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Control of properties and geometric characteristics of selectively formed GaAs nanowires within the FIB treatment area on Si(111)

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Abstract. In this paper we present the results of experimental studies on the selective formation of GaAs nanowire arrays on the Si(111) substrate surface and the control of their properties. It has been shown that pre-treatment of the Si(111) surface with a native oxide layer by a focused Ga-ion beam with further low-temperature annealing and high-temperature growth allows the formation of selective GaAs nanowire arrays with a different set of parameters that can be controlled by changing the dose of ion-beam treatment. We also demonstrated the possibility of obtaining arrays with a yield of vertically oriented nanowires at the level of almost 100% and very high density (up to 8 μm^{-2}). At the same time outside the modified areas, the formation of nanowires was almost completely suppressed. Moreover, based on Raman spectroscopy study we have found that our approach allows to obtain nanowire arrays with clear zinc-blende crystal phase in wide range of nanostructure sizes.

Keywords: nanowires, gallium arsenide, focused ion beam, molecular beam epitaxy, A3B5

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Материалы конференции
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Управление свойствами и геометрическими характеристиками селективно сформированных нитевидных нанокристаллов GaAs в области обработки ФИП на подложке Si(111)

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Аннотация. В данной работе представлены результаты экспериментальных исследований селективного формирования массивов нитевидных нанокристаллов GaAs на поверхности подложки Si(111) и их свойств. Было показано, что предварительная обработка поверхности Si(111) со слоем естественного оксида фокусированным пучком ионов Ga с последующим низкотемпературным отжигом и высокотемпературным ростом позволяет локально формировать массивы нитевидных нанокристаллов GaAs с различным набором параметров, которыми можно управлять, изменяя дозу ионно-лучевой обработки. Продемонстрирована возможность получения массивов с выходом вертикально ориентированных нитевидных нанокристаллов на уровне практически 100% и очень высокой плотностью (до 8 мкм$^{-2}$). При этом вне области обработки образование нитевидных нанокристаллов было практически полностью подавлено. Результаты анализа образцов спектроскопией комбинационного рассеяния света показали возможность получения массивов нитевидных нанокристаллов со структурой цинковой обманки в широком диапазоне размеров наноструктур.

Ключевые слова: нанопроволоки, арсенид галлия, фокусированный ионный пучок, молекулярно-лучевая эпитаксия, A3B5

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Introduction

Currently, A3B5 nanowires (NWs) are of great interest as key elements for creating promising photonic and nanoelectronic devices [1, 2]. The availability of technology capable of precisely controlling the NW position and their various properties and geometric parameters is required for the creation of various devices [3]. To date, one of the most perspective technologies for this purpose is focused ion beam (FIB) treatment of the substrate surface prior to NW growth [4–7]. However, the processes of NW epitaxial growth on the surface prepared in this way, as well as the influence of substrate processing parameters by the FIB method on the resulting characteristics of the formed NW arrays remain poorly understood and require additional research. In this paper, we study the selective growth of GaAs NW arrays within the FIB treatment area on the Si(111) surface with a native oxide layer at a high growth temperature and the dose effect on their properties and geometric characteristics.

Materials and Methods

Experimental studies were carried out on Si(111) p-type epi-ready substrate with a native oxide layer. The Ga ions were implanted into the substrate at an accelerating voltage of 30 kV according to a template consisting of several 5×5 μm square areas in which the dose ranged from 0.052–52 pC/μm^2. Then annealing was performed at a temperature of 600 °C for 1 hour. After that, the NW growth was carried out with substrate temperature of 750 °C with a nominal deposition rate of 0.25 ML/s for 48 minutes by the MBE method. The sample was analyzed by SEM and Raman spectroscopy methods. The Raman spectra were measured at room temperature using a Horiba LabRam HR800 setup equipped with a 532 nm laser.

Results and Discussion

SEM images analysis of the surface after NW growth shows that GaAs NW arrays selectively form within areas treated with an ion beam (Fig. 1). At the same time, their growth is practically suppressed outside the modification area and only the formation of low-density GaAs crystallites is observed (Fig. 1, *d*). It is also seen that changing the dose allows to control key NW morphological characteristics, such as: density, length, diameter and yield of vertical NWs (Fig. 1, *a*, *b*, *c*). The character of the dose effect on the NW parameters is presented through the dependences plotted based on SEM images statistical processing (Fig. 2, *a*, *b*).

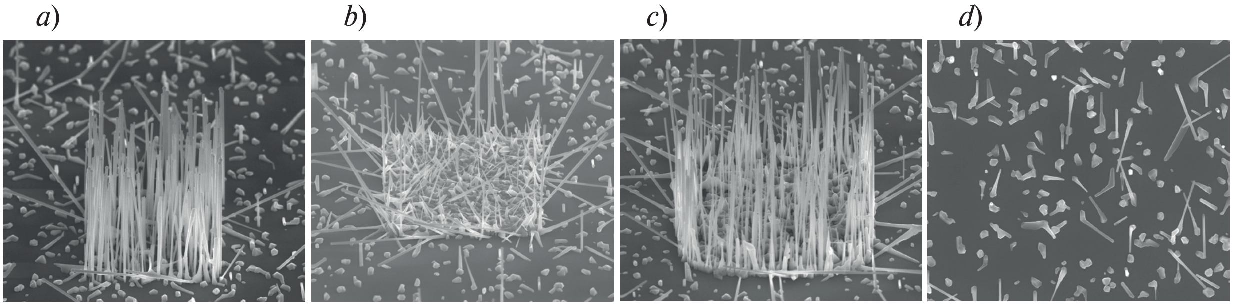

Fig. 1. Tilted SEM-images of modified areas after GaAs nanowire growth for ion doses: 0.052 (*a*), 5.2 (*b*), 52 (*c*) pC/μm^2 and for unmodified area (*d*). The size of the SEM images is 10×10 μm

The analysis of the obtained dependences shows that the curves change character from the FIB dose is rather complex and nonlinear. So, selective formation of an NW array with almost 100% verticality value is observed at the beginning of the ion dose range (0.052 pC/μm^2 see Fig. 1, *a*, 2, *a*). This is an unexpected result considering that the growth occurs on the substrate surface with a native oxide layer [8]. The value of the NW density in this case is ~ 5 μm^{-2}. The deviation of some NWs within the array from the vertical position (angle less than 90° between the surface and the NW itself) is due to the fact that this NWs were formed in the transition area between the FIB surface treatment and the reference region without modification. Such NWs were categorized as non-vertical. A slight deviation and connection between neighboring NWs near their top are due to the impact of the electron beam on them in the process of SEM surface analysis [9]. It is also worth noting that in the whole range of considered ion doses, only for a certain dose value (0.052 pC/μm^2) the NW formation with maximum average values of length (3.6 ± 0.25 μm) and diameter (65 ± 4 nm) within the array is observed (Fig. 2, *b*). At the same time, the NW diameter is practically equal to the reference values (71 ± 4 nm) whereas the length is 2.25 times greater than that outside the processing area (1.6 ± 0.2 μm). Then, as the ion dose rises, the NW density slightly increases (up to ~ 7 μm^{-2}) and the values of the NW verticality, length and diameter begin to decrease (Fig. 2, *a*, *b*). However, the verticality also remains in the region of high values (about 80% for 0.52 pC/μm^2) compared to the unmodified area (20%). A further increase in the dose leads to a sharp decrease and stabilization of all key NW characteristics in the region of minimum values within the dose range of 1.56 – 26 pC/μm^2. The values stabilize at: 5.4 μm^{-2} for density, 10% for verticality, 29 ± 2 nm and 0.7 ± 0.12 μm for diameter and length, respectively (Fig. 2, *a*, *b*). This can be attributed to the formation of a GaAs polycrystalline base (Fig. 1, *b*) that changes the conditions and mechanism of NW growth on the surface within the treatment area [10]. Meanwhile, it is also interesting to note that this stabilization is aborted by a subsequent increase in ion dose (52 pC/μm^2). This leads to a sharp increase in all NW characteristics and the formation of an array with a maximum density (Fig. 1, *c*) equal to 8 μm^{-2} which is 20 times greater than that outside the treatment area (0.42 μm^{-2}). It is also worth noting that the curves of the length, diameter and verticality of NWs show a similar character of dependence on the FIB dose. The density values, in contrast, change slightly and fluctuate mainly in the range from 5 to 7 μm^{-2}, except for the last point in the considered dose range. Mechanisms underlying the FIB dose effect on the NW parameters is reflected in [11].

Furthermore, it is important to mention that the technology developed and applied in this work, on the one hand, allows to obtain high-density NW arrays with 100% verticality and, on the other hand, allows to obtain arrays with high selectivity on the silicon surface with native oxide layer. An important feature of this approach is the absence of the need for templates, masks and the use of complex lithographic techniques for surface preparation before growth. We assume that such selectivity is achieved primarily by the by using a combination of low-temperature annealing and high-temperature growth. This allows to reduce the number of pores formed on the substrate surface in the native oxide layer outside the modification area during the annealing stage. Simultaneously, this temperature facilitates their formation within the ion beam treatment area through the chemical interaction of embedded Ga ions diffusing to the substrate surface with oxide atoms [11]. The high growth temperature reduces the probability of nucleation outside the modification area while increasing it within the FIB treatment area due to the abundance of nanopores and active diffusion of Ga atoms over the Si surface.

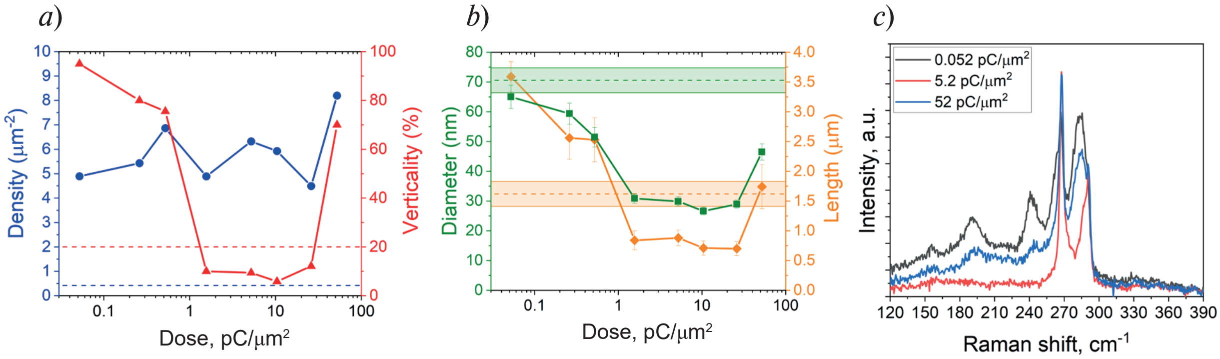

Fig. 2. Dependence of the NW density and verticality (*a*) and diameter and length (*b*) on Ga ion dose. Dash lines correspond to values for unmodified area. Raman spectra from NW arrays formed within the area with different FIB dose (*c*)

The obtained results analysis of NW arrays structural studies by Raman spectroscopy shows the presence of the main intense peaks at frequencies 267 cm^{-1} and 291 cm^{-1} in the whole ion dose range (Fig. 2, *c*). These peaks are typical for transverse (TO) and longitudinal (LO) optical phonons, respectively, in a GaAs bulk crystal with a cubic zinc-blende (ZB) lattice [12]. We can also distinguish the peak formation (low-frequency shift in the LO mode region) with the maximum value of its intensity varying with increasing ion dose in the range of 281 – 287 cm^{-1}. This peak is associated with surface optical (SO) phonons in the ZB lattice of GaAs [13]. The SO peak position dependence on the ion dose is related to the change in the NW geometrical characteristics (Fig. 2, *b*) as the dose increases [14]. It is important to note that the peaks described above are typical only for the cubic crystal lattice of GaAs. The presence of wurtzite (WZ) hexagonal insertions in ZB GaAs NW (polytypism) is usually determined by the presence of an additional peak on the spectra located in the region of 258 cm^{-1} (E2 mode) [15]. As can be seen from the spectra in Figure 2, *c*, the peak responsible for the E2 mode is completely absent in this frequency region which generally indicates that the NW arrays formation occurs in a single ZB crystalline phase of sphalerite, regardless of the FIB dose applied.

Conclusion

Thus, it was shown that the developed approach based on the preliminary preparation of Si(111) surface with a native oxide layer by focused Ga ion beam in combination with optimal annealing and growth parameters allows to form selective GaAs NW arrays and to control their characteristics within a wide range by changing the ion dose. At the same time, for certain dose values the vertical NW yield can be maintained above 80% and increased up to almost 100%. Based on the results of Raman spectroscopy it was also revealed that the developed technique allows to form NWs with a single zinc-blende crystalline phase regardless of the applied FIB dose. It is worth noting that this approach does not require the use of additional templates, masks, resist and chemical etchants and allows to perform all necessary operations in a single technological cycle. This makes this technology fully compatible with vacuum equipment and relatively simple and cheap which is an extremely important factor in the creation of the integrated photonics element base.

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