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# Experimental study of nanoholes formation using local droplet etching of FIB-modified GaAs (001) surface

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**Abstract.** In this work, we study of the effect of focused ion beam (FIB) and pre-growth treatment based on local droplet etching (LDE) techniques combination on the regular nanohole array formation on GaAs (001) surface, which can act as template for selective quantum dot formation in future. The results of the influence of the regimes of method combination on the nanohole shape and size are presented. Based on the analysis of Raman spectra, we have shown that the use of LDE-based technique makes it possible to almost restore the crystal structure of FIB-modified regions completely. The possibility of obtaining highly symmetrical, faceted by {101} and {011} planes nanoholes of various diameters and depths in selected surface points in one technological cycle is shown.

**Keywords:** focused ion beam, quantum dots, GaAs, molecular beam epitaxy, nanopatterning, local droplet etching

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# Экспериментальное исследование образования наноуглублений с помощью локального капельного травления модифицированной поверхности GaAs (001) фокусированным ионным пучком

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**Аннотация.** В данной работе представлены результаты экспериментальных исследования влияния сочетания модификации поверхности GaAs(001) методом фокусированных ионных пучков (ФИП) и последующей предростовой обработки на основе техники локального капельного травления на процессы формирования упорядоченных массивов углублений с целью их использования в дальнейшем для селективного роста квантовых точек. Представлены результаты исследований режимов в рамках используемого подхода на размеры и форму формируемых углублений. С помощью рамановской спектроскопии показано, что капельное травление позволяет практически полностью восстановить кристаллическую структуру подложки в области ФИП-модификации.

Также продемонстрирована возможность получения высокосимметричных, ограненных набором плоскостей {101} и {011} углублений различных размеров в заданных точках поверхности в рамках единого технологического цикла.

**Ключевые слова:** фокусированный ионный пучок, квантовые точки, GaAs, молекулярно-лучевая эпитаксия, наноструктурирование, локальное капельное травление

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## Introduction

To date, research is being actively conducted aimed at the possibility of flexible control of the parameters of quantum dots (QDs), which underlie the creation of a promising elemental base of quantum communications (sources of single and entangled photons) and quantum computing (quantum registers based on quantum dots) [1- 9]. The dependence of the functional characteristics of quantum dots on their composition, size, shape, and mutual arrangement in arrays requires the development of methods and technologies that allow one to effectively control the processes of formation of quantum dots and their final characteristics.

One of the most promising approaches in this respect is the use of combinations of epitaxial techniques with methods of pre-growth surface modification by forming an array of nanoholes at given points on the substrate. For pre-growth modification, electron-beam [10] and nanoimprint lithography [11] are most widely used today. However, traditional lithographic techniques are poorly compatible with subsequent epitaxial growth processes due to increased defect formation and/or surface contamination and do not provide the required quality of nanostructures.

Against this background, the technology of focused ion beams (FIB) compares favorably, which makes it possible to locally modify the sample surface under high vacuum conditions, without the use of resists, masks, and subsequent chemical surface treatment [12]. At the same time, ion bombardment of the surface during the FIB-treatment significantly damages the crystal structure of the substrate, which complicates the formation of optically active QDs in such nanoholes. Therefore, the use of FIB for these tasks requires the development of methods for reducing the defectiveness to an acceptable level or complete restoration of the substrate crystal structure.

In this work, to form ordered arrays of nanoholes for the subsequent selective QD growth, we propose to use a combination of modification of the GaAs(001) surface by the FIB method and subsequent pre-growth treatment based on the local droplet etching (LDE) technique. We have experimentally shown that, in this combination, the FIB method can be effectively used to localize the formation of Ga droplets with precision, and subsequent processing of samples based on droplet etching can be used to subsequently create highly symmetric nanoholes at modification points [13]. In this case, the droplet etching process is accompanied by the selective removal of amorphized and defects saturated near-surface regions at modification points. Experimental dependences of the influence of the dose of ion-beam treatment on the characteristics of the formed nanoholes in a single technological process are obtained.

## Materials and Methods

For experimental study we used epi-ready GaAs(001) substrates. FIB-modification of GaAs surface was carried out using a Nova NanoLab 600 scanning electron microscope (SEM) equipped with a FIB system with a Ga ion source. For this we formed point arrays 5×5 μm in size with distance of 1 μm between points using FIB treatment. We used ion beam with accelerating voltage of 10 kV and beam current of 0.3 pA. The Ga ion dose was given by changing number of beam passes in each point. The passes number N was varied from 1 to 300.

Then we used pre-growth treatment based on combination of high temperature annealing and LDE technique in SemiTEq STE 35 MBE setup to obtain arrays of local nanoholes at FIB-modification points on the GaAs substrate. All samples were studied by the SEM, AFM, and Raman spectroscopy before and after pre-growth treatment.

## Results and Discussion

An analysis of the AFM results showed that immediately after the FIB modification, starting from $N = 5$, an array of nanoholes is formed on the GaAs surface. In this case, the nanohole diameter increases with the increase in the number of FIB passes (and, accordingly, the dose of FIB-treatment) from 64 nm at $N = 5$ to 160 nm at $N = 300$. At same time the depth of the nanohole increases from 4.8 nm to 65.1 nm, respectively. Pre-growth treatment based on a combination of high-temperature annealing and local droplet etching leads to a transformation in the size and shape of the nanoholes. The structure diameter increases from 126 nm (at $N = 5$) to 310 nm (at $N = 300$), while the depth increases from 46 to 126 nm, respectively. In this case, as can be seen from the AFM profiles, the nanoholes become faceted. Analysis of the AFM profiles of nanoholes (Fig. 1, *a*) in different directions made it possible to determine the angle between the main faceting planes and the substrate plane, which is 45°.

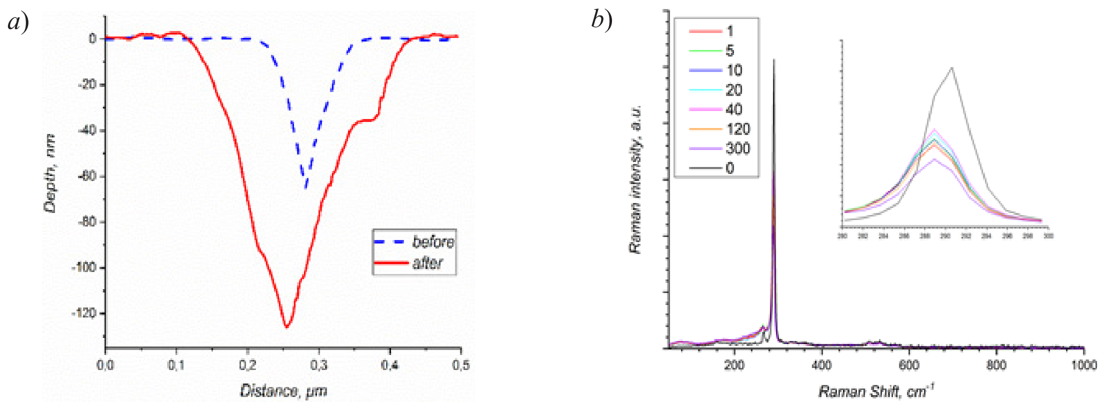


Fig. 1. AFM profiles of nanoholes before and after LDE-based treatment (*a*); Raman spectra from FIB-modified areas with different passes number (*b*)

The results of the study of samples by Raman spectroscopy are shown in Fig. 1, *b*. As can be seen from the presented spectra, an increase in the number of passes (dose of ion-beam treatment) leads to a decrease in the intensity of the LO-phonon line of crystalline GaAs – 291 $cm^{-1}$ – by about 1.5 times, which is due to saturation of the near-surface layers by defects in the crystal structure during processing. At the same time, at the points of modification, the LO-GaAs peak shifts by about 2 $cm^{-1}$ to the left relative to the unmodified surface, which can also be associated with distortions of the crystal structure that occur in the regions adjacent to nanoholes. It is important to note that the intensity of the line decreases sharply even at the 1 pass, further decreasing insignificantly (Fig. 1, *b*). This may indicate that the main contribution to the reduction is due precisely to the defective region, and not to the amorphous layer directly on the surface at the etch points. In this case, the length of the defect regions is determined mainly by the energy of the ions, which depends on the accelerating voltage. Thus, we can say that the dose affects the concentration of defects within the region specified by the beam accelerating voltage.

Analysis of SEM images (Fig. 2) showed that after pre-growth treatment based on local droplet etching, highly symmetric nanoholed are formed on the surface at modification points, which correlates with AFM data. Taking into account the previously measured angles between the main facets and the surface plane, as well as the mutual orientation relative to the wafer base cuts, we found that the main facets of the nanoholes belong to the {101} and {011} plane families (Fig. 2 *a*, *b*). Moreover, it is important to note that as the number of passes and, as a consequence, the size of the nanohole increase, the {111}A and {111}B planes begin to appear additionally (Fig. 2, *c*). In addition, as can be seen from the presented SEM images, at small passes, the

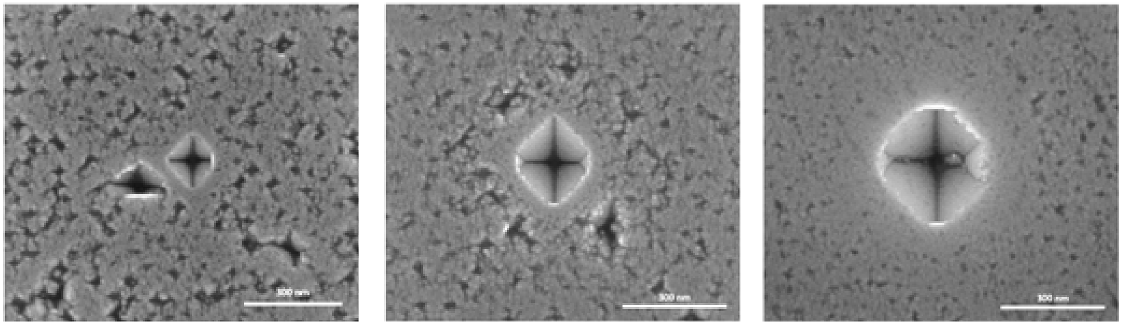

Fig. 2. SEM images of the GaAs (001) surface with nanoholes formed after LDE-based treatment of FIB-modified points with different number of FIB passes *N*: 5 (*a*), 40 (*b*), 300 (*c*)

surface around the nanoholes is inhomogeneous and has many disordered pits comparable in depth (up to 20 nm). However, as the treatment dose increases, an area of reduced roughness appears around the pits, which increases with the number of passes and the size of the hole. The high roughness of the unmodified areas is due to the processes of removal of native GaAs oxide at high temperatures. The formation of areas with reduced roughness is apparently due to the redeposition of the sputtered material during the FIB treatment, which at the LDE stage helps to remove the oxide, suppressing the etching processes on the surface.

Analysis of SEM images, taking into account information about the angles between the main faceting planes, made it possible to calculate the actual dimensions of the nanoholes and plot the corresponding dependencies (Fig. 3). As can be seen from the presented data, the nanohole diameters measured by AFM and those determined from SEM data are practically the same (Fig. 3, *a*). In this case, the lateral size of the structures after droplet etching increases by almost a factor of 2 compared to the initial one.

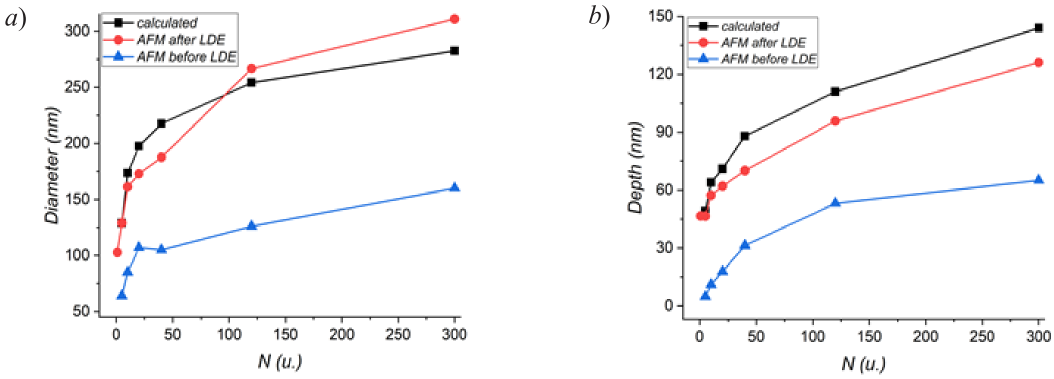


Fig. 3. Experimental dependences of the diameter (*a*) and depth (*b*) of the obtained nanoholes on the number of FIB passes before and after LDE-based treatment. Calculated – data based on SEM images analysis

We also showed a significant (many times) increase in the nanohole depth at the points of FIB-modification. If after FIB the nanohole depth changed, as mentioned earlier, from 4.8 to 65 nm (according to AFM data), then after LDE the calculated depth smoothly increases from 54 to 138 nm, i.e. 10 times – at low doses, and more than 2 times – at high ion doses. At the same time, as can be seen from the dependences, AFM underestimates the depth by approximately 10% in the entire measured range, which is due to the finite curvature of the AFM probe tip.

We attribute such a sharp and significant increase in the size of the modified cavities during pre-growth treatment to the anomalously high rate of anisotropic etching of the substrate by the Ga liquid droplet. This is due to the fact that, in contrast to the conventional LDE process, when the surface of the epitaxial layer with a high crystal structure perfection is subjected to local etching, in this case, much less stable regions with a disturbed crystal structure, saturated with defects and an excess of implanted Ga ions are etched. Thus, it can be assumed that the pre-growth treatment based on LDE technique proposed by us makes it possible to selectively remove almost the entire defective area around the modification points. This opens broad prospects for using the proposed approach for creating templates with the aim of subsequently obtaining site-controlled optically active quantum dots. And the possibility of obtaining highly symmetric nanoholes makes this technique suitable for controlling the shape of quantum dots, which is very important for creating sources of single and entangled photons.

## Conclusion

Thus, the results of experimental studies allow us to conclude that the use of a combination of the FIB and LDE methods is promising for creating ordered and highly symmetric nanoholes for obtaining regular (site-controlled) arrays of quantum dots of a given shape, size, and density. In addition, we have shown the possibility of obtaining holes of various sizes and shapes in a single technological cycle.

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