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Study of GaAs epitaxial growth on Si substrates modified by focused ion beams

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In this paper, we present a study of the effect of the silicon substrate modification by focused ion beams on subsequent growth of GaAs layers by molecular beam epitaxy. We demonstrate that when samples exposed to the ion irradiation at various accelerating voltages and ion beam passes are annealed in the absence of the arsenic flux, an increase in the depth of the modified Si substrate areas occurs. At the same time, crystallization of gallium accumulations during annealing in the arsenic flux leads to the filling of holes formed during the ion bombardment. We reveal that the growth of GaAs on substrates with areas modified at an accelerating voltage of 30 kV and subjected to subsequent annealing in the arsenic flux at a temperature of 600°C is accompanied by the formation of nanowires, the density of which increases within areas with a large number of ion beam passes. The results of the conducted research can be used for the development of technological approaches to the formation of GaAs epitaxial layers on Si substrates.

Keywords: molecular beam epitaxy, monolithic integration, gallium arsenide, silicon, focused ion beams.

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1. Introduction

Due to unique optical characteristics inherent to semiconductors of the A_3B_5 group, which are based on GaAs, these materials are actively used in modern optoelectronic devices. However, relative costliness of the A_3B_5 semiconductor heterostructures limits its further wide distribution. At the same time, due to its abundance and fabricability silicon forming the basis of the majority of semiconductor devices does not have similar optical properties in connection with an indirect band gap [1]. In connection therewith, more attention is paid to epitaxial growth of A_3B_5 semiconductor compounds on silicon substrates, in particular, to a monolithic integration method, which will supposedly combine light emission sources with high-speed data processing devices into a single chip [2,3]. It is expected that this will combine advantages of the GaAs technology (high-performance laser sources) and the Si technology (high-speed data processing) [4–7].

However, the qualitative GaAs growth on the silicon substrates is substantially limited due to a huge difference in parameters of the substrate lattice and the growth layer, thereby leading to generation and germination of non-conformance dislocations [7–9]. Moreover, the growth of an A_3B_5 polar semiconductor on a non-polar Si substrate leads to generation of anti-phase domains [7,8], so does the difference in thermal expansion factors of the materials — to intense generation of the dislocations and flaws, which can lead to cracking in a growing layer [10]. Using different methods of profiling and amorphization in combination with pregrowth surface preparation and formation of buffer layers allows not only localizing the structure on a certain area of the substrate, but reducing in orders a dislocation density in growing layers while reducing the thickness of the layers being grown [2,11–13]. However, development of the technology of growing qualitative GaAs layers on the Si substrates is significantly held by a lack of elaborated approaches to profiling and amorphization of the surface with subsequent preparation for the growth.

In the present work, we study initial stages of the formation of the GaAs layer on the Si substrates, which are profiled using a focused ion beams method (FIB). We evaluate the influence of parameters of ion irradiation used in the FIB method for formation of modified areas, and of subsequent annealing modes on nucleation and growth of the GaAs layer.

2. Experimental methods

The samples were produced using the molecular beam epitaxy system SemiTEq STE 35 (CJSC „NTO") with solid-state sources. The studies were carried out on the Si substrates with orientation (100) with areas of local

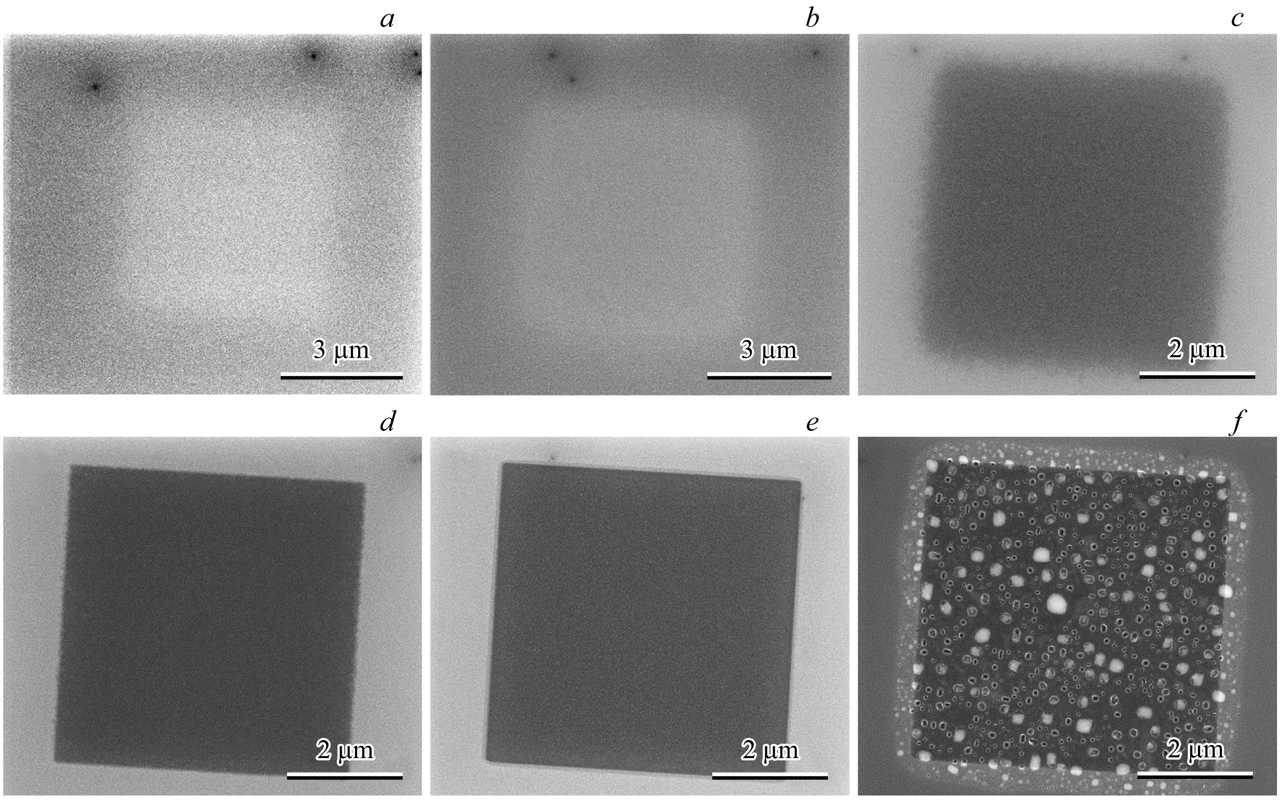

Figure 1. SEM-images of the silicon sample's surface areas exposed to FIB at different parameters: *a* — 5 kV, 5 passes; *b* — 5 kV, 30 passes; *c* — 5 kV, 200 passes; *d* — 30 kV, 5 passes; *e* — 30 kV, 30 passes; *f* — 30 kV, 200 passes — with subsequent annealing in the absence of the arsenic flux.

modification as arrays of squares of the sizes $5 \times 5\,\mu$m. The surface was modified by the FIB method using the scanning electron & ion microscope (SEM) Nova Nanolab 600 (FEI Company) at the modes of local implantation of Ga ions into the Si substrate. For the first group of the samples, the acceleration voltage was 5 kV (amperage — 29 pA), and for the second group — 30 kV (amperage — 30 pA). Each group of the samples was treated by FIB with a number of the passes: 5, 30 and 200.

The natural oxide was removed from the Si surface by annealing at 900°C in vacuum during 30 min [14]. Then the samples were annealed at $T = 600^\circ$C during 60 min in a no-arsenic medium or in the flux of As_4 of the pressure $P = 4 \cdot 10^{-5}$ Pa. Then, the high-temperature (600°C) GaAs layer of the thickness 200 nm was applied to the substrate surface at the rate of 0,25 of the monolayer per second by the molecular beam epitaxy method.

The morphology of the structures being formed was investigated by the SEM method and by the atomic force microscopy (AFM) as well in a probe nanolaboratory NTEGRA (CJSC „NT-MDT").

3. Results and discussion

The analysis of the SEM-images shown in the Fig. 1 means that changing a value of the acceleration voltage of the ion beam leads to the qualitative change of the morphology of the modified areas despite equal doses of ion irradiation. When the acceleration voltage is 5 kV, the boundaries of the squares are diffused (Fig. 1, *a*–*c*), whereas at 30 kV the modification is still uniform even after annealing (Fig. 1, *d*–*e*). With 200 passes of the ion beam at the voltage of 30 kV (Fig. 1, *f*), the surface included evident pores and foreign drops of various forms and sizes. Based on a number of ions injected into the surface during bombardment, it is logical to suppose that gallium clusters form drops, which etch the substrate and partially evaporate from the surface during the high-temperature annealing, leaving pores of a different depth. We correlate no similar morphology at 200 passes of the ion beam at the voltage of 5 kV (Fig. 1, *c*) to the fact that in this case the material is not so deep as in the case of 30 kV, thereby resulting in its more intense evaporation during the annealing. On the other hand, at the high acceleration voltage the depth of an implanted region is big, the material gradually comes out to the surface and fails to be fully desorbed during the annealing. Surface availability of modified pore areas can also be correlated to significant deformation of the Si surface during FIB treatment. It should be noted that during annealing in the absence of the arsenic flux, surfacing of the gallium atoms out of the depth of the substrate can increase defectiveness of the modified layer.

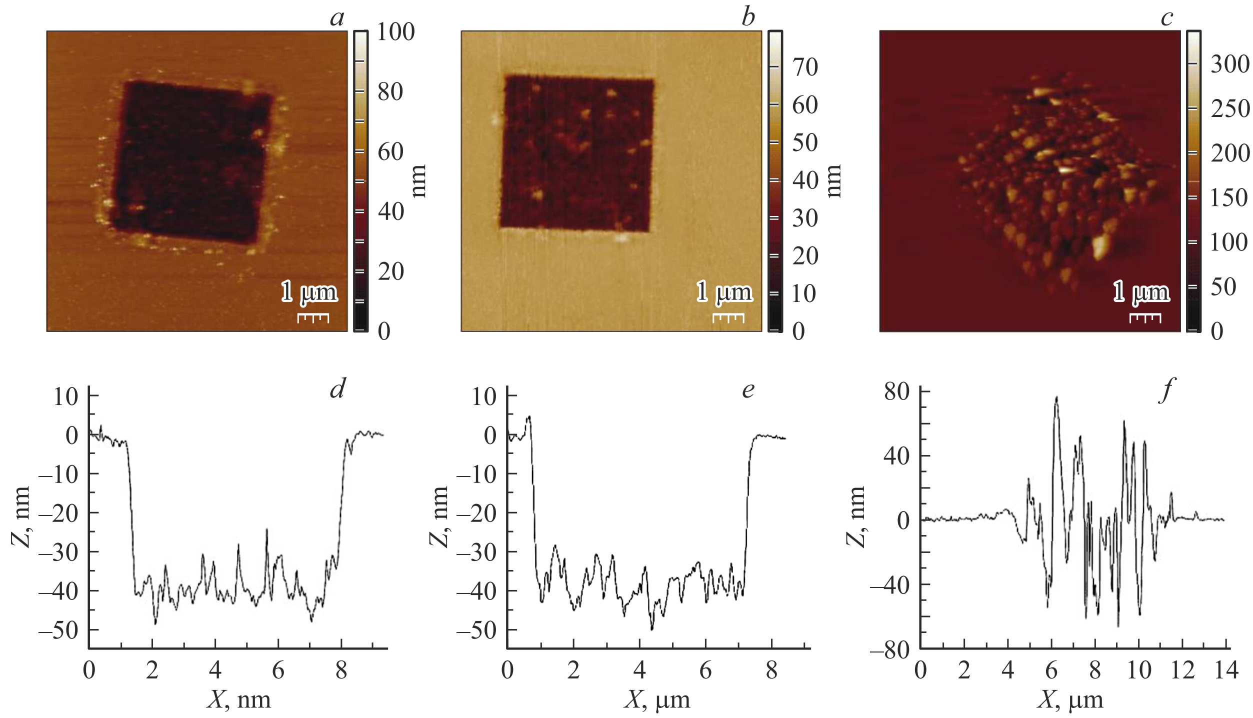

Figure 2. AFM-images of the silicon sample's surface areas exposed to FIB at the acceleration voltage of 30 kV and with 200 passes of the ion beam: *a* and *d*) prior to annealing, *b* and *e*) with subsequent annealing in the absence of the arsenic flux, *c* and *f*) with subsequent annealing in the arsenic flux.

The samples exposed to the ion irradiation at the acceleration voltage of 30 kV were additionally investigated by the AFM method (Fig. 2). With the increase in the number of the passes of the ion beam, the depth of the modified areas increases from 1,2 nm (5 passes) to 39 nm (200 passes) (Fig. 2, *a, d*). The subsequent annealing of the samples led to the increase in the depth of the areas to 41 nm (Fig. 2, *b, e*) due to etching of the Si substrate with the implanted Ga atoms. With the increase in the number of the passes from 5 to 200, the roughness of the modified areas increases as well from 1.6 to 27 nm for an unannealed sample (Fig. 2, *d*) and from 1 to 18 nm for the sample with subsequent annealing in the absence of the arsenic flux (Fig. 2, *e*).

At the next stage, we investigated the influence of availability of the arsenic flux during annealing the samples. It supposedly contributes to crystallization of gallium clusters within the modified areas by generating nucleation centers for subsequent formation of the epitaxial GaAs layers (Fig. 3). The availability of the arsenic flux can lead to the decrease in intensity of Ga evaporation from the surface and the decrease in drop merge probability, thereby resulting in no evident typical pore on the surface (see Fig. 1,*f*), but in a big number of crystallized structures (Fig. 3,*f*).

A crystal nature of islands to be formed during annealing in the arsenic flux may be judged by a typical crystal faceting, as it is evident on the SEM-images obtained (Fig. 4, *b*). There is no faceting during annealing in the absence of the arsenic flux (Fig. 4, *a*), thereby meaning that annealing in the arsenic flux results in crystallization of the implanted Ga on the surface. Thus, exposure of the samples to the arsenic flux during annealing leads to formation of crystal GaAs nanostructures, which can subsequently act as nucleation centers for further growing of the GaAs layers.

The results of the AFM studies of the samples exposed to ion irradiation and subsequent annealing in the arsenic flux have revealed no significant change in parameters of the modified areas, which were obtained at 5 and 30 passes, relative to the samples with annealing in the absence of the arsenic flux, except for the decrease in roughness from 1 to 0.5 and from 5 to 3 nm, respectively. However, the irradiation at 200 passes of the ion beam detects significant increase in roughness of the modified area from 18 to 175 nm (Fig. 2, *b, c, e, f*) and no pronounced cavity to be typical for the sample with annealing in the absence of the arsenic flux (Fig. 2, *e*). The obtained results of the studies mean that processes of crystallization of clusters of gallium atoms prevail over processes of high-temperature etching of the substrate by the gallium atoms. The crystallization results in natural increase in a volume of the material accumulated in the modification region and substitution of the cavity space with a layer containing GaAs crystallites. Injected into the Si substrate, such crystallites are capable of being centers of nucleation and further growth of the epitaxial GaAs layer.

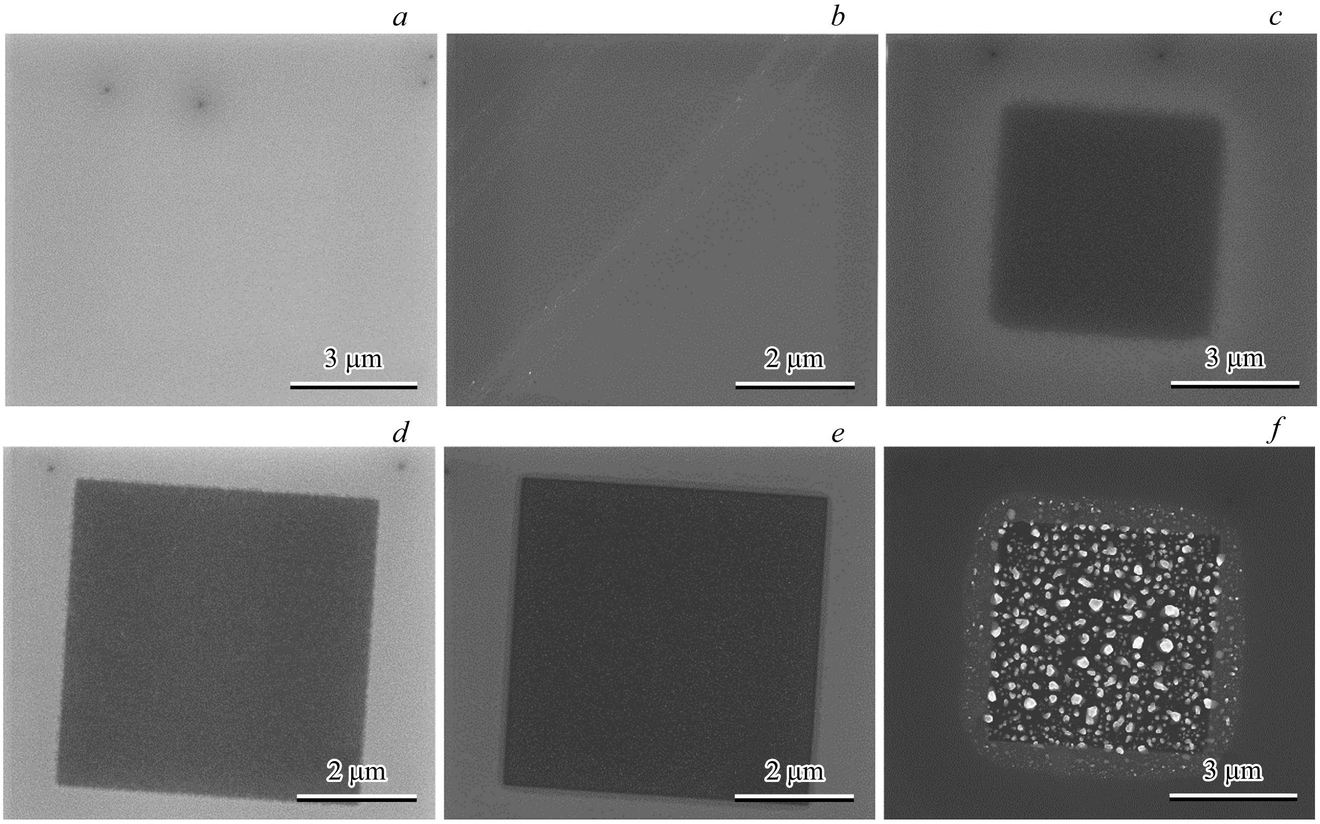

Figure 3. SEM-images of the silicon sample's surface areas exposed to FIB at different parameters of irradiation: *a*) 5 kV, 5 passes, *b*) 5 kV, 30 passes, *c*) 5 kV, 200 passes, *d*) 30 kV, 5 passes, *e*) 30 kV, 30 passes *f*) 30 kV, 200 passes — with subsequent annealing in the arsenic flux.

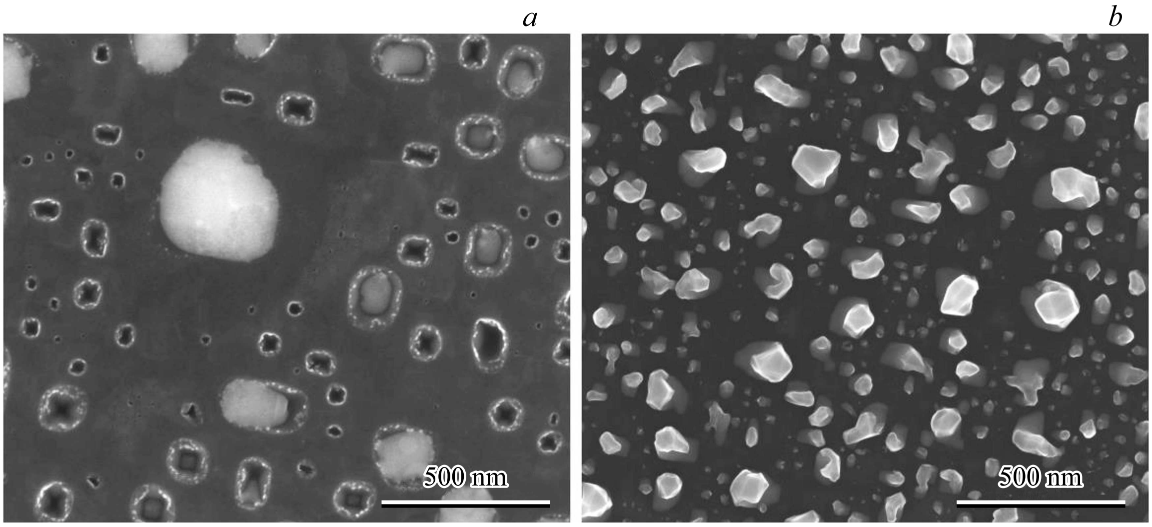

Figure 4. SEM-images of the silicon sample's surface areas exposed to FIB (30 kV, 200 passes) at the different annealing modes: *a*) annealing in the absence of the arsenic flux, *b*) annealing in the arsenic flux.

Analysis of the samples showing crystallization of the gallium clusters can be based upon to make a conclusion that annealing in the arsenic flux is a more preferable method of preparing the FIB-implanted surface for subsequent GaAs growth than annealing in the absence of the arsenic flux. In connection therewith, the next stage was taken to investigate the processes of GaAs growth on the FIB-modified areas exposed to high-temperature annealing

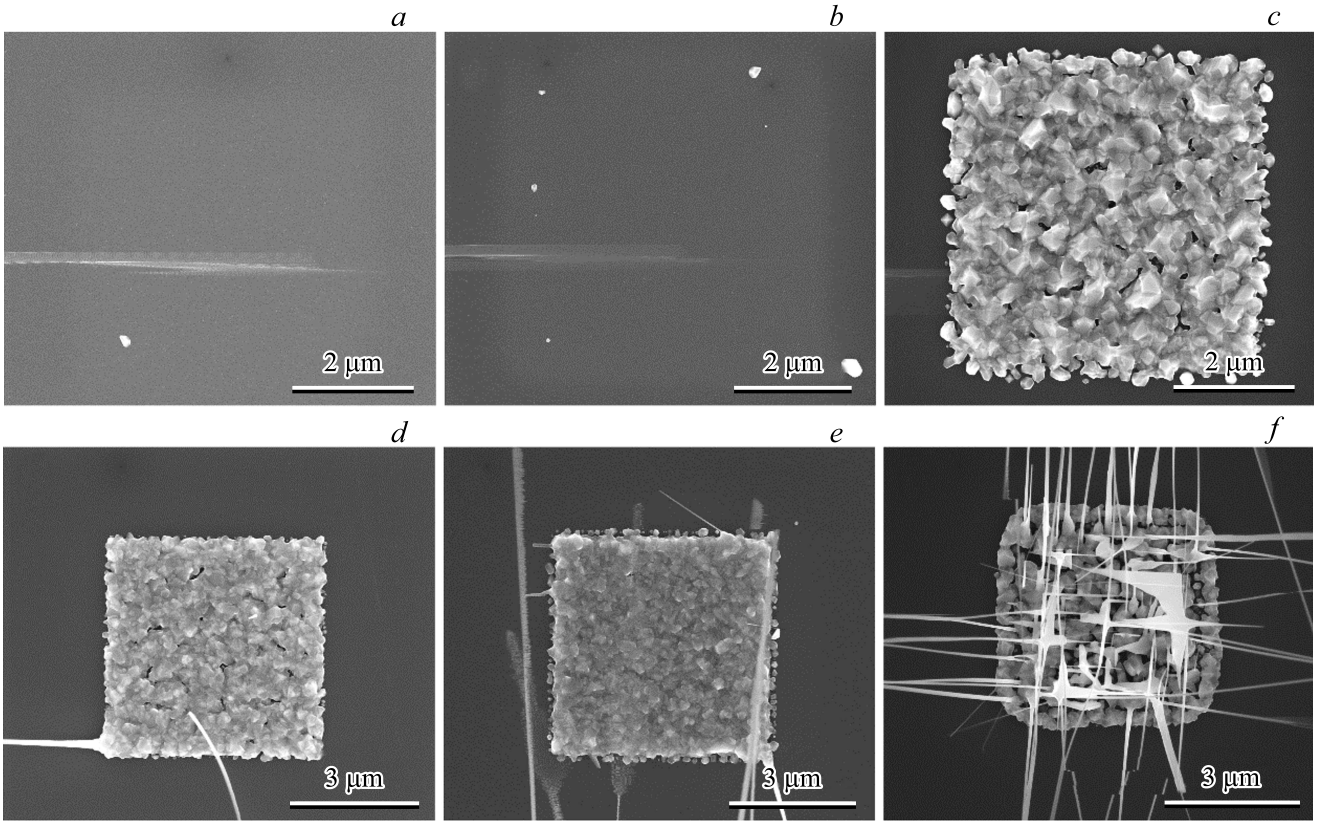

Figure 5. SEM-images of the silicon sample's surface areas exposed to FIB at different parameters of irradiation: *a*) 5 kV, 5 passes; *b*) 5 kV, 30 passes; *c*) 5 kV, 200 passes; *d*) 30 kV, 5 passes; *e*) 30 kV, 30 passes; *f*) 30 kV, 200 passes — with subsequent annealing in the arsenic flux and further growth of the epitaxial GaAs layer of the thickness of 200 nm.

in the arsenic flux. It has been revealed that the presence of the regions exposed to ion irradiation at 5 and 30 passes and acceleration voltage of 5 kV did not lead to localization of GaAs growth (Fig. 5, *a, b*) and, therefore, did not allow using preliminary structuring of the surface in order to provide for formation of the qualitative epitaxial layers. It seems to be correlated to diffusion of implanted gallium atoms to the substrate surface, their bonding to arsenic particles during annealing and further free migration over the surface, what is also confirmed by images in the Fig. 3, *a, b*.

Due to a large scope of crystallized regions in the areas exposed to ion irradiation at the voltage of 30 kV and 200 passes, here, it expected to form the GaAs areas to be growing together to a solid layer. However, Fig. 5,*f* shows the opposite. The GaAs growth on such areas is accompanied by generation of nanowires, which are oriented in various directions to be predominantly perpendicular to each other: [110], $[1\bar{1}0]$, $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$. It may be correlated, on the one hand, to excessive Ga atoms in the modified regions resulted from ion injection into the substrate, while, on the other hand, to possible delay in GaAs nucleation processes on the Si surface, which can also lead to local change of the Ga and As_4 flux ratio towards a metal component even in the conditions of initial excess of arsenic. It should be also noted that such local shift of the flux ratio towards Ga excess remained during the whole growth period, thereby resulting in an average length of the GaAs nanowires of 7.1 μm.

With decrease in the number of the passes of the ion beam, the surface nanowire density reduces from $3 \cdot 10^8\,cm^{-2}$ (Fig. 5,*f*) to 0 (Fig. 3, *a–c*), which is correlated to decrease in the gallium flux, whose excess with respect to the arsenic flux contributes to nucleation and growth of the oriented nanowires [15–17]. Moreover, it is clear from the Fig. 5 that a degree of occupation of the modified area surface with the GaAs layer is minimum for 30 kV and 200 passes.

The results of the study of the GaAs growth processes on the FIB-implanted surfaces are analyzed to be generally concluded that the pre-treatment of the surface with the gallium ions at 200 passes contributes to nucleation and further growth of nanocrystalline GaAs layers. And in combination with the effective methods of growing of the buffer layers, it can provide for high-quality monolithic integration with the Si substrates. Nevertheless, further thorough study is required for the structure and electronic & optical properties of the crystal layers.

4. Conclusion

Thus, the results of the studies carried out have established that during annealing in the absence of the arsenic flux, the Si substrates treated by the FIB method at the acceleration voltage of 30 kV and 200 passes of the ion beam accumulate the implanted Ga in drops, which partially evaporates, leaving pores at its place. The substrates exposed to the ion treatment of lesser intensity (at the voltage below 30 kV and doses below 200 passes) show no evident drop on the surface of the modified areas after annealing in the absence of the arsenic flux. It is attributed to the fact that it is energetically unfavorable for the material to surface and evaporate at 600°C.

The exposure of the samples in the arsenic flux during annealing leads to crystallization of gallium drops and generation of centers of nucleation for further GaAs growth. However, the results of the studies demonstrated that on the areas exposed to the FIB treatment at the voltage of 30 kV and 200 passes of the ion beam the GaAs growth was accompanied by intense formation of the nanowires. Decrease in the ion irradiation dose leads to decrease in the surface nanowire density and increase in the degree of occupation of the areas with the GaAs layer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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