Single- and Double-Stage Growth of GaInP Nanostructures on Silicon Substrates from the Vapor Phase

© A.S. Vlasov[1], L.B. Karlina[1], R.V. Levin[1], V.V. Lysak[1], M.V. Uchaev[1], I.P. Soshnikov[1,2,3]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] Alferov University,
St. Petersburg, Russia
[3] Institute for Analytical Instrumentation of the Russian Academy of Sciences,
St. Petersburg, Russia

E-mail: vlasov@scell.ioffe.ru

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We present studies of one- and two-stage growth of GaInP nanostructures on (111)-oriented silicon substrates from saturated phosphorus and indium vapors in a quasi-closed volume. Growth was achieved sequentially by formation of a primary nucleation layer consisting of GaInP nanostructures on a silicon substrate, followed by additional gallium deposition. Studies of the vibrational properties and photoluminescence spectra revealed that the second stage of the process, using additional deposition of a metal catalyst layer and various sources, allows for the obtaining structures with a composition different from that of the nucleation layer. Photoluminescence mapping measurements revealed that the two-stage growth method significantly improves the compositional homogeneity of the nanostructures compared to a single-stage approach, and also demonstrates the relationship between the morphology and the composition of the primary and secondary layers.

Keywords: GaInP nanostructures, self-catalytic vapor-phase growth, III-V on Si.

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1. Introduction

A two-stage growth is not common in growing nanostructures (NS), but its use may significantly improve homogeneity, density and crystalline quality of binary and ternary nanowires III-V and to obtain the optimal composition of nucleation layers [1–3]. The ways for the implementation of these objectives may be completely different. Thus, for example, there are studies that demonstrate the effectiveness of the two-stage sequence of growth temperature variation (growth starts at a relatively higher temperature and continues at a relatively lower one) in respect to GaAsSb compound as a promising approach to produce nanowhiskers (NW) of high density at higher content of Sb [1]. Growing GaN NWs on graphene substrates by the method of molecular beam epitaxy found a different approach. In this case the two-stage growth procedure consisted of the first stage at the relatively low temperature, which is followed by the second stage at a higher temperature. At the same time the clear advantage of the two-stage growth was observed from the point of view of the initial (incubation) period reduction and improvement of the NW height homogeneity [2]. In process of self-catalytic growth of GaP on Si(111) substrates using the method of molecular beam epitaxy, it was found that the increase of the vertical yield and diameter of NW could not be achieved simultaneously within one-stage growth. However, this limitation may be overcome in the two-stage approach with the reduction of V/III flow ratio at the second stage of growth after the formation of the NW rods at a higher ratio of V/III and growth temperature. In this case the subsequent expansion of the catalyst drop result in the increase of the NW diameter, and the even radial growth made it possible to obtain NW with the vertical side walls [3].

Branched NWs from $A^{III}B^{V}$ compounds are of great interest both from the fundamental point of view and for the development of electronic and optoelectronic structures with the expanded functionality. In paper [4] an interesting approach is presented to the synthesis of branched NWs AlGaAs with the use of catalytic gold drops in the growth of the layers of molecular-beam epitaxy directly on Si(111) substrates. The second and third deposition of gold on the substrate with NW resulted in the formation of the first and second generations of branches.

In our previous paper [5] we demonstrated the ability to produce nanocrystals of GaInP solid solutions of various composition by the method of growth from vapor phase. The obtained nanostructures (NS) had a noticeable degree of heterogeneity, especially in the field of $x_{Ga} \sim 0.4-0.6$ compositions, which depends on the different size of catalytic gallium drops used in self-catalytic growth.

Our method has certain features that prevent independent regulation of indium, gallium and phosphorus flows. The ratio of V and III group vapors in the vapor phase is determined by the process temperature, i.e. the source phase diagram diagram. Therefore, the additional sputtering of gallium for the second stage of GaInP growth was selected as the most optimal solution. Influence of the repeated gallium sputtering on the morphology and optical properties

of GaInP NS, obtained in the quasi closed volume, is not available in the references known to us. This paper presents the results of the studies aimed at the ability to obtain NS of more homogeneous composition, and also vertical NWs, due to the use of the two-stage growth. The studies of the morphology of the produced structures, their vibrational properties and photoluminescence are provided.

2. Experimental method

The first stage of the self-catalyic growth of GaInP NS of solid solutions on the substrates of single-crystal silicon doped with phosphorus with orientation (111) was carried out using the method specified in our previous paper [5]. Catalytic drops on the silicon surface with a thin layer of „native“ oxide were formed by sputtering of a gallium film of different thickness and its subsequent annealing in the hydrogen atmosphere outside the growth chamber. The thickness was controlled by selecting the corresponding gallium evaporant charge in the range of 0.5−1 mg. Figure 1 presents the histogram of catalytic Ga drop size distribution on the silicon substrate, with orientation (111) after annealing. When 0.5 mg of gallium is sputtered (red strips), the drop dimensions were 20−70 nm. Increase of the thickness of the sputtered layer (1.0 mg of gallium, green strips) results in the increase of the average drop size to 50−100 nm, and at the same time the density of the drops did not change significantly and was $\sim 10^{10}$ cm^{-2} for both sub-samples.

The samples with the catalyst drops formed on their surface were placed in the growth chamber, which is a quasi-closed cell, where in the close proximity there is a source of saturated vapors (In−InP or Sn−InP melts) and a sample. The initial period of temperature rise was 20 min, after which upon achievement of 560 °C, the temperature in the growth chamber was stabilized at 10−30 min. The ratio of the phosphorus and indium vapor flows was determined by the Sn−InP and In−InP state diagrams at the specified temperature. The growth of the structures with various thickness of the sputtered gallium film was carried out in one mode with the purpose to determine the effect of the size of catalytic drops on the thickness and morphology of the nucleation layer. The second stage of growth was carried out after sputtering of 0.5 mg of gallium on the already grown primary nucleation layer of NS. Additional annealing of drops in this case was not carried out. The structure was heated to the growth temperature (560 °C) in the hydrogen flow, in process of which the catalytic drops were formed, and subsequent growth directly on the nucleation layer took place.

The morphology and composition of grown NS were studied with the help of a scanning electron microscope (SEM) SUPRA 25 Carl Zeiss, equipped with the energy disperse spectroscopy unit Ultim Oxford Instruments. Oscillatory properties were studied by the methods of Raman scattering spectroscopy using a single-frequency laser with wavelength of 532 nm. Optical properties and homogeneity

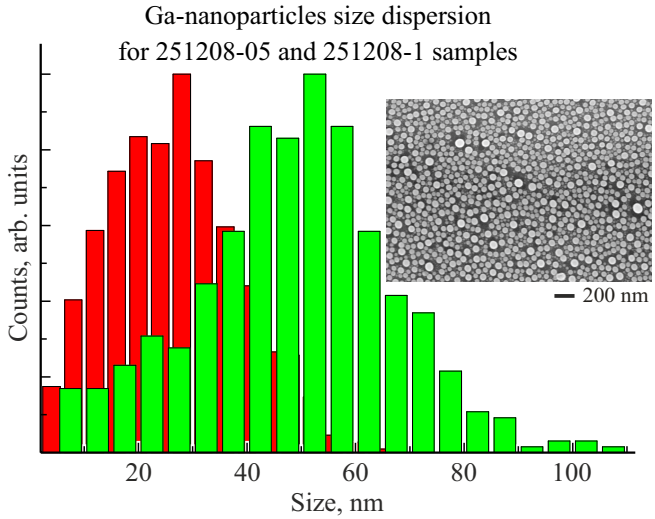

Figure 1. Distribution of catalytic Ga droplets on the silicon substrate, with (111) orientation, after annealing at sputtering of 0.5 mg of gallium (red strips) and 1.0 mg of gallium (green strips). On the insert — example of the SEM horizontal section (plan view) of the Si(111) surface with the formed ensemble of nanodisperse Ga droplets as a result of annealing of the film obtained after the deposition of 1 mg.

by composition of synthesized NS were studied by the method of photoluminescent spectroscopy (PL) with the possibility of spatial scanning with submicron lateral resolution. High resolution is achieved by using a confocal optical microscope (NT-MDT) coupled with a spectrometer. As a source of excitation, a single-frequency laser was used with the wavelength of 532 nm. Collection of luminescence from the sample was carried out with a lens with magnification of 100×, numerical aperture 0.7 and diaphragm 100 μm, providing for the lateral resolution of $\sim 1\,\mu$m.

3. Discussion of results

Based on the results specified in our previous paper [5], the following composition was selected for the first stage of growth: catalytic drops (0.5 mg Ga), source of In−InP. In this case it was possible to control the optical properties of the layers with sufficient accuracy after the first and second growth stages. The selection of the Sn−InP source for the second stage of growth was caused by hígh pressure of phosphorus vapors (and, accordingly, its lárger flow), and the repeated application of gallium corrects the composition of crystallites that grew at the first stage. In this case the growth occurs or takes place on a nucleation GaInP layer, which provides for better wetting and low energy barrier for subsequent crystallization [6,7].

Figure 2 presents a cleavage face and a surface of silicon with the nucleation GaInP layer made of crystallites with specific average dimensions of 70−120 nm and density of $\sim 5 \cdot 10^9$ cm^{-2}, which were formed with the use of catalytic gallium drops with the size of 20−70 nm. According to

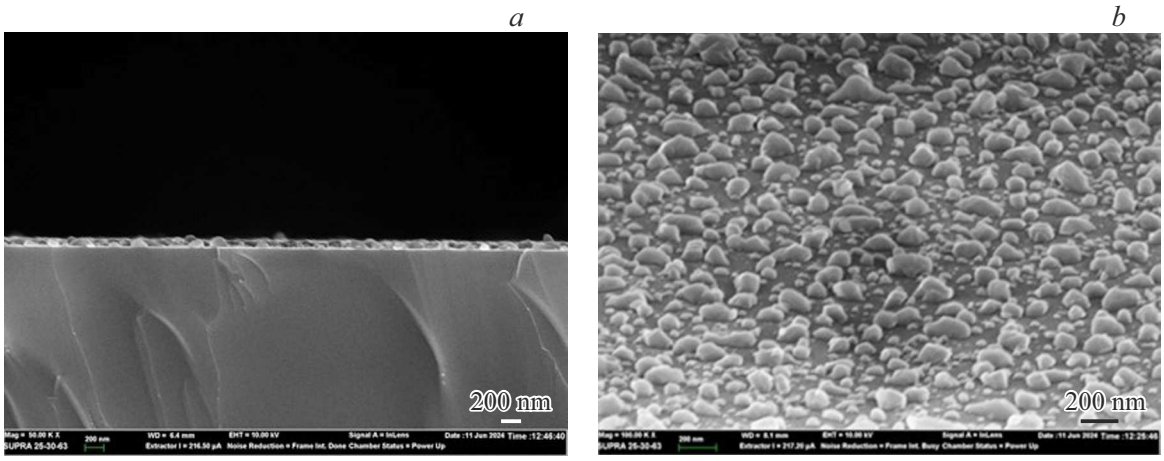

Figure 2. SEM-image of the silicon surface with nucleation layer of GaInP-nanostructures after the first stage of growth in the projection: *a* — cross section and *b* — isometry (inclination of 20° to the surface).

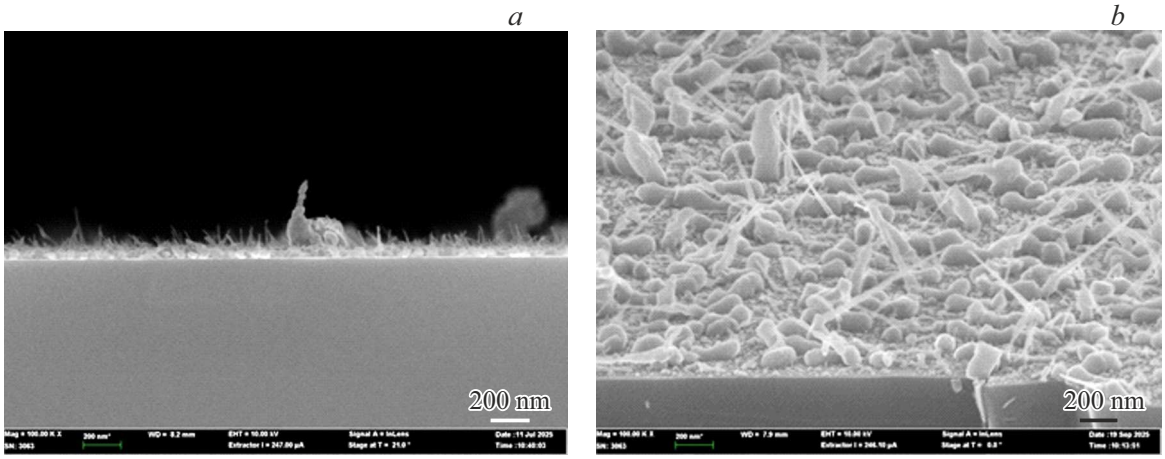

Figure 3. SEM-image of GaInP-nanostructures (sample NW451, Table 1) after the second stage of growth in the projections: *a* — cross section and *b* — isometry.

the results obtained by the method of scanning electron microscopy, we observe the formation of GaInP crystallites with the ratio of components close to 3 : 1 : 4, i. e. indium is present in the composition, and the composition of the solid solution is close to stoichiometric one.

The second stage of growth included the repeated sputtering of gallium on a structure with the nucleation GaInP layer. Nanostructures were growing under the same temperature-time conditions as the first stage. Therefore, the morphology of the structure after the first stage of growth is a nucleation layer with isolated crystallites of island type with specific dimensions presented in Figure 1. After the second stage of growth, mixed morphology is observed: apart from nanocrystallites, nanoscale whiskers appear, i. e. the growth is combined.

Analysis of SEM images and comparison with the data of photoluminescence made it possible to assume that the homogeneity of the structures obtained after the second stage of growth will to a certain degree depend on the morphology of the first stage of growth. Larger catalytic drops formed from sputtering of 0.7 mg of gallium, and NS that contain more gallium, display high heterogeneity for both stages of growth.

The SEM image in Figure 3 contains both nanocrystals and NWs. The presence of NWs indicates that at the second stage the mechanism of vapor–liquid–crystal (LCP) is implemented with the participation of newly formed gallium drops on a relief nucleation layer. Specific dimensions and density of NW are from 100 to 700 nm in length and from 5 to 25 nm in diameter with density of $\sim 4 \cdot 10^8\,\mathrm{cm}^{-2}$. Despite high density of primary islands ($\sim 5 \cdot 10^9\,\mathrm{cm}^{-2}$), the NW density turns out to be an order lower, which indicates the selective nucleation of drops only on some crystallites, probably having a certain crystallographic facet pattern or size.

The growth of NWs occurs from nanocrystallites (the crystalline nature of the objects is confirmed by the facet pattern presence) with the specific dimensions of ~ 200 nm. It may be noted that NW growth occurs from the edges and certain structural features of the crystal of

Table 1. Growth conditions of considered samples

Sample	Stage I		Stage II	
	Catalyst	Source	Catalyst	Source
NW466	Ga, 0.5 mg	In–InP, 30 min	–	–
NW451	Ga, 0.5 mg	In–InP, 10 min	Ga, 0.5 mg	Sn–InP, 30 min
NW452	Ga, 0.7 mg	In–InP, 10 min	Ga, 0.5 mg	Sn–InP, 30 min

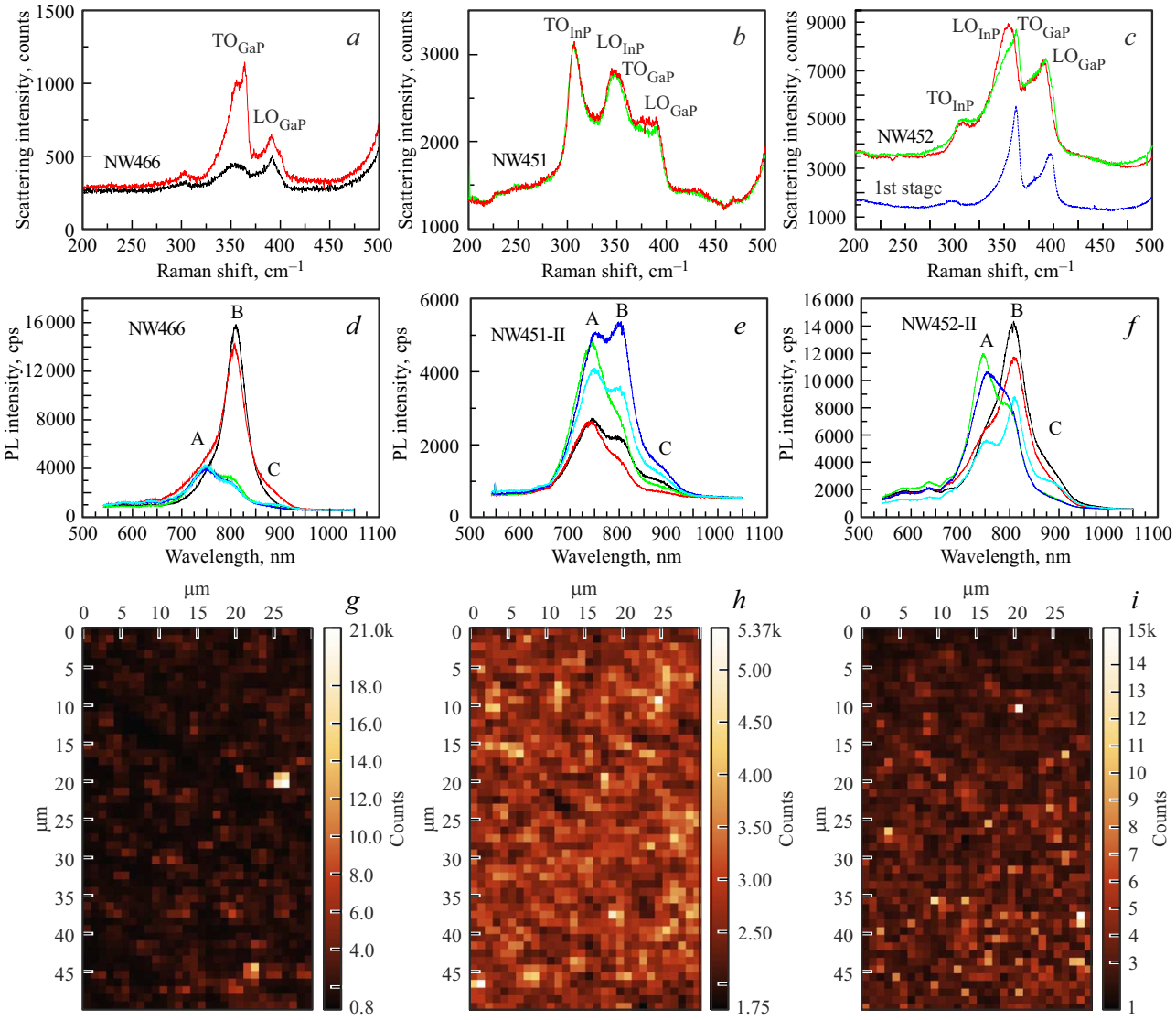

Figure 4. Raman scattering spectra (*a–c*), photoluminescence spectra (*d–f*) and photoluminescence intensity distribution maps (*g–i*) of NW466 (*a, d, g*), NW451 (*b, e, h*) and NW452 (*c, f, i*) samples (see Table 1).

crystallites. Also the morphology of the nucleation layer changes, which indicates the possibility of occurrence of the additional mechanism of vapor–solid growth. Considerable lateral growth from the vapor phase may occur along the side walls of the crystallites [8]. The mechanism for the formation of homogeneous drops on the toporgaphic or textured layer requires a separate study, however, one can assume that the decisive role is played by the migration of group III adatoms towards the ledges of the primary crystallites in process of heating, or NS partial dissolution is observed with the subsequent recrystallization in process of growth. The details on the conditions of growth of the considered samples are assembled in Table 1.

Figure 4, *a-c* presents the specific spectra of Raman scattering of NS after the first and second stages of growth. As it was shown previously, the one-stage method of growth

Table 2. Relative change of signal intensity for various bands and integral intensity of photoluminescence spectra

Band	NW466	NW451	W452
A	4.22	1.182	1.41
B	14.5	2.366	3.688
C	7.339	1.984	7.157
Integral Intensity of PL	2.868	0.98	1.917

makes it possible to obtain NS of direct-band composition, however, high heterogeneity of the layer is observed at the same time [5]. Figure 4, *a* shows two scattering spectra of NW466 sample measured in two random points. Considerable changes of the mode composition are seen in the area of frequencies of longitudinal and transverse vibrations of Ga−P-type. Raman scattering spectra after the second stage of growth are presented in Figure 4, *b*−*c*, samples NW451, NW452. One can note amplification of transverse vibrations of InP-type (TO_{InP}), especially in NW451 sample. Processes happening in two-stage growth turn out to a large degree to be related to the structure of the primarily formed layer: differences in NW451 and NW452 samples consist only in the thickness of the primary layer: to grow NW-452, at the first stage a thicker layer of catalyst (sub-sample of 0.7 mg) was used to form NS (see Table 1). This results in formation of larger NSs with higher concentration of Ga, which further affects the formation of final NSs. Besides, a shift is observed in the longitudinal vibrations of GaP-type (LO_{GaP}), which may indicate the interaction between the catalyst and NS in the process of the second stage of growth and recrystallization of NS of a different composition. This process is most visible in the NW452 structure, where the increased initial content of Ga was used. The specific spectrum of scattering of the NW452 structure after the first stage of growth is presented in Figure 4, *c* with a dotted line.

The homogeneity of the layer is more visual in PL spectra presented in Figure 4, *d*–*f*, and PL intensity distribution maps (Figure 4, *g*–*i*). Despite the fact that all structures emit approximately in the same spectral range and demonstrate a similar structure of three main bands, the apperance of which is most probably related to the jump-like change of the NS composition, the homogeneity of the signal from the NW-466 sample is noticeably worse than in the NW451 and NW-452 samples. The homogeneity of PL intensity is more visual in the data of Table 2, which represent a relative range of $(I_{max} - I_{min})/I_{average}$ signal intensity variation. Table 2 includes data both for separate radiation bands and for the total PL intensity. One can note that the sample produced by one-stage method has the widest intensity spread. PL maps, as well as Raman scattering spectra, demonstrate the differences in the homogeneity between NW451 and NW452 samples. The highest homogeneity in the NS composition and size is observed in the NW451 sample.

4. Conclusion

Therefore, the technology was developed for the two-stage growth of GaInP nanostructures from the saturated In, P vapors using Ga as a catalyst. It was established that the use of the two-stage self-catalytic growth of GaInP solid solutions from saturated vapors of indium and phosphorus on silicon substrates significantly increaases the homogeneity of the composition and results in emergence of vertical nanostructures. The effect of sample morphology after the first stage of growth on the NS properties after the second stage was demonstrated. It is shown that the optimization of growth conditions enables control of the NS composition and dimensions homogeneity. The optimal conditions were determined for the production of NS layers of the maximum degree of homogeneity.

Conflict of interest

Authors declare no conflict of interest.

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