux.

![Figure 4](image4.png)

**Figure 4.** AFM image of GaAs quantum dot regular array obtained on LAO modified GaAs(001) surface by droplet MBE.

After the formation of Ga droplets, their crystallization in the As$_4$ flux was carried out at a constant surface temperature. On unmodified areas of samples, Ga droplets were transformed into disc-shaped structures with pits in the place of droplets (Fig. 3b). The height of the disk was 20 nm above the level
of the initial surface of epitaxial layer. The average radius of the formed disks was $262 \pm 37$ nm and is limited, apparently, by the diffusion length of Ga adatoms under the given conditions. It should be noted that the set value correlates well with the work data [20, 21].

On modified LAO sites, after annealing in the As$_4$ flux, regular arrays of GaAs quantum dots were formed, whose density was equal to the density of the formed pits and amounted to $4.6 \cdot 10^8$ cm$^{-2}$ (Fig. 4). The size of the formed quantum dots was $78 \pm 6$ nm, and the degree of filling of the pits was 89%. As can be seen from the presented data, the density of Ga droplets (and GaAs quantum dots) is 2.5 times higher in comparison with unmodified areas, and the size of the structures is 3 times smaller. The obtained ratios of the values of the densities and the diameters of the structures for different sample regions are in good agreement with the redistribution of the material during the Ga deposition due to the stimulated by high temperature and low growth rate in the absence of arsenic and desorption. Since the distances between LAO-formed pits (500 nm) are less than twice the value of the diffusion length of Ga adatoms, determined earlier by us, the growth of structures is suppressed by diffusion gathering into the pits.

4. Conclusion
Experimental studies of the droplet epitaxy of arrays of self-organizing GaAs nanostructures (droplets and quantum dots) on an As-stabilized GaAs(001) surface are carried out. The possibility of obtaining ordered arrays of Ga droplets with a density up to $4 \cdot 10^{11}$ cm$^{-2}$ is shown. The possibility of independent control of the density and size of the structures formed by droplet epitaxy is experimentally confirmed. The regimes for the formation of regular arrays of Ga droplets and GaAs quantum dots with reduced dispersion on the LAO-modified surfaces at relatively high growth temperatures are determined. Moreover, it was shown, in this case the density of the structures is set, in the first place, by the parameters of the modified substrate.

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References
[1] Kianpoura M, Sabbaghi-Nadooshanb R and Navic K 2014 J. Computer and System Sc. 80 1404–14
[2] Karimia M J, Rezaei G and Nazaria M 2014 J. of Luminescence 145 55–60
[3] Ageev O A, Solodovnik M S, Balakirev S V, Eremenko M M and Mikhailin I A 2016 J. of Phys.: Conf. Series 741(1) 012012
[4] Shahazadeh M and Sabaeian M 2014 Superlattices and Microstructures 75 514–522
[5] Ageev O A, Konoplev B G, Rubashkina M V, Rukomoikin A V, Smirnov V A and Solodovnik M S 2014 Nanotech. in Rus. 8 23–28
[6] Ramos E, R. Franco R, Silva-Valencia J and Figueira M S 2014 Physica E 64 39–44.
[7] Ageev O A, Solodovnik M S, Balakirev S V and Eremenko M M 2016 Phys. of the Solid State 58(5) 1045–1052
[8] Sayahian J A and Rezarei G 2015 Physica B 456 103–107
[9] Wang Z M 2008 Self-assembled quantum dots (Springer) 468 p
[10] Atkinson P, Schmidt O G, Bremmer S P and Ritchie D A 2008 C.R. Physique 9 88–803
[11] Lee B C, Lin S D, Lee C P, Lee H M, Wu J C and Sun K W 2002 Appl. Phys. Lett. 2. 326–328
[12] Ageev O A, Smirnov V A, Solodovnik M S, Rukomoikin A V and Avilov V I 2012 Semiconductors 46(13) 1616–1621
[13] M. Zander M, Nishinaga J, Iga K and Horikoshi Y 2011 J. Cryst. Growth 323 9–12
[14] Panyakeow S 2009 Engineering J. 13(1) 51–56
[15] Mano T, Watanabe K, Tsukamoto S, Fujioka H, Oshima M and Koguchi N 1999 Jpn. J. Appl. Phys. 38 1009–11
[16] Lee J H, Wang Z M and Salamo G J 2009 IEEE Transactions on Nanotech. 8(4) 431–36
[17] Avilov V I, Ageev O A, Smirnov V A, Solodovnik M S and Tsukanova O G 2015 Nanotech. in Rus. 10(3-4) 214–219
[18] Atkinson P, Schmidt O G 2009 J. Cryst. Growth 311 1815–18
[19] Asaoka Y 2003 J. Cryst. Growth 251 40–45
[20] Ageev O A, Solodovnik M S, Balakirev S V, Eremenko M M and Mikhailin I A 2017 J. Cryst. Growth 457 46–51
[21] Ageev O A, Solodovnik M S, Balakirev S V and Eremenko M M 2016 J. Vac. Sci. Technol. B 34(4) 041804