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Multistage droplet epitaxy for the fabrication of InAs/GaAs quantum dots with ultra-low density

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Abstract. In this paper, we demonstrate a novel technique enabling fabrication of small-sized InAs/GaAs quantum dots with a very low surface density during droplet epitaxy. In contrast to the traditional two-stage approach, we introduce an additional stage of exposure to the ultra-low arsenic flux which enables partial diffusion decay of droplets with a large initial size. While exposure of droplets to large arsenic fluxes leads to their transformation into rings, disks and holes, exposure to the ultra-low flux makes it possible to reduce the volume of droplets maintaining their initial surface density. At the following stages of crystallization and annealing, In droplets are converted into InAs quantum dots with an average diameter below 30 nm and a surface density below 10^8 cm^{-2}. The standard deviation of quantum dot diameters is found to be less than 5%. Furthermore, we demonstrate that the growth procedure is well-reproducible, which makes it a promising method of quantum dot fabrication for advanced nanophotonic devices.

Keywords: droplet epitaxy, InAs/GaAs, nanostructures, quantum dots

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Многостадийная капельная эпитаксия для формирования квантовых точек InAs/GaAs со сверхнизкой плотностью

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Аннотация. В данной статье демонстрируется новая методика, позволяющая получать квантовые точки InAs/GaAs малого размера с низкой поверхностной плотностью в процессе капельной эпитаксии. Особенность подхода заключается во введении дополнительной стадии экспозиции капель в ультрамалом потоке мышьяка, которая позволяет обеспечить частичный диффузионный распад капель с большим исходным размером при сохранении их исходной поверхностной плотности, после чего на стадиях кристаллизации и отжига капли In преобразуются в однородные массивы квантовых точек InAs с диаметром менее 30 нм и поверхностной плотностью менее 10^8 см$^{-2}$.

Ключевые слова. капельная эпитаксия, In/GaAs, наноструктуры, квантовые точки

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Introduction

Today, studies of physical processes and phenomena in epitaxial nanostructures, such as quantum dots and rings, nanowires, tunnel-coupled heterostructures etc., are on their top because of their possible applicability in promising widely used quantum photonic and nanoelectronic devices [1]. Both fundamental and applied aspects of the nanostructure fabrication are also of great importance [2]. Although various methods of A3B5 quantum dot formation have been developed for their further use in high-efficiency semiconductor devices [3], a method of droplet epitaxy remains one of the most advantageous due to its flexibility and possibilities for the growth of various nanostructures excluding wetting layer formation [4, 5]. Because droplet epitaxial growth of nanostructures is carried out in two main stages – deposition of metal atoms forming droplets and their crystallization in the group-V vapor – it becomes possible to alter surface density and geometrical parameters of nanostructures independently [6, 7]. Low-density droplets are usually obtained at high substrate temperatures leading to a concomitant increase in their size [5, 8]. Large droplets cannot be then converted to compact quantum dots suitable for photonic and electronic applications. Meanwhile, quantum dots with ultra-low density are actively used for the fabrication of single and entangled photon emitters, in which case they must be well-isolated from each other [9].

In this paper, we demonstrate a technique of multistage droplet epitaxy which makes it possible to form single InAs quantum dots with an appropriate size (~25 nm) and an ultra-low density ($\sim 3 \cdot 10^7$ cm^{-2}). The peculiarity of our technique consists in the introduction of an additional stage of droplet epitaxy between droplet formation and crystallization, namely exposure of indium droplets to the arsenic flux of an ultra-low value (10^{-7}–10^{-6} Pa) which we demonstrated previously [6]. As a result of this exposure, indium atoms diffuse out of the droplets inducing their reduction in volume. Subsequent high-temperature crystallization of shrunk droplets enables formation of low-density semiconductor quantum dot arrays suitable for production of single quantum dot single and entangled photon sources on their basis.

Materials and Methods

The samples were grown in a SemiTEq STE35 molecular beam epitaxy system with solid-state sources on epi-ready GaAs substrates with the (001) orientation. The native oxide was removed by heating the substrate to 600 °C under a pressure of As_4 $P = 4 \cdot 10^{-5}$ Pa. Then, a GaAs buffer layer with a thickness of 250 nm was grown at a temperature of 580 °C at a growth rate of 1 monolayer (ML) per second. Next, the substrate was cooled down to the deposition temperature T = 300 °C with the arsenic valve completely closed. In order to monitor the growth process *in situ* and calibrate the growth rates, a reflection high-energy electron diffraction system was used in the growth chamber.

At the first stage of droplet epitaxy procedure, 1.5 equivalent ML of indium were deposited on the surface of the GaAs(001) substrate at a growth rate of 0.25 ML/s. At the next stage, droplets formed on samples A were exposed to an As_4 flux of various values (P/P_0 from 1 to 929 where $P_0 = 7 \cdot 10^{-8}$ Pa is a background pressure) and were kept in the growth chamber during 5 minutes after closing the arsenic valve. Substrates with droplets on samples B were brought to T = 200 °C, 300 °C, 400 °C and 500 °C and then exposed to the arsenic flux P/P_0 = 714 with immediate substrate heating to 500 °C. For two of group B samples, a period t between substrate heating and arsenic supply was 60 and 180 seconds. Droplets on samples C were exposed to an ultra-low arsenic flux, after which they were arsenized at $T = 500$ °C and $P/P_0 = 714$.

At the last stage, all samples were unloaded and characterized using FEI Nova Nanolab scanning electron microscope (SEM) and NT-MDT NTEGRA atomic force microscope (AFM).

Results and discussion

The average diameter of droplets obtained after deposition of 1.5 ML of indium on the GaAs(001) surface at $T = 300$ °C is found to be 98 nm (Fig. 1, *a*). Exposure of the droplets to the arsenic flux leads to the formation of various nanostructures and their complexes [10]. A low arsenic flux is traditionally applied to transform In droplets into InAs rings [11] or to etch the surface under the droplets [12–14]. However, we use fluxes of ultra-low values (below 10^{-6} Pa) to demonstrate that droplets can be reduced in size under their exposure due to the phenomenon of diffusion decay [6]. As a result, a decrease in the droplet size from 98 to 18 nm is observed after exposure to the arsenic flux of various values P/P_0 in a range from 1 to 2.9. Because of the crystallization at a boundary of three phases, the formation of InAs ring also occurred around the original droplet circle (Fig. 1, *b*) The ring diameter does not change significantly with increasing P confirming the assumption about the nature of its formation.

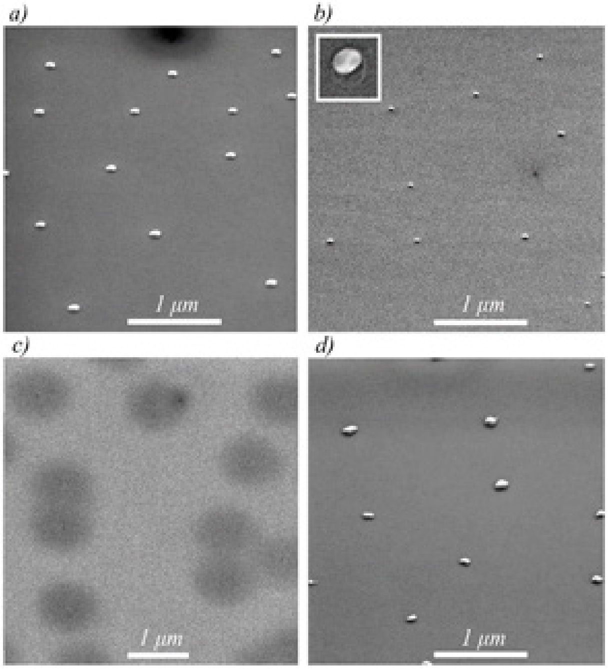

Fig. 1. SEM images of nanostructures obtained after deposition of 1.5 ML of indium and subsequent exposure to the arsenic flux P/P_0: 1 (*a*); 1.4 (*b*); 500 (*c*); 714 with the simultaneous substrate heating up to 500 °C (*d*). Inset area is 150×150 nm².

An increase in the arsenic flux P/P_0 from 4 to 10 induces droplet etching of the surface leading to the formation of a hole under the initial droplet position. The droplet etching, also known as "nanodrilling", is a process typical for high-temperature droplet epitaxy [15]. However, it is also observed in a range of low temperatures when the exposing arsenic flux is not very large [6]. The holes are found to have a diameter of about 40 nm surrounded by the original droplet ring with the depth of approximately 2 nm.

A significant increase in the arsenic flux (P/P_0 from 70 to 929) leads to the complete diffusion decay of droplets with their spreading over the surface within a disk-shaped area (Fig. 1, *c*). The average diameter of these disks ranges from 674 to 885 nm. More thorough consideration of the disk areas allows another observation of crystallized InAs rings at the place of original droplets. This indicates that the three-phase boundary crystallization has a higher rate among all the microscopic processes. At the same time, we found out previously that the droplet decay without ring formation is still possible in case of minimum arsenic fluxes when droplets have a larger size [6].

A transition to high-temperature exposure (at $T = 500$ °C) leads to a qualitative change in the growth system. Droplets do not decay into monolayer-high disks but convert into faceted nanostructures (dots) (Fig. 1, *d*). The average diameter of dots obtained after the high-temperature arsenic exposure without a pause between the arsenic supply and substrate heating (heating expectation time $t = 0$ s) is 102 nm. However, we also study the dependence of the dot parameters on this time period. An increase in t from 0 to 60 and 180 seconds leads to a decrease in the diameter of dots from 102 to 87 nm and to 38 nm, respectively (Fig. 2). The reduction of dots with increasing expectation time is attributed to the fact that droplets decay during the arsenic exposure without heating rather than crystallize. However, as soon as the substrate reaches a certain temperature, crystallization becomes more preferable than the diffusion decay, and the remainders of droplets convert into faceted dots. The surface density of dots increases with increasing t from $3 \cdot 10^7$ to $9 \cdot 10^7$ cm^{-2} which is associated with the fact that droplets may break up into several parts during the high-temperature exposure.

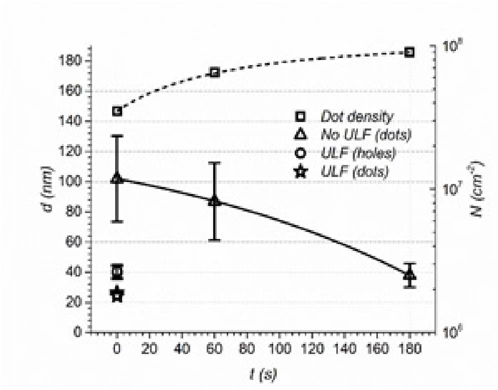

Fig. 2. Heating expectation time dependences of the diameter (triangles) and surface density (squares) of nanostructures obtained after deposition of 1.5 ML of indium and subsequent exposure to the arsenic flux $P/P_0 = 714$. Circles and stars denote diameters of holes and dots, respectively, obtained after two-stage exposure of droplets to the arsenic flux.

To obtain small-sized quantum dots with a value of the initial droplet density, we implement a two-stage exposure in the arsenic flux. At the first stage, the droplet volume is reduced to an optimal value under the influence of the ultra-low arsenic flux. At the final stage, a droplet with required parameters is crystallized into a semiconductor dot. Taking into account that the low-temperature arsenic exposure leads to the droplet decay and the high-temperature exposure allows fixation of the droplet shape with its further crystallization, we can select parameters at which dots have a size below 30 nm.

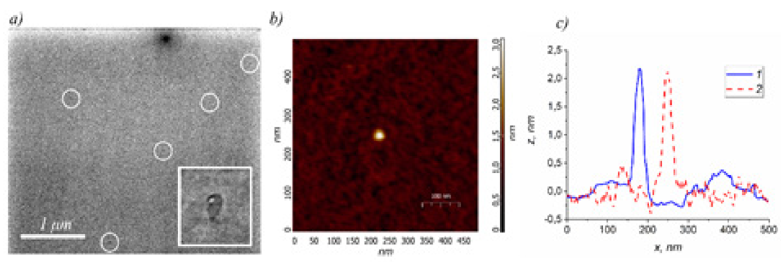

Fig. 3. SEM (*a*) and AFM (*b*) images of nanostructures obtained after deposition of 1.5 ML of indium and subsequent two-stage exposure to the arsenic flux. AFM (*c*) sections of typical nanostructures from Figure 4 *a*, *b*, *c*: 1) $P/P_0 = 2.0$, 2) $P/P_0 = 2.9$. Inset area is 150×150 nm^2

Figure 3 demonstrates our results of the two-stage exposure of droplets with various values of the ultra-low arsenic flux as an intermediate stage: $P/P_0 = 2$ (Fig. 3, *a*) and $P/P_0 = 2.9$ (Fig. 3, *b*). We observe that the resulting nanostructures represent dot-hole complexes wherein shallow holes surround nanodots. An average hole diameter is 40 nm, but it is not expected to have a significant influence on the optoelectronic properties of final structures. The main result consists in the formation of small-sized dots located at a great distance from each other (more than 1 μm on average). The surface density of dots is found to be $3 \cdot 10^7$ cm^{-2} whereas their average diameter/height is 27/2.8 nm for $P/P_0 = 2$ and 24/2.5 nm for $P/P_0 = 2.9$ (Fig. 3). The dots have a small size dispersion with 4% and 5% standard deviation of their diameter for $P/P_0 = 2$ and $P/P_0 = 2.9$, respectively. Moreover, it is important to note that the technological procedure has good reproducibility which is confirmed by the fact that low-density of small-sized dots were formed on various samples with different values of the ultra-low arsenic flux.

Conclusion

Using the multistage droplet epitaxial technique, we demonstrated the possibility of fabrication of low-density arrays of droplets that can be reduced in size and then transformed into semiconductor quantum dots. In contrast to the one-stage crystallization in the arsenic vapor, nanostructures obtained after the pre-exposure of large droplets to the ultra-low arsenic flux have a small size and a small size dispersion. Because an initial droplet array is set to have a low surface density, crystallized dots are also located at a large distance from each other making it possible to easily find and separate them. Furthermore, the process is demonstrated to be well-reproducible which is especially important in semiconductor technology. Thus, the results obtained open up great opportunities for the fabrication of single quantum dots for modern quantum photonic and nanoelectronic devices.

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