*Physics of the Solid State, 2022, Vol. 64, No. 8*

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# Study of the effect of ultra-low arsenic flux on the formation of In(As)/GaAs nanostructures by droplet epitaxy

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*Received April 12, 2022*
*Revised April 12, 2022*
*Accepted April 19, 2022*

In this paper, we present the results of studying the influence of arsenic pressure in the range of ultra-low values ($10^{-7}-10^{-6}$ Pa) on the processes of modification of In/GaAs(001) droplets with various initial sizes obtained by droplet epitaxy. We experimentally demonstrate that exposure of droplets to the ultralow arsenic flux makes it possible to reduce the droplet size to subcritical sizes while maintaining the initially specified surface density. The exposure of droplet nanostructures in the arsenic flux can be accompanied only by a decrease in their size, which is more typical for droplets obtained at large amounts of indium deposited material. For droplets with a smaller initial size, the formation of rings along the perimeter of the initial droplets and holes inside the rings is typical along with the droplet reduction. We also reveal that the dependence of the relative volume of droplets subjected to diffusion decay in the arsenic flux becomes more significant with a decrease in their initial size.

**Keywords:** droplet epitaxy, nanostructures, In(As)/GaAs, arsenic flux.

DOI: 10.21883/PSS.2022.08.54609.345

## 1. Introduction

The growing interest to semiconductor nanostructures, including quantum dots, and making of devices on their basis are largely conditioned by the transition of micro- and optoelectronics to the use of various quantum size effects occurring in such structures [1,2]. Thereat, nanostructures' functional characteristics are determined not only by their structural and physical/chemical properties, but also by their morphology — shape and size [3–5]. A special part in the technology of self-organizing semiconductor nanostructures is played by control of their surface density: depending on device purpose, structures both with high-density and low-density arrays of quantum dots are required [6–9]. In particular, high-efficiency sources of single and entangled photons of the near infrared band should be created using structures with single InAs/GaAs quantum dots, which presupposes the formation of quantum dot arrays having a low surface density (not higher than $10^8-10^9\,\text{cm}^{-2}$) to enable their subsequent isolation from each other [10,11]. However, the traditional method for the making of InAs/GaAs quantum dots using the Stranski–Krastanov mechanism has several shortcomings chiefly related to the fundamental limitation (due to the mechanism of their formation) of possibilities for independent control of nanostructures' surface density, shape and size [12,13]. At the same time, this shortcoming is eliminated in the droplet epitaxy technology [14], where the formation of $A^3B^5$ quantum dots is multi-stage with a number of phases: deposition of droplets of group III atoms, correction of shape and crystallization in a flow of group V molecules, as well as annealing of the obtained nanostructures. A selection of process parameters at each growth stage ensures control of nanostructures' shape, size and surface density in a wide range [7,15,16]. However, even in case of the said approach there is the still unsolved and topical problem of creation of quantum dot arrays in an InAs/GaAs system, which have ultra-low density ($< 10^8\,\text{cm}^{-2}$) and small structure sizes ($< 30\,\text{nm}$) at the same time (such parameters are necessary for the making of nanoelectronics and nanophotonics devices on their basis) [17].

Thanks to the multi-stage nature of droplet epitaxy, this method can be used to form quantum dots [7,11], quantum-dot molecules [18], quantum rings [19], nanosized recesses [20] and other types of nanostructures [21]. As a rule, the arsenic flux is used in the droplet epitaxy method to change the nanostructure shape and/or transform metal droplets into semiconductor nanostructures. Quantum dots are traditionally obtained using relatively large arsenic fluxes ($> 10^{-5}-10^{-4}$ Pa) and low temperatures ($< 250^\circ$C) [7,22], which largely hinders the attainment of a high optical quality of nanostructures [23]. At the same time, relatively small arsenic fluxes and high temperatures are used for formation of quantum rings and nanosized recesses (droplet etching) [21,24]. We have demonstrated [25], that ultra-low arsenic fluxes can be used to stimulate the diffusional decay of droplet In/GaAs nanostructures, while chiefly suppressing the crystallization processes in the droplet bulk which cause the formation of InAs. As a result, droplets become smaller while retaining a constant surface density value.

In this paper we study the dependence of size of indium drops, obtained at the first phase of droplet epitaxy after deposition of different material amounts (i.e., with different deposition thicknesses $H$), on ultra-low arsenic flux $P$ that acts on the droplets during the second phase of droplet epitaxy. It is experimentally demonstrated that the arsenic flux most significantly affects small-sized droplets obtained at near-critical deposition thicknesses, but, at the same time, impact on larger droplets allows for better process controllability.

## 2. Experimental methods

Samples were grown in a SemiTEq STE35 molecular beam epitaxy unit (CJSC „NTO") with solid-state sources on GaAs substrates with orientation (001), „epi-ready"class. After the standard removal of the oxide, a buffer GaAs layer 400 nm thick was grown at 580°C with the rate of 1 monolayer (ML) per second. Then the substrate was cooled to the deposition temperature $T = 300°$C, the arsenic valve being fully closed.

Then indium was deposited in the thickness range corresponding to $1-3$ equivalent InAs monolayers, accompanied with formation of droplets having different sizes but approximately the same surface density. Right after the formation, the droplets were exposed to ultra-low arsenic flux assigned by the growth chamber pressure in the value range from $7.0 \cdot 10^{-8}$ to $1.1 \cdot 10^{-6}$ Pa.

An analysis of patterns of reflection high-energy electron diffraction (RHEED) has revealed absence of the initial reconstruction $(2 \times 4)$ on the GaAs surface after indium deposition. Subsequent exposure of indium droplets in an ultra-low arsenic flux did not cause a noticeable change in the RHEED pattern.

Sample morphology was studied using a Nova Nanolab 600 scanning electron-ion microscope (SEM) (FEI Company) and Ntegra atomic-force microscope (NT-MDT Spectrum Instruments).

## 3. Results and discussion

The results of the experimental studies have shown that the lower boundary of the size of droplets, formed after indium deposition on the GaAs(001) surface, is limited by the critical thickness of droplet formation [26] (Fig. 1). Reduction of the deposited material amount allows for a significant reduction of the average droplet diameter $d$ (e.g., from 155 to 65 nm at $T = 300°$C), but further size reduction is impossible due the nucleation threshold which increases with decrease of temperature of the substrate used for deposition [26,27]. The experimental dependences in Fig. 1 show shat, despite the gradual approach of the dependence of the average diameter of droplets, obtained at the critical deposition thickness, on substrate temperature to the saturation value, the minimum stable size of structures increases to values which prevent droplet transformation into optically active quantum dots. Droplet size reduction requires a substrate temperature reduction which inevitably causes an increase of nanostructures' surface density. At the same time, further reduction of the stable size of droplet nanostructures at a given substrate temperature by reduction of equivalent deposition thickness is impossible.

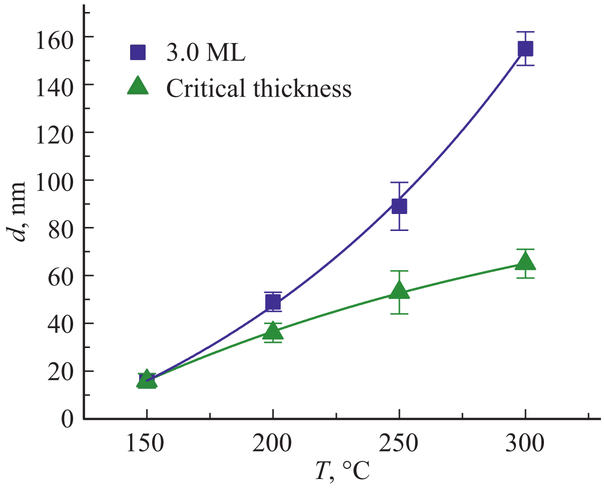

**Figure 1.** Average diameter of droplets obtained after deposition of 3.0 ML (blue square) and after deposition of a critical indium thickness (green triangles) vs. substrate temperature.

Our studies have shown that the limitation of the minimum droplet size can be overcome by post-correction of size of the already formed structures using an ultra-low arsenic flux. Fig. 2 shows the SEM-images of droplet nanostructures obtained after indium droplet exposure in different arsenic fluxes. The initial sizes of the droplets obtained at the thicknesses of 3.0 (Fig. 2, *a*) and 1.5 ML (Fig. 2, *d*), differ in more than 1.5 times (155 and 98 nm respectively). An increase of arsenic pressure at the droplet exposure phase leads to reduction of their average size due to diffusional decay caused by migration of metal (indium) atoms from the droplet to adjoining surface regions being enriched with arsenic. The equilibrium between a metal droplet and the metal-stabilized surface established directly after the formation of indium droplets is disrupted by the supplied arsenic flux due to the surface stabilization with arsenic. This results in a gradient of indium atom concentration between the droplet and the surface, which causes the diffusional decay of droplets.

The size of the droplet nanostructure, formed upon deposition of 3 ML of indium, occur initially (up to $P = 2.9 \cdot 10^{-7}$ Pa) without the formation of ring structures along the perimeter of the initial droplets (Fig. 3). However, rate of droplet crystallization at the boundary of three phases sharply increases at a certain arsenic flux ($P \geq 4.2 \cdot 10^{-7}$ Pa), and the droplet transforms into a „droplet-ring" complex (Fig. 2, *b, c, e–f*). Thereat, ring diameter does not decrease with an increase of arsenic flux pressure (Fig. 3), which confirms the nature of its formation related to crystallization of a droplet of the initial size at a triple point. At the same time, droplet structure size sharply decreases when ring structures appear and stabilizes

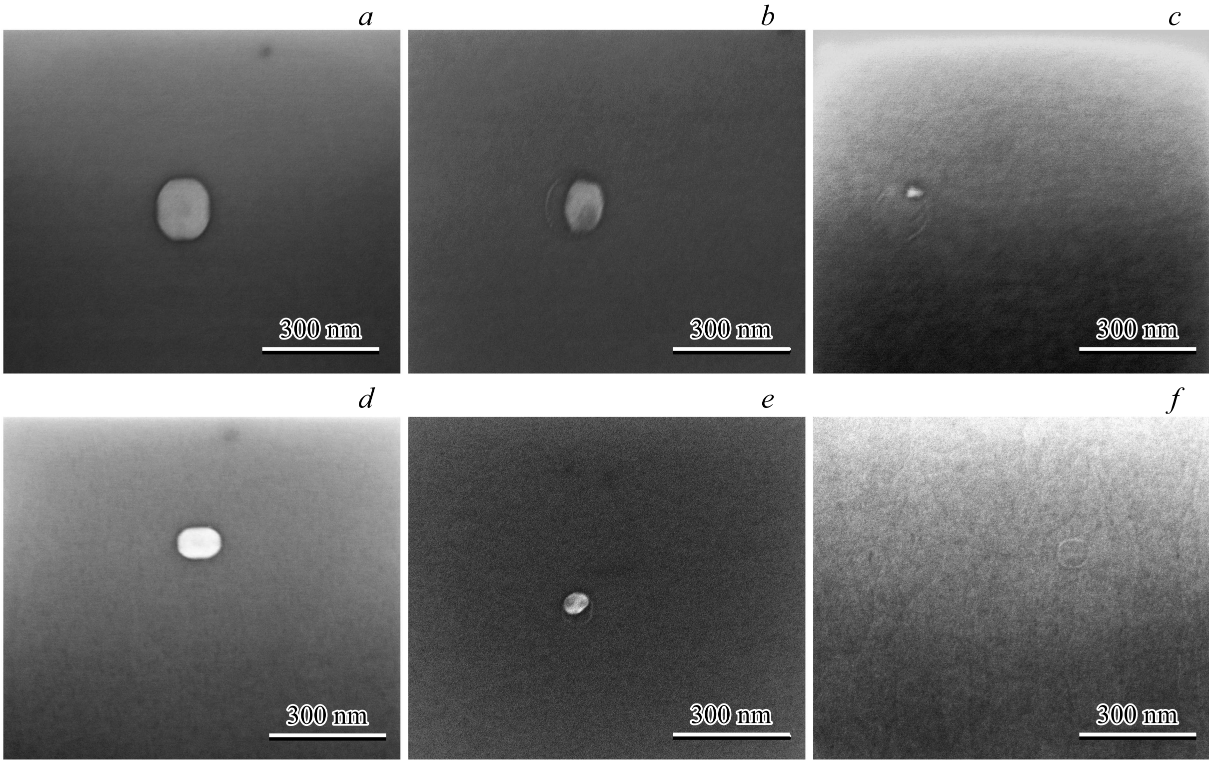

**Figure 2.** SEM-images of nanostructures obtained after deposition of 3.0 ML (upper row) and 1.5 ML (lower row) of indium, followed by exposure in arsenic flux at different pressures: *a*) $7.0 \cdot 10^{-8}$ Pa (3.0 ML), *b*) $4.2 \cdot 10^{-7}$ Pa (3.0 ML), *c*) $5.7 \cdot 10^{-7}$ Pa (3.0 ML), *d*) $7.0 \cdot 10^{-8}$ Pa (1.5 ML), *e*) $1.4 \cdot 10^{-7}$ Pa (1.5 ML), *f*) $2.9 \cdot 10^{-7}$ Pa (1.5 ML).

in the vicinity of about 30–35 nm, and does not change subsequently. We believe that stabilization can be caused by complete crystallization of the „droplet–ring“complex, i.e. an InAs „quantum dot–ring“complex forms.

The threshold value of arsenic flux, at which the formation of ring structures begins, for indium droplets, obtained at $H = 1.5$ ML, with a smaller initial size (98 nm at $T = 300°$C), shifts to the left (Fig. 3) and decreases to $1 \cdot 10^{-7}$ Pa due to a smaller initial volume of the droplet and, consequently, faster attainment of critical arsenic supersaturation in the droplet. Moreover, when the pressure $P = 2.9 \cdot 10^{-7}$ Pa is reached, nanosized recesses start forming due to activation of etching of the epitaxial layer surface by the droplet material (Fig. 3).

It should also be noted that when arsenic pressure increases to values over $5.7 \cdot 10^{-7}$ Pa, the surface is free even from traces of droplets obtained after depositing 1.5 ML of indium. Apparently, this is due to the fact that the rate of droplet diffusional decay considerably exceeds both the rate of crystallization and the rate of droplet etching.

Then several additional studies were performed with formation of droplets having an initial size from 65 nm (for $H = 1.0$ ML) to 155 nm (for $H = 3.0$ ML) with the interval of 0.5 ML. Then measurements of the droplet geometrical parameters were used to calculate their initial volume $V$ (before the arsenic flux impact), as well as residual volume $\Delta V$ — after the impact of various arsenic fluxes. Fig. 4 shows the relative residual volume of droplets vs. value of the acting arsenic flux (Fig. 4, *a*) and vs. deposition thickness at which the initial droplets were obtained (Fig. 4, *b*).

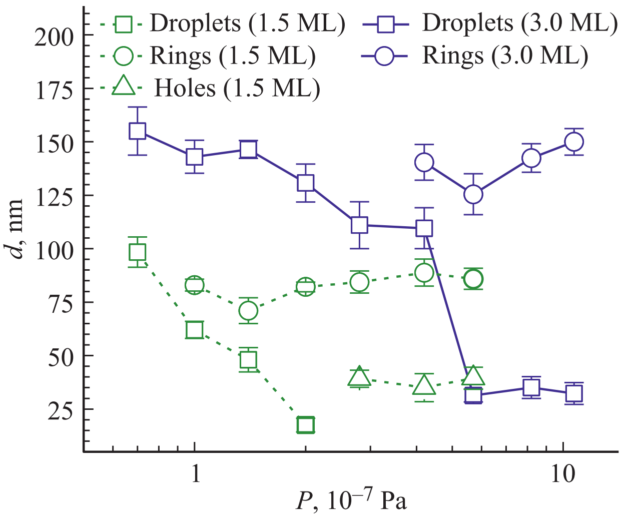

**Figure 3.** Dependences of average diameter of droplets, rings and recesses formed after the deposition of 3.0 ML (blue markers) and 1.5 ML (green markers) of indium, followed by exposure in different ultra-low arsenic fluxes.

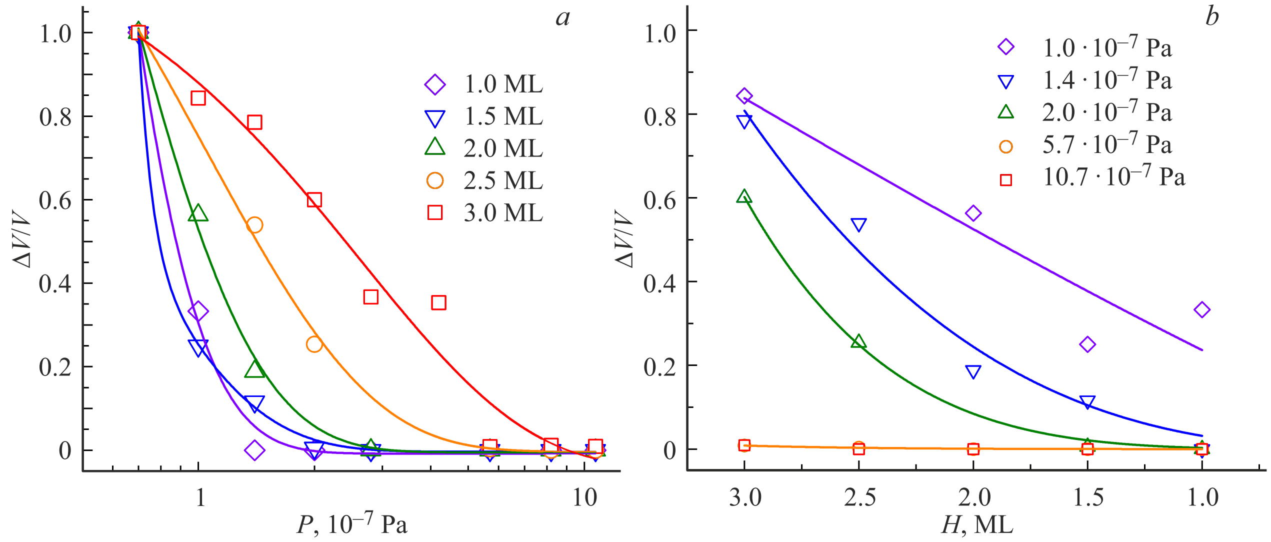

**Figure 4.** Average relative volume of droplets formed after deposition of different indium amounts, followed by exposure in different ultra-low arsenic fluxes: *a*) vs. value of arsenic flux, *b*) vs. deposited material amount.

The dependences shown in Fig. 4 make it possible to assume that sensitivity of indium droplets to arsenic flux considerably increases as the deposited material amount decreases. While the droplet volume in case of droplets obtained upon deposition of 3.0 ML of indium can be controlled in a wide range of arsenic pressures, diffusional decay of droplets obtained upon deposition of 1.0 ML of indium, which is the critical In/GaAs thickness for the given temperature [26], occurs almost instantaneously and is poorly controlled. However, an advantage of droplets with the smallest preliminary size is the minimization of indium material amount, which can distribute across the surface and affect the optical and electronic properties of a heterostructure with quantum dots forming in it [28]. From this viewpoint, a trade-off between the degree of control of droplet size reduction and reproducibility, on the one hand, and minimization of adverse impact of excessive material outside the nanostructures (in the wetting layer) — on the other hand, the thickness of 1.5 ML seems to be the optimal value of deposited material amount.

The dependences in Fig. 4, *b* also show that droplets having a large initial size are less exposed to the impact of an ultra-low arsenic flux — for $H = 3.0$ ML a change in the relative volume is from 0.843 to 0.009 in the pressure range of $1.0 \cdot 10^{-7}$ to $1.1 \cdot 10^{-6}$ Pa. As deposition thickness decreases and, consequently, the initial size of droplet nanostructures decreases, $\Delta V/V$ decreases from 0.843 to 0.333 at $P = 1.0 \cdot 10^{-7}$ Pa, which is due to intensified diffusional decay under the action of an ultra-low arsenic flux. We have also found that an arsenic pressure exceeding $1.1 \cdot 10^{-6}$ Pa results in almost complete decay of the droplets, which formed at any of the deposition thicknesses under consideration, when residual volume in relation to the initial volume is maximum 0.9%.

## 4. Conclusion

Thus, the performed studies have experimentally demonstrated that arsenic flux in the range of ultra-low values significantly affects the sizes of indium droplets obtained at different deposition thicknesses. Increase of the arsenic flux results in diffusional decay which leads to droplet volume decrease, while further increase also results in crystallization at the boundary of three phases with the formation of rings and droplet etching, accompanied with the formation of nanosized recesses in the regions where the droplets are initially located. Intensity of droplet volume decrease increases for droplets, obtained at smaller deposition thicknesses, which hinders their size control but allows for keeping the surface free from excessive material.

### Funding

The study was supported by the Russian Science Foundation (grant No. 19-79-10099) at Southern Federal University.

### Conflict of interest

The authors declare that they have no conflict of interest.

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