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Investigation of the influence of the ion-beam treatment dose of the Si(111) surface on the GaAs nanowires growth processes

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This paper presents the results of experimental studies of the effect of the Ga ion dose during ion-beam treatment of the Si(111) surface using the focused ion beam technique on the Ga^+ nanowires epitaxial growth processes. A significant difference is revealed between the parameters of nanowire arrays formed on modified and unmodified areas of the Si substrate in this way. It is shown that changing the Ga ions dose from 0.052 to 10.4 pC/μm^2 during ion-beam treatment makes it possible to form GaAs nanowires arrays with a different set of parameters in a single technological cycle with a high degree of localization. The regularities of the influence of the dose of Ga ions during surface modification on the key characteristics of GaAs nanowires (density, diameter, length, and orientation with respect to the substrate surface) are experimentally established.

Keywords: Focused ion beam, nanowires, GaAs, molecular beam epitaxy.

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1. Introduction

The $A^{III}B^V$ nanowires (NWs) are promising items for creating various elements and devices of the photonics, micro- and nano-electronics, micromechanics and sensorics due to a combination of their unique electronic, optical and mechanical properties [1–4]. Creation of the NW-based devices requires development of technologies of controlling their main characteristics (both together and separately): the sizes (a length, a diameters), the shape, the chemical composition, doping, the density [5]. If for NW formation the „vapor-liquid-solid" (VLS) mechanism is used, then it is achieved by adjusting the main parameters of the metal nanodroplets acting as catalytic centers of NW growth, i.e. their size and location on the substrate surface.

As a rule, various combinations of epitaxial and lithographic procedures are used for it — a hetero- or self-catalyst one– depending on a variety of the VLS mechanism used and, consequently, on the metal as a catalyst [6,7]. The electron-beam lithography [8–10], the nano-imprint lithography [11,12] and the so-called nano-sphere lithography [6,13] are the most widespread lithographic procedures for NW formation.

However, the pre-growth treatment of the substrate surface using traditional technological processes based on the lithographic operations (which usually includes the operations liquid and (or) plasma etching) either fails to ensure the required parameters of the obtained structures [14,15], or is poorly compatible with the growth processes [16], or characterized by high cost and low capacity [17–19]. That is why the task of effective control of the various NW parameters (the length, the diameter, the density, etc.), including by the pre-growth surface preparation, is still relevant.

Recently, an alternative method to control the NW parameters with elimination (or minimization) of the main disadvantages of the above-described approaches, is actively studied. This method represents local ion-beam surface treatment by means of the focused beam of the Ga ions [20–23]. This method is designed to perform the technological operations of the local ion-beam etching with high spatial resolution in high-vacuum conditions without the need of applying the resists, the masks and chemical etching [24–27]. At the same time, the focused ion beam (FIB) method can be used both for forming depressions both in a masking oxide layer in the SiO_2/Si structures (with subsequent localization of catalyst droplets therein) [20] and for direct local formation of the catalyst centers — in case of using the Ga ion beams and of the self-catalyst VLS growth [21]. In the second case, in the subsequent annealing, the Ga ions embedded into the substrate at the FIB-treatment stage form, at beam-affected points, the Ga droplets acting as catalyst center for the GaAs NW growth [22]. By changing the various technological parameters of the FIB-treatment and the pre-growth annealing, it is possible to effectively control the size, the density and the position of the formed metal droplets, thereby largely predetermining the characteristics of the post-growing GaAs NWs [23]. At the same time, it is still little known about issues related to mutual influence of the main parameters of the ion-beam treatment (the dose, the accelerating voltage and the current of the beam, the treatment topology, etc.) and the epitaxial synthesis (the temperature and the time of annealing and growth, the ratio of the growth components, etc.) on the key characteristics of the GaAs NWs, as well as about the mechanisms underlying the NW growth using the FIB-treatment, thereby primarily requiring the experimental studies in this field.

The purpose of this study is to investigate the influence of the ion dose when treating the Si(111) surface with the focused Ga^+ ion beam on the processes of the formation of the GaAs NW arrays.

2. Experimental procedure

The substrates were taken to be the Si(111) plates, which are preliminary cleaned in acetone and isopropyl alcohol to be subsequently flushed in deionized water and dried. The ion-beam treatment of the substrate surface was performed using the scanning electron microscope (SEM) Nova NanoLab 600, equipped with the FIB system with the Ga ion source. The FIB-modified areas were squares with the size of $5 \times 5\,\mu$m and were given using a template generated in the control program by the ion beam. The surface of all the areas was modified at fixed values of the accelerating voltage of the ion beam (30 kV) and the current (30 pA). Under the FIB impact, the Ga ion dose varied from 0.052 to 10.4 pC/μm^2 and was specified by changing the number of passes of the ion beam as per the template-specified topology with invariability of the other FIB parameters. With the FIB treatment of the Si surface within the said dose range, the surface etching is almost suppressed (approximately several nanometers for the dose of 10.4 pC/μm^2) and there is predominantly evident implantation of the Ga ions to the subsurface layer of the substrate [28].

The self-catalyst GaAs NWs have been grown by the molecular beam epitaxy (MBE) on the unit SemiTEq STE 35. The Si(111) substrates with the FIB-modified surface areas were pre-annealed in the ultra high vacuum conditions at the temperature of 600°C during 60 minutes. This stage included the initiation of the processes of segregation of Ga embedded to the substrate crystal structure, with subsequent formation of the catalyst centers. At the same time, the masking layer of the intrinsic Si oxide was not removed, thereby simultaneously forming the GaAs NWs outside the modified areas to be subsequently used as a reference array of the structures [29]. Then, the GaAs NWs were grown at the same substrate temperature (600°C) with the equivalent deposition rate and thickness of GaAs, which are equal to 0.25 m/s and 200 nm, respectively. The ratio of the flowrates of Ga and As_4 pre-calibrated on the GaAs(001) substrate was 1 : 4.

The morphology of the produced structures was controlled by the SEM methods. The geometric parameters of the GaAs NWs (the length, the diameter, the density) were analyzed based on the SEM images using the special software SIS Software Scandium.

3. Results and discussion

The analysis of the obtained SEM-images of the Si(111) surface with the FIB-modified areas has shown the substantial influence of the Ga ion dose on the processes of the formation of the GaAs NW arrays and the geometric parameters thereof (Fig. 1). The low doses exhibit the formation of the highly-dense (up to ~ 13.6 pcs./μm^2) Ga droplet arrays (Fig. 1, *a*). At the same time, the growth of GaAs NWs as well as the GaAs crystallites of the parasite phase was almost suppressed in comparison with even the unmodified surface. The increase in the dose of the Ga ions results in the increase in the GaAs NW density and intensification of the processes of the parasite growth of the GaAs crystallites (Fig. 1, *b*) up to the formation of a solid polycrystal base (Fig. 1, *c*).

Fig. 2 shows the quantitative analysis of the geometric parameters of the GaAs NW arrays based on the SEM images and the subsequent statistical processing of the obtained data allowed plotting the dependences of the main parameters of the nanostructures: the array density, the average values of the length and the diameter, as well as their vertical position (a portion of the normally oriented NWs of their total number) on the dose of the Ga ions during the FIB-treatment of the Si(111) surface.

As it is clear from the presented dependences, at the very low doses of treatment (~ 0.052 pC/μm^2), as previously said, the NW growth is substantially suppressed and the NW density is 0.36 pcs./μm^2, which is almost by order less than the density of the array formed on the unmodified surface (2.56 pcs./μm^2 — Fig. 2, *a*). At the same time, the density of the Ga droplets in the modification area is up to 13.6 pcs./μm^2, but the NWs do not develop therefrom (Fig. 1, *a*). The increase in the dose in the FIB-treatment results in the sharp increase in the GaAs NW density (Fig. 2, *a*) with the peak value of 7.8 pcs./μm^2 (at the dose of 5.21 pcs./μm^2), and then to the gradual decrease to 5.76 pcs./μm^2 (Fig. 1, *c*). However, within the whole range of the doses (except for the first point) the NW density exceeds their density on the unmodified surface in more than two times.

The nature of the dependences of the length and the diameter of the GaAs NWs on the FIB-treatment dose (Fig. 2, *b* and *c*, respectively) is the same. Namely, the increase in the dose of Ga ions first of all leads to a sharp decrease in the length and the diameter of the NWs simultaneously, with subsequent, starting from the dose of 1.56 pC/μm^2, getting to saturation and with stabilization of the values within the ranges $0.9-1.17\,\mu$m and $27-29$ nm, respectively. It is in ~ 4.3 and ~ 2.2 times less than the length and the diameter of the GaAs NWs formed outside the modified areas, which are equal to 4.44 μm and 61 nm, respectively. The NW density in this range of the dose values has a clear trend to decrease (Fig. 2, *a*) at the constant values of the length and the diameter of the structures, which is caused by the intensification of the growth of the parasitic structures within the high doses (Fig. 1). At the same time, the portion of GaAs NWs normally oriented in relation to the substrate first of all increases sharply to 70% (at the dose of 0.52 pC/μm^2), and then decreases sharply as well, and starting from the dose of 5.21 pC/μm^2, it is stabilized at a value within the range $6-10$%. At the

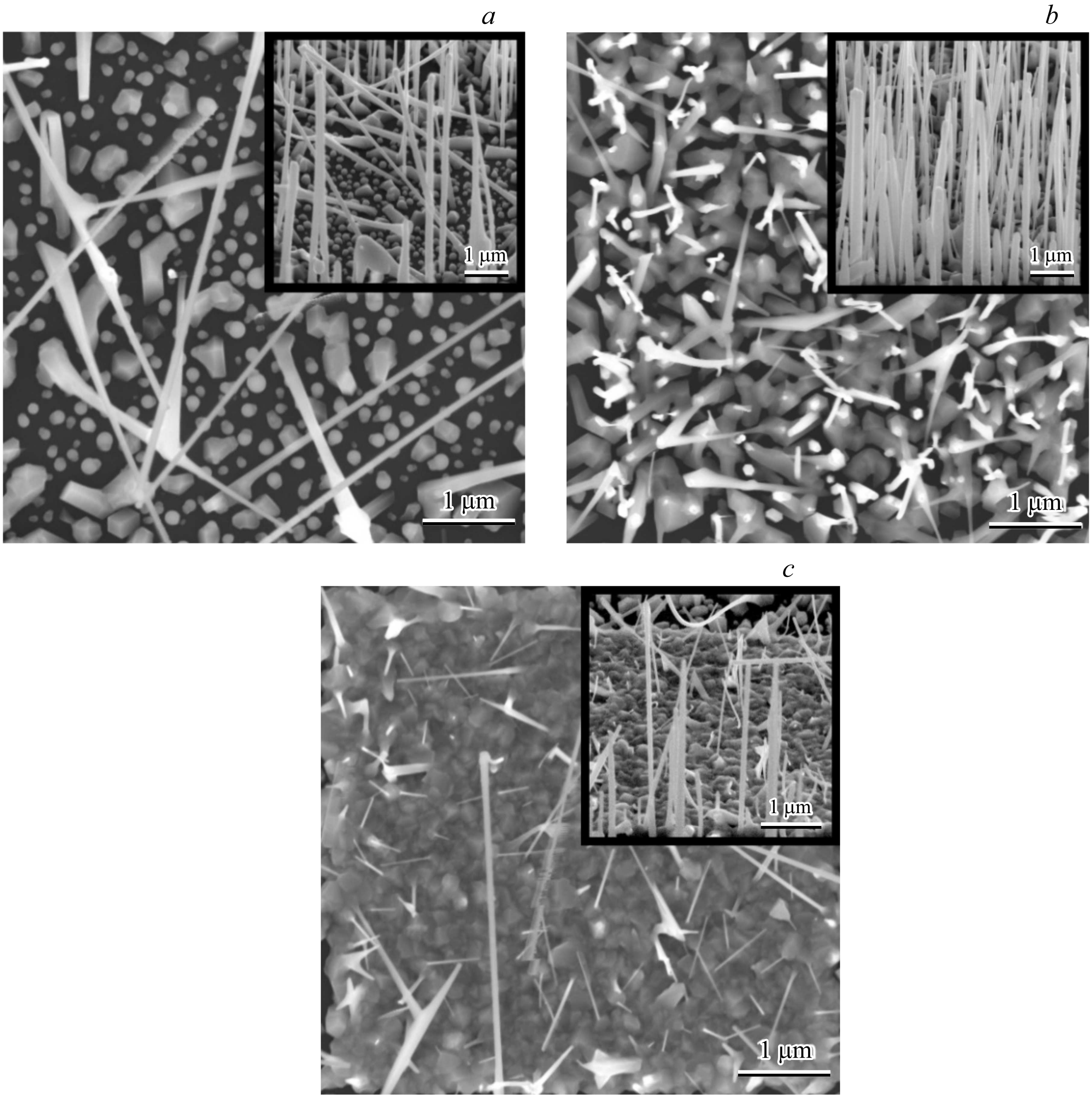

Figure 1. SEM-images (top view, the inserts show the images at the angle of 52°) of the GaAs NW arrays obtained on the FIB-modified areas with the various dose of the Ga ions: *a* — 0.052, *b* — 0.26, *c* — 10.4 pC/μm^2.

same time, outside the FIB-modified area, the portion of the normally oriented GaAs NWs is $\sim$ 50%.

In doing so, the dose range 0.26−0.52 pC/μm^2 is interesting, because its NW density increases in more than two times in comparison with the reference values — from 2.56 to 6.56 pcs./μm^2, at the actually unchanged diameter ($\sim$ 60 nm), although with the decrease in their length by the 20−35% — from 4.44 to 3−3.5 μm. At the same time, the yield of normally (vertically) oriented NWs also increases by 20% in comparison with the reference values (from 50 to 70%) in the same dose range.

Such an unusual nature of the influence of the irradiation dose value of the surface with the Ga ions (almost full suppression of the catalyst growth of the GaAs NWs within the small doses and the growth of the highly-dense strongly disordered NWs of small diameters and lengths at the high irradiation doses) is apparently caused by the specifics of the interaction of the ions with the substrate crystal structure at the various levels of the FIB impact intensity.

When irradiating the surface with the low doses, the ions predominantly penetrate the crystal structure of the subsurface layer of the Si substrate. However, while being enriched with ions and defects generated thereby, the crystal lattice still retains its structure [30]. The relatively low (in comparison with the areas of the higher irradiation dose) defect concentration in these regions not only complicates rebuilding of the crystal structure of the substrate at the annealing stage, but also makes difficult for the interstitial ions (atoms) of Ga to surface, thereby suppressing the formation of the catalyst droplets (centers of nucleation of

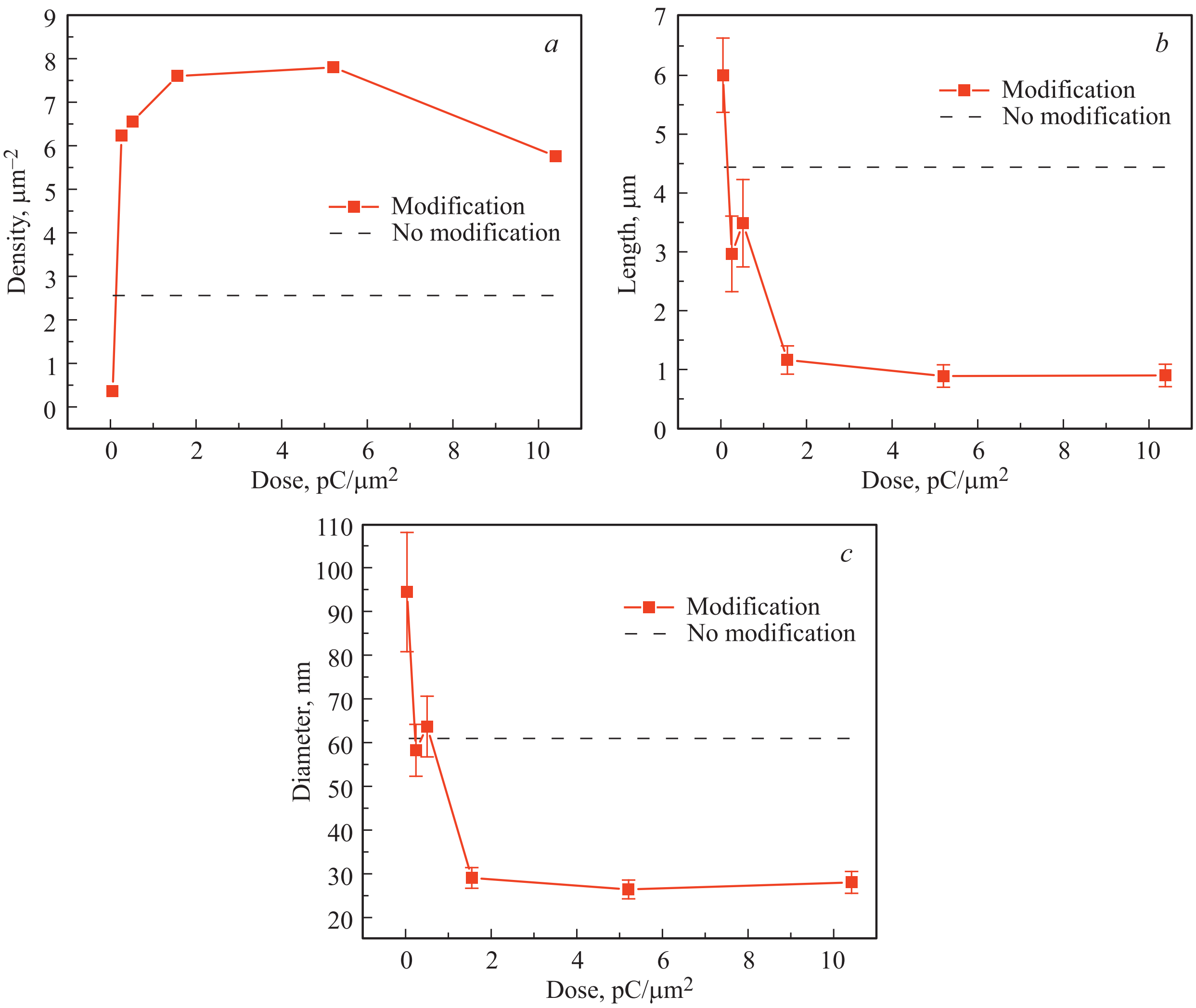

Figure 2. Dependences of (*a*) the density, (*b*) the length and (*c*) the diameter of the GaAs NW on the FIB-treatment dose.

GaAs NWs) by the interstitial material. The experimental detection of the high density of the Ga droplets at the areas with the dose of 0.052 pC/μm^2 (Fig. 1, *a*) at almost full suppression of the directly catalyst growth with their involvement (Fig. 1, *a* and 2, *a*) might indicate that they are formed at feeding the growth components (the Ga atoms and the As molecules) at the initial stage of the growth. It can be assumed the NW nucleation stage at these areas in these growth conditions was for some reasons kinetically decelerated and (or) stretched in time, which could lead to outflow of the material to the adjacent areas, where the initial stage of the NW formation was significantly faster. In turn, it resulted in no development of the GaAs NWs from the formed Ga droplets despite continuously supplying the epitaxial material to the substrate.

The fivefold increase in the irradiation dose (from 0.052 to 0.26 pC/μm^2) is accompanied by the increase in the defectiveness of the subsurface layer of the modified area, thereby resulting in the intensification of the processes of rebuilding of the crystal lattice at the annealing stage, which is accompanied by segregation of the interstitial ions (atoms) Ga at the Si substrate surface and, as a result, to the formation of the catalyst droplets [31]. In turn, it results in the intensification of the processes of the catalyst and parasit growth, which lead to the sharp increase in the NW density (in more than two times) and that of the GaAs crystallites, respectively (Fig. 1, *b* and 2, *a*). At the same time, the length and the diameter of NWs consistently decrease in comparison with the structures on the unmodified surface — 2.97 μm and 58 nm, respectively (Fig. 2, *b* and *c*), which is caused by the redistribution of the epitaxial material primarily between the NWs. At the same time, the portion of the Ga As NWs normally oriented to the substrate gains its maximum ($\sim$ 70%).

Further on, with the increase in the surface irradiation dose in the FIB-modification to 10.4 pC/μm^2, not only the concentration of the interstitial Ga ions increases, but their surfacing rate increases as well. Consequently, the modified surface is more and more enriched with the Ga atoms, thereby resulting in the increase in the density and the sizes of the catalyst droplets. It results in the suppression of the catalyst growth responsible for the NW formation and to stimulation of the parasitic growth — the density and the size of the GaAs crystallites are increasing. Thus, theoretically, the GaAs NW density should decrease. However, as it follows from Fig. 1, *c* and 2, *a*, the experiment indicates the opposite — the NW density is changing insignificantly to remain highly above the reference values.

We relate this system behavior to the change of the GaAs NW nucleation mechanism. In the conditions in which the parasitic growths dominates (when the 3D GaAs crystallites are formed on the surface), when the coverage degree of the GaAs crystallites is 100% (Fig. 1, *c*), the formation of the excessive metal component and the formation of the catalyst centers are possible only due to an additional, totally uncompensated flux of the Ga atoms, which is caused by continuing processes of the segregation of the Ga ions embedded into the subsurface layer of the Si substrate at the FIB-modification stage. This assumption agrees well with the results of the experimental studies. First of all, the segregation flux of the excessive Ga to the surface is quite small, which makes the size of the formed catalyst centers quite and, consequently, the diameter of the growing NWs quite small, in our case the NW diameter at the saturation portion (Fig. 2, *c*) is in more than two times less than the reference values (61 nm). Secondly, this flux should decrease in time due to a finite number of the interstitial Ga ions. As it is clear from the Fig. 1, *c*, the GaAs NWs have a clear conical shape and a relatively small length (0.91 μm). At the same time, as it follows from the dependences of the length and the diameter of the NWs that starting from the dose of 1.56 pC/μm^2, the sizes of the nanocrystals almost cease to depend on the irradiation dose. Thirdly, as in this case the Ga droplets form already not on the Si(111) surface, but on various faces of the randomly-oriented GaAs crystallites, then the portion of the GaAs NWs oriented normally to the substrate is sharply decreasing. This assumption is also confirmed experimentally— the portion of the normally oriented NWs at the doses above 1.56 pC/μm^2 does not exceed 20%.

4. Conclusion

Thus, the experimental studies have been conducted to show that it is possible to control the various NW parameters with the FIB method by varying the dose of implantation of the Ga ions into the Si(111) substrate. There is a sharp difference between the NW arrays formed on the modified and unmodified areas of the Si substrate. It has been shown that the change in the dose of the Ga ion implantation within the range from 0.052 to 10.4 pC/μm^2 allows controlling the NW length within the range 1–6 μm, the density — within the range 0–7.8 pcs./μm^2, the diameter — within the range 28–95 nm, the portion of the normally oriented NWs — within the range 5–70%. It has experimentally demonstrated the change of the modes and the mechanisms of formation of the catalyst centers and the initial stage of the GaAs NW growth, which is caused by differences in the nature of structural disruptions of the Si substrate and the segregation of the interstitial Ga ions on the surface at the various modes of the FIB-modification. It has experimentally shown the possibility of forming GaAs NW arrays, which are substantially different in their geometric parameters in a single sample within one technological cycle. It has been also shown that by selecting the FIB-modification parameters it was possible to substantially increase, at the same time, the density and the portion of the normally oriented NWs with their unchanged diameter and insignificant reduction of the length.

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Conflict of interest

The authors declare that they have no conflict of interest.

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