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Self-catalytic growth of GaInP nanostructures on silicon substrates from vapor phase: choice of source composition and catalytic droplets

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The article presents studies of self-catalytic growth of GaInP nanostructures on (111) oriented silicon substrates from saturated vapors of phosphorus and indium in a quasi-closed volume, aimed at studying the methods for controlling the composition of the obtained structures. Studies of vibrational properties and photoluminescence spectra have shown that choosing the optimal combination of source and catalytic droplet compositions makes it possible to obtain GaInP nanostructures emitting in the range from 1.37 to 1.9 eV. Differences in the morphology of the obtained nanostructures depending on the conditions of their formation have been established.

Keywords: GaInP nanostructures, self-catalytic growth from vapor phase, $A^{III}B^{V}$ on Si.

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1. Introduction

The ternary GaInP solid solution with a band gap varying from 1.34 eV (InP) to 2.24 eV (GaP) at room temperature has found wide application in numerous optoelectronic devices and solar power engineering [1]. Moreover, since the work on integration of structures based on $A^{III}B^{V}$ compounds with silicon progresses rapidly, the use of GaInP nanostructures with their characteristics controlled by adjusting the ratio of indium and gallium in their composition is very promising. This study is a continuation of our series of papers on catalytic growth of $A^{III}B^{V}$ compounds on gallium arsenide and silicon substrates from saturated indium and phosphorus vapors [2].

The synthesis of GaInP solid solutions with a wide range of compositions is a challenging task. The method of preliminary seed synthesis in solution (solution phase synthesis) was used in [3] to form nanowires (filamentary nanocrystals) from a gallium indium phosphide alloy ($In_xGa_{1-x}P$) with an indium/gallium ratio and, consequently, the physical and electronic structure varying over the entire range of compositions from $x = 0$ to $x = 1$.

GaInP nanowires with the In content varying smoothly from 12 to 73 % were obtained via chemical vapor deposition on a single silicon substrate; their photoluminescence peak shifted from 580 to 780 nm, respectively. The method is based on obtaining a composition gradient by tilting the substrate horizontally in a specific way to achieve a temperature gradient.

It is known that self-catalytic growth (i.e., growth with no additional catalysts) of $A^{III}B^{V}$ nanocrystals is the most promising [4,5]. Using the methods of metal-organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE), adjusting the growth temperature and the ratio of fluxes of group V and III elements, and introducing additional dopants in the process of growth, one may induce a change in the composition of GaInP nanowires (NWs). However, each NW growth technology has its specifics. In the present case, this specific feature is a limited number of independent process parameters that may be used to alter the nature of nanostructure growth. The phosphorus/indium vapor pressure ratio is actually determined by the process temperature. Thus, existing growth theories [4,5], which assume the possibility of independent alteration of the ratio of group V and III elements, cannot be used directly to explain and predict the composition and processes occurring during synthesis in a quasi-closed volume from saturated vapor.

The possibility of synthesis of nanocrystals from GaInP solid solutions with a composition close to the indirect-gap one was demonstrated in our previous study [2]. As the indium content increases, it becomes possible to vary the band gap within a wide range.

In the present study, the research aimed at controlling the composition of GaInP NWs through the use of various vapor phase sources and catalytic droplets with a complex composition was continued. The morphology of the obtained structures, their vibrational properties, and their photoluminescence were examined.

2. Experimental procedure

The present study was focused on the initial period of growth of GaInP nanocrystals (NCs). They were grown on boron-doped single-crystal silicon substrates with the (111) orientation in accordance with the procedure detailed in [2]. The initial period of temperature growth during synthesis was 20-min-long. Following that, when 560 °C was reached, the temperature in the growth chamber was stabilized for 30 min. The ratio of phosphorus and indium vapor fluxes corresponded to the state diagrams of Sn-InP and In-InP [6].

The morphology and composition of the grown NWs were studied using a SUPRA 25 (Carl Zeiss) scanning electron microscope (SEM) fitted with an energy-dispersive X-ray spectroscopy attachment (Ultim, Oxford Instruments). In certain cases, SEM images revealed the partial presence of catalytic droplets on top of nanostructures. This suggests that the nanostructures grew by the vapor–liquid–solid mechanism. Vibrational properties were studied using Raman scattering spectroscopy with a single-frequency laser operating at a wavelength of 532 nm. Raman spectra were recorded in the backscattering geometry with polarization $z(xy)$-z in order to suppress the forbidden acoustic vibration signal from the silicon substrate. Photoluminescence (PL) spectra were measured at a temperature of 70 K with an optical resolution no worse than 1.5 μm.

3. Discussion

The table presents the considered combinations of source and catalyst droplet compositions. Two sources (In-InP and Sn-InP solutions-melts) and two catalyst types (Ga and Ga-In) were used. The results of preliminary experiments revealed that the use of indium catalyst droplets in combination with the chosen sources is impractical under the given temperature and time conditions (due possibly to an insufficient phosphorus vapor pressure).

Catalyst droplets were formed using a VUP-5 setup by thermal evaporation in vacuum from a molybdenum boat onto the structure without substrate heating and with subsequent annealing in hydrogen (10 min, 400 °C). Droplets of a complex (Ga-In) composition were formed by sequential deposition of metal layers (first In, then Ga). The possible source–catalyst combination are listed in the table. When catalyst droplets of a mixed composition were used, different component ratios were analyzed.

The growth of nanostructures was not observed in experiments with the In-InP source and droplets of a complex composition.

Combinations of sources and catalyst droplets

Catalyst		Source (solution-melt)	
		Sn-InP	In-InP
	Ga	Option A	Option B
	Ga-In	Option C	–

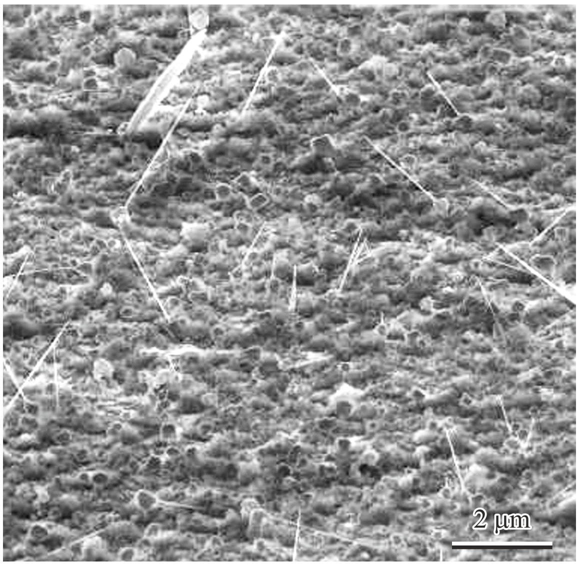

Figure 1. SEM image of an array of GaInP nanostructures (option A).

Option A

The phosphorus vapor pressure is sufficiently high in this case. The phosphorus/indium ratio in the vapor phase promoted both the formation of a nucleation layer and individual GaInP nanostructures. The formation of nanowires on the surface of the sublayer was observed (Figure 1). The characteristic dimensions of these NWs were ~ 20–50 nm (diameter) and 3–7 μm (length) at a density of ~ 10^6 NW/cm^2. The growth process was detailed in [2]. The nucleation layer and NCs had an indirect-gap composition.

Option B

As before, the morphology of the obtained structures revealed a nucleation sublayer and NCs with characteristic dimensions of ~ 40–100 nm (diameter) and up to 500 nm (length). NCs were typically oriented along the surface of the sample. Catalytic droplets were observed in the form of contrasting (bright) areas on top of NCs.

Since the nucleation sublayer corresponded to an indirect-gap composition, it produced no photoluminescence signal. At the same time, nanostructures with a significantly higher indium content were mostly direct-gap and emitted within the range of 600–720 nm (Figure 2). A large spread in positions of the PL maximum in different nanostructures was noted. Apparently, the composition of nanostructures depends largely on the size of the formed droplet.

Option C

The formation of multiple NCs faceted along low-index planes (Figs. 3, a, c) was observed in this case. The characteristic sizes of NCs ranged from 50 to 300 nm. Different

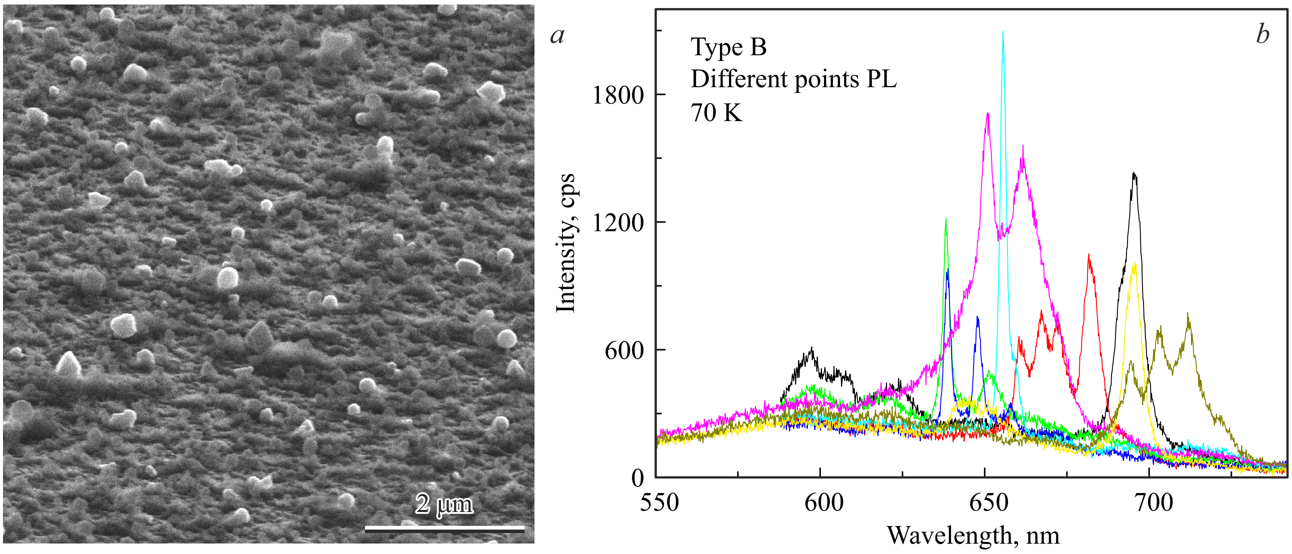

Figure 2. *a* — SEM image of an array of GaInP nanostructures (option B); *b* — photoluminescence spectra measured at different points on the surface.

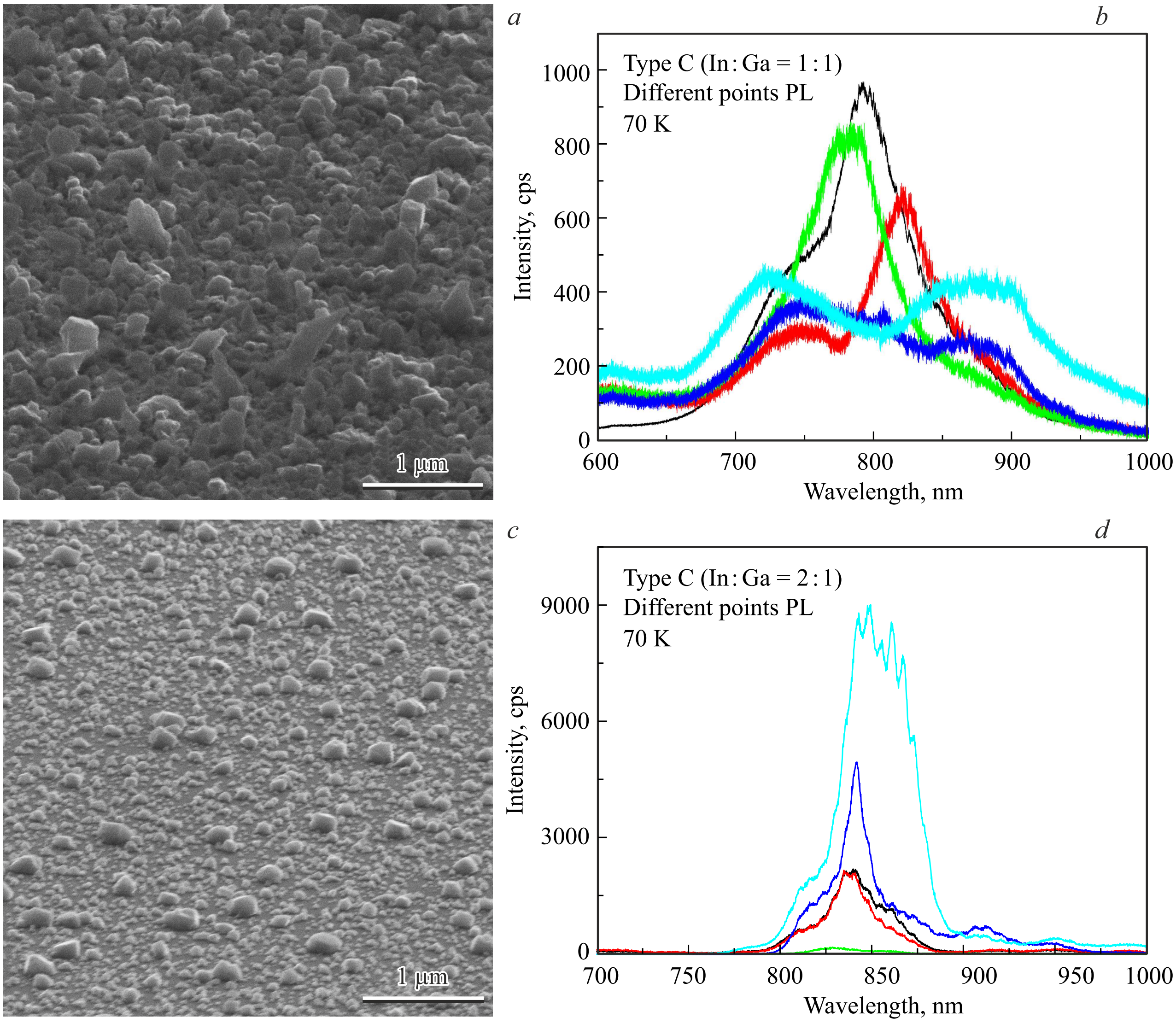

Figure 3. *a, c* — SEM images of the surface (option C) and photoluminescence spectra of nanostructures (*b, d*).

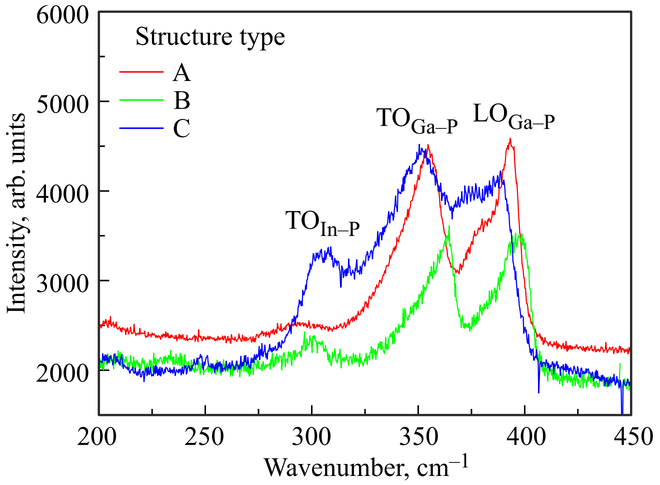

Figure 4. Characteristic Raman spectra of structures type A, B, and C.

ratios of indium and gallium in a droplet corresponded to different morphologies of the resulting structures. The random nature of nucleation translated into a significant size dispersion. Figure 3 presents two types of nanostructures obtained using catalytic droplets of a mixed composition: the Ga : In ratio was close to 1 : 1 in the top panels (*a, b*) and 1 : 2 in the bottom panels (*c, d*). In the former case, the surface morphology was very similar to option B (see above), and the presence of indium in catalyst droplets led to a shift of the photoluminescence maximum (Figure 3, *b*). The position of the maximum, the number of peaks, and their width were also characterized by a significant heterogeneity, but the existence of separate nanostructures of a direct-gap composition is out of the question in this case. Photoluminescence was observed at every point of the sample. As the indium concentration in catalyst droplets increased, the PL shifted further toward InP. The spread of nanostructure compositions was constrained noticeably in the process: the PL maximum at all points fell within the range of 850 ± 30 nm (Figure 3, *d*).

Figure 4 shows the typical Raman spectra. Since the size of a focused laser beam exceeds significantly the size of nanostructures, the signal from the nucleation layer is dominant in the scattering spectrum. Option C, where the density of nanostructures increases significantly, was the only one revealing clearly the emergence of additional vibrations ($310-315\,cm^{-1}$), corresponding to a solid solution with a high indium content. The spectrum featured signals of longitudinal (LO) and transverse (TO) phonons of the Ga-P type (at frequencies of $360-400\,cm^{-1}$) and the mixed Ga-P+In-P type ($348-363\,cm^{-1}$).

Despite the large width of bands, which is attributable to heterogeneity of the composition of different nanostructures, one may trace the influence of growth conditions on the maximum Ga content in the nucleation layer. Specifically, when Ga droplets and the Sn-InP source were used, the average composition of the nucleation layer was $X_{Ga} \sim 0.8-0.85$. When indium was added to the composition of nucleation droplets (option C), the concentration of Ga in the nucleation layer decreased predictably, and a signal emerged within the frequency range of In-P-type vibrations ($300-340\,cm^{-1}$), indicating the formation of NCs with a composition close to InP. When Ga droplets and the In-InP source were used, average Ga content X_{Ga} did, on the contrary, increase to $X_{Ga} \sim 0.9$. This may be attributed to a reduction of the phosphorus vapor pressure and a sequential formation of the nucleation layer and NCs; however, the initial growth processes have not been analyzed in detail.

4. Conclusion

It was found that the composition of nanostructures grown from saturated phosphorus and indium vapors on silicon substrates may be controlled efficiently by setting the optimal combination of sources, droplets, and the conditions for their formation. The obtained results demonstrated that the adjustment of growth conditions provides an opportunity to synthesize nanostructures emitting within the range from 1.37 to 1.9 eV.

Conflict of interest

The authors declare that they have no conflict of interest.

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