08

GaInP on silicon nanostructures self-catalyst growth from vapor phase

© L.B. Karlina [1], A.S. Vlasov [1], R.V. Levin [1], A.V. Malevskaya [1], V.V. Zabrodskiy [1], I.P. Soshnikov [1–3]

[1] Ioffe Institute, St. Petersburg, Russia
[2] Alferov University, Russian Academy of Sciences, St. Petersburg, Russia
[3] Institute of Analytical Instrument Making, Russian Academy of Sciences, St. Petersburg, Russia
E-mail: karlin@mail.ioffe.ru

Received November 22, 2024
Revised January 16, 2025
Accepted January 20, 2025

Here we report the results of the study of GaInP nanowires obtained by the self-catalytic growth method from saturated vapors of phosphorus and indium in a quasi-closed volume on silicon substrates with the (111) orientation. The morphology and composition of the obtained structures were studied by scanning electron microscopy. It was found that the presence of silicon in the catalytic gallium droplets affects the morphology and composition of the nanostructures. The Raman spectroscopy Studies of the obtained nanostructures were performed.

Keywords: GaInP, nanowires, VLS growth from the vapor phase, III-V on Si

DOI: 10.61011/0000000000

A triple solid solution GaInP, the width of the band gap of which varies from 1.344 eV (InP) to 2.24 eV (GaP) at room temperature, is a promising material for multiple applications in optoelectronics and solar photovoltaics. Integration of the structures based on III-V compounds with silicon is one of the relevant tasks, which at the current stage of microelectronics development is solved by different methods, which usually require complicated and expensive equipment [1]. Previously we proposed the original method to grow III-V nanowires (NW) on silicon substrates in quasi-equilibrium conditions using vapor–liquid–crystal (VLC) mechanism with gold droplets as a catalyst and sources of phosphorus and indium vapors based on the solution-melt Sn–InP, located directly in the growth chamber [2,3]. Using self-catalytic (Ga in our case) growth to obtain NW of GaInP solid solutions on silicon seems to be more preferable. However, in order to understand and optimize the process of self-catalytic growth of GaInP NWs by the method proposed by us, additional research is needed.

This paper studies the features of the GaInP NW growth nature, and also the role of silicon, which may penetrate into the catalytic droplets of gallium from the silicon substrate at the stage of their formation. Besides, the morphology and the vibrational properties of the obtained structures were studied.

GaInP NWs were grown on (111) oriented substrates of single crystal silicon doped with boron. The standard procedure of silicon cleaning in the buffered HF solution was carried out before growth. The gallium film was deposited by method of thermal evaporation in vacuum using installation VUP-5 from a molybdenum boat onto the structure without substrate heating. The source of the material was gallium with purity of 7N. The Ga layer was sputtered at pressure of $(1-1.6)\cdot 10^{-6}$ Torr.

To study the initial stage of formation of catalytic gallium droplets on the silicon substrates and impact of this stage at the further growth of GaInP solid solution NWs, the catalytic droplets were formed by two methods.

1. After sputtering of the gallium film, the specimen was placed directly in the growth chamber, where the catalytic droplets were formed in the presence of phosphorus and indium vapors during temperature rise to the specified value.

2. The droplets were formed by additional annealing of the gallium film in a separate installation at temperature of 400 °C for 10 min in the hydrogen atmosphere. It is known that at temperature of 400 °C the maximum concentration of the dissolved silicon in gallium is estimated at 1 at.%. [4].

Growth experiments were carried out in a specialized installation using a quasi-closed cell described previously as a source of vapors [3]. GaInP NW synthesis was carried out in the hydrogen flow atmosphere. The source of indium and phosphorus vapor was a saturated Sn–InP solution-melt located directly in the growth chamber.

The initial period of temperature rise in the process of growth was 20 min, and then after reaching the 560 °C the temperature in the growth chamber was stabilized for 30 min. The ratio of phosphorus and indium vapor flows in the vapor phase in accordance with the Sn–InP system phase diagram was within 8–10 [5].

The morphology and the composition of the grown NWs were studied using scanning-electron microscope (SEM) SUPRA 25 Carl Zeiss, equipped with energy-dispersive X-ray spectroscopy unit by Ultim Oxford Instruments. SEM-images in certain cases demonstrated the particles of catalytic droplets on the tops of nanostructures. This allows to conclude on the growth of nanostructures based on VLC mechanism. Vibrational properties were studied by the Raman scattering spectroscopy methods using a single-frequency laser with wavelength of 532 nm. The

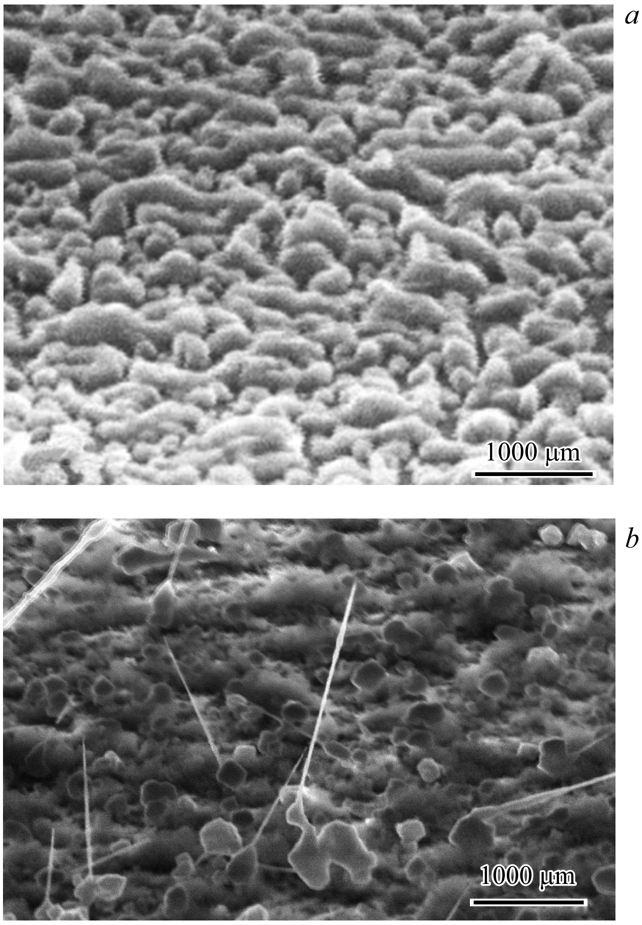


Figure 1. SEM-image of the array of GaInP nanostructures grown using catalytic droplets of gallium. *a* — without pre annealing, *b* — after pre annealing of catalytic droplets in an individual installation.

unpolarized Raman scattering spectra were measured in the backscattering geometry.

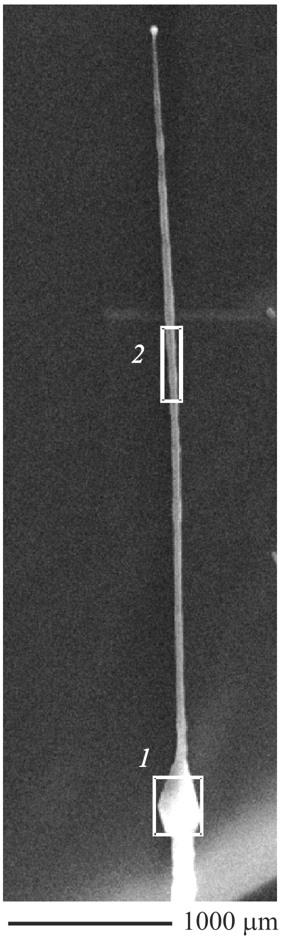
Silicon substrates with different methods of catalytic droplets formation were simultaneously placed into the growth chamber. The morphology of the specified structures is shown in fig. 1. As you can see in fig. 1, in both cases the surface of Si-substrate is irregularly covered with islands (crystallites) having somewhat different morphology. And substantial differences are observed.

Fig. 1, *a* (specimen without annealing) shows rounded structures without clear faceting extended along the surface. Extended structures have preferential direction close to $\langle 110 \rangle$. Specific density of structures with size of 10−50 nm is $\sim 10^{10}\,\text{cm}^{-2}$, extended to 250 nm — $10^9\,\text{cm}^{-2}$. The average composition of layer $Ga_xIn_{1-x}P$ may be defined as $x \sim 0.75{-}0.83$. It should be noted that the presence of individual metal droplets indirectly confirms our assumption on VLC-mechanism of growth.

Fig. 1, *b* (specimen after prior annealing for 10 min) shows crystallites faceted with planes of type (110) having specific dimensions of around 50−150 nm with density of around $10^9\,\text{cm}^{-2}$. Some crystallites demonstrate growth of NW with diameter of 10−30 nm and length of more than 1000 nm. The density of such NWs is around $10^7{-}10^8\,\text{cm}^{-2}$. The shape of NW complies with the hexagonal prism so that the side facets correspond to planes of type (110). By composition the obtained structures (and surface crystallites and FNCs) are solid solutions $Ga_xIn_{1-x}P$. A difference is noted in the composition of surface crystallites and NWs: for crystallites, the higher content of gallium is specific ($x \sim 0.7{-}0.8$), and for NWs — high content of indium ($x \sim 0.2{-}0.35$).

Energy-dispersive spectra of X-ray diffraction show the presence of In, Ga, P and Si atoms in the obtained structures. Content of III/V (In+Ga:P) is approximately 1:1. The ratio In:Ga in the surface nanostructures and individual NWs differs and is $1:(3-5)$ and $(2-3):1$ accordingly, 2D-layers are enriched with gallium, and NWs are enriched with indium. It does not seem possible to assess the presence of silicon in these structures by this method due-to contribution of the substrate signal to the overall picture.

It may be assumed that additional annealing (fig. 1, *b*) promotes more effective penetration of the silicon atoms from the substrate into the droplet, thus changing the chemical potential in the liquid phase and the corresponding speed of NW nucleation in the self-catalytic process. Paper [6] presents the thermodynamic consideration of the quantitative estimate of the chemical potential change in the liquid phase and corresponding speed of nucleation of triple single layers of NW during the self-catalytic VLC process under the influence of the presence of Si atoms for InGaAs and AlGaAs systems. Based on the analysis of the proposed growth model of triple solid solutions A_3B_5 it may be assumed that in our case the process of GaInP NW formation will be influenced by the presence of silicon atoms in the droplet. Comparison of the morphological features of NW self-catalytic growth on the silicon substrates from the droplets formed by different methods confirms our assumption experimentally. Increase of the NW nucleation speed in the presence of silicon promotes the combination of 2D- and 3D-growth and actual increase of GaInP layer thickness. This assumption is related to the near-surface layer of NW. Fig. 2 shows the image and energy-dispersive spectra for dedicated areas of a single NW transferred on a carbon film. The spectra are normalized to the maximum intensity value corresponding to the aluminum peak. Aluminum and copper peaks in the spectrum are artifacts due to the interaction of the scattered electrons with the materials of the supporting net and holder (table) of specimens, and they are excluded from the analysis when considered. The composition of NW defined using the spectra shown in the figure corresponds to Ga:Si:P:In — 37:7:50:6 (*1*) and 41:0:48:11 (*2*). Comparison of the spectra/composition shows the appearance of the silicon signal in the area *1*, adjacent to the substrate. At the same time the area *2*, corresponding to the main body of NW, does not contain the silicon signals that are noticeable for the energy-dispersive studies.



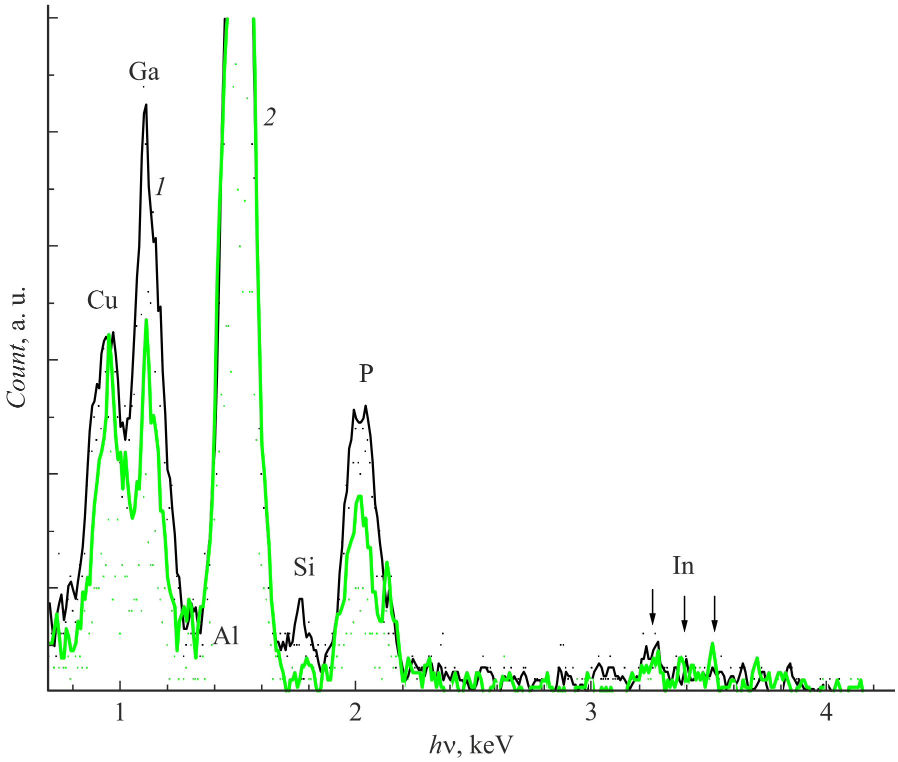


Figure 2. SEM-image of NW transferred to a perforated carbon film, and energy-dispersive spectra for areas near the surface (*1*) and in the middle part of NW (*2*).

Thus, it is shown experimentally that the morphology of the structures may be controlled by adding silicon in the composition of the catalytic gallium droplets, thus receiving the additional controlled parameter of the growth process.

The mechanism of formation of the vertical NWs on the surface of the already grown 2D-layer is not quite clear yet. It may be assumed that the indium droplets formed from the vapor phase on the surface of the grown layer may serve as catalytic drops [7]. Another mechanism of formation of such vertical structures may be the mechanism specified in papers [8,9], where indium is pushed out of crystallites in process of crystallization under compressing stresses and forms NW with high indium content. The final conclusion may be made on the basis of additional experiments.

The impact of the initial stage of droplet formation at the composition and speed of growth of nanostructures may be seen in the Raman scattering spectra (fig. 3). The spectra include longitudinal modes of GaP and InP type LO_1 and LO_2 and common transverse oscillation (TO_m). The spectra have the shape specific for GaInP nanostructures [10]. The vibrational frequency of the sample after annealing indicates the composition of the solid solution $x \sim 0.8$, which matches the data of the X-ray microanalysis [11]. It seems to be impossible to assess the composition of the solid solution of crystallites in the sample without annealing due-to high heterogeneous broadening, caused most probably by the difference in the composition. Besides, the difference in the spectra intensity attracts attention: the spectrum of the specimen without annealing has the intensity that is lower by more than two orders of magnitude. Probably, this is due to small quantity of the solid solution and large quantity of metal drops, which may explain the observed round shapes of nanostructures. Such difference in the intensity may indicate the substantial increase of growth speed in the structures with the previously formed drops.

Therefore, the paper for the first time studied the self-catalytic growth of GaInP solid solutions using VLC mechanism on Si (111) substrates by growth method from the saturated vapors of indium and phosphorus using catalytic gallium droplets. The influence of the silicon presence in the catalytic gallium droplets on the composition, morphology and speed of NW growth was shown experimentally. The vibrational properties of the obtained structures were

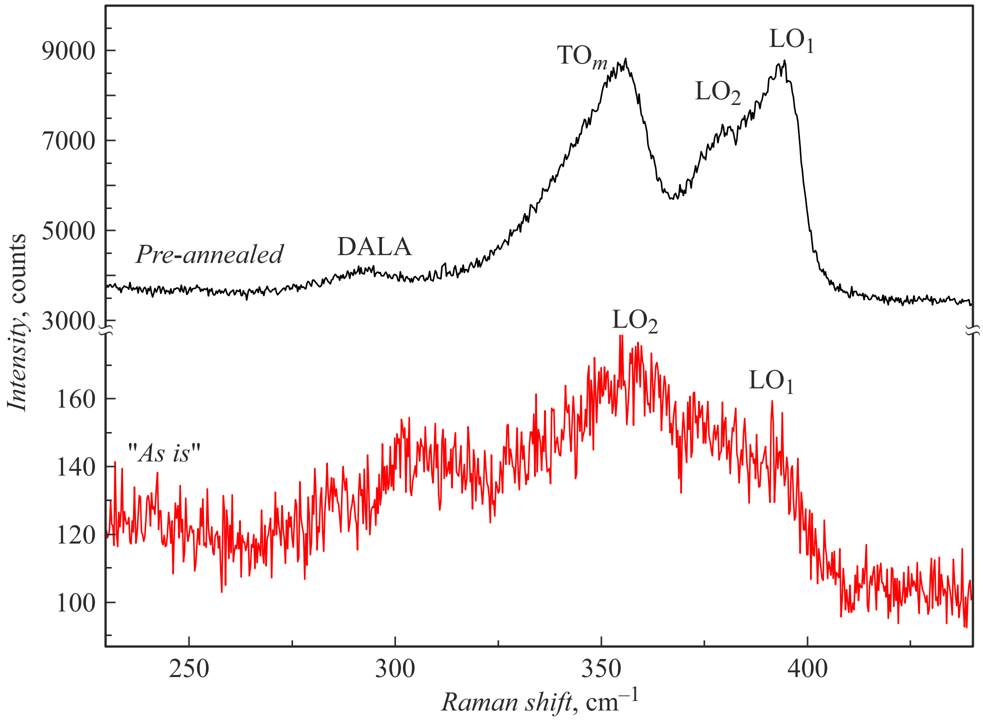


Figure 3. Raman scattering spectra of specimens with (*Pre-annealed*) (top curve) and without pre annealing („*As is*“) (bottom curve).

measured, which confirmed the formation of GaInP NWs of different composition.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S. Saurabh, M.Kh. Hossain, S. Singh, S.K. Agnihotria, D.P. Samajdar, RSC Adv., **13**, 9878 (2023). DOI: 10.1039/d3ra00039g

[2] L.B. Karlina, A.S. Vlasov, I.V. Ilkiv, A.V. Vershinin, I.P. Soshnikov, Semiconductors, **57** (7), 521 (2023). DOI: 10.61011/SC.2023.07.57414.5037C.

[3] A.S. Vlasov, L.B. Karlina, B.Ya. Ber, N.A. Bert, M.E. Boiko, D.Y. Kazantsev, A.A. Levin, A.B. Smirnov, I.P. Smirnova, I.P. Soshnikov, Mater. Today Commun., **31**, 103232 (2022). DOI: 10.1016/j.mtcomm.2022.103232

[4] M.K. Sunkara, S. Sharma, R. Miranda, G. Lian, E.C. Dickey, Appl. Phys. Lett., **79** (10), 1546 (2001). DOI: 10.1063/1.1401089

[5] Yu.P. Khukhryanskiy, V.I. Panteleev, Neorgan. materialy, **13** (5), 785 (1977) (in Russian).

[6] H. Hijazi, M. Zeghouane, V.G. Dubrovskii, Nanomaterials, **11**, 83 (2021) DOI: 10.3390/nano11010083

[7] G. Miao, D. Zhang, Nanoscale Res. Lett., **7** (1), 321 (2012). DOI: 10.1186/1556-276X-7-321

[8] S.A. Kukushkin, A.V. Osipov, A.V. Redkov, V.M. Stozharov, E.V. Ubiyvovk, Sh.Sh. Sharofidinov, Tech. Phys. Lett., **48** (2), 65 (2022). DOI: 10.21883/TPL.2022.02.53584.19056.

[9] V.O. Gridchin, K.P. Kotlyar, E.V. Ubyivovk, V.V. Lendyashova, A.S. Dragunova, N.V. Kryzhanovskaya, D.S. Shevchuk, R.R. Reznik, S.A. Kukushkin, G.E. Cirlin, ACS Appl. Nano Mater., **7** (15), 17460 (2024). DOI: 10.1021/acsanm.4c02561

[10] I. Mediavilla, J.L. Pura, V.G. Hinojosa, B. Galiana, L. Hrachowina, M.T. Borgström, J. Jimenez, ACS Nano, **18**, 10113 (2024). DOI: 10.1021/acsnano.3c12973

[11] O. Pagés, A. Chafi, D. Fristot, A.V. Postnikov, Phys. Rev. B, **73**, 165206 (2006). DOI: 10.1103/PhysRevB.73.165206

Translated by M.Verenikina