Formation of single and heterostructured nanowires based on $InAs_{1-x}P_x$ solid solutions on Si(111)

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We study the growth of nanowire arrays based on InAsP on silicon substrates. It was found that during the growth process two structural phases are formed: a cubic structure of the sphalerite type and a hexagonal structure of the wurtzite type. The epitaxial relations between InAsP and Si were determined: $[0001]_{NWs} \parallel [111]_{Si}$, $[11\bar{2}0]_{NWs} \parallel [1\bar{1}0]_{Si}$. A decrease of the radial growth rate and the formation of an axial heterojunction were revealed with the formation of thin (< 100 nm) segments of the $InAs_{1-x}P_x$ solid solution and maintaining a sufficiently high partial pressure of the As flow (at least 50%).

Keywords: InAsP, nanowires, molecular beam epitaxy.

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1. Introduction

One of the challenges facing the development of electronics and information technology is the problem of integrating $A^{III}B^{V}$ and Si semiconductors. The integration of these compounds will make it possible to combine the capabilities of silicon integrated technology and the possibilities of creating optoelectronic devices based on heterostructures of compounds $A^{III}B^{V}$: optical sensors, communication lines and signal processing [1,2]. A variant of solving this problem is the transition from heterostructures of planar geometry to heterostructures based on nanowires (NW) [3]. Nanowires based on solid solutions $InAs_{1-x}P_x$ are attractive in this field. The InAs compound is a narrow-gap semiconductor ($E_g = 0.35$ eV) and is characterized by a high charge carrier mobility of $40\,000\,cm^2/(V \cdot s)$ and a long lifetime of minority carriers, which makes it widely used in microwave transistors [4], as well as in near-infrared photodetectors ($1.2-3.6\,\mu m$) [5]. Epitaxial InAsP NWs and hetero-structured InAsP/InAs-based NWs formed by the self-induced mechanism, which consists in the formation of structures in the vapour–solid method [6] without the use of a catalyst drop, which favorably affects the electrophysical properties of these compounds, were chosen as the object of this study, as the formation of NWs by the self-induced mechanism excludes the incorporation of foreign material (for example, Au, which acts in some cases as a catalyst in the growth of NWs from a droplet) into the structure of NWs, and the formation of deep levels, which play the role of charge traps, is excluded. However, the self-induced mechanism imposes limitations on the range of possible growth parameters and, as a consequence, on the morphology of the formed NW arrays.

2. Experiment procedure

Epitaxial arrays of InAsP nanowires were synthesized by molecular-beam epitaxy on a Veeco GEN III machine on *p*-Si(111) substrates with disorientation in 4° towards $\langle 11\bar{2} \rangle$. The silicon wafers were cleaned by a modified Shiraki [7] method before being placed in the loading chamber. In the final step, silicon oxide was formed by boiling the substrate in an ammonia-peroxide solution ($NH_4OH : H_2O_2 : H_2O(1:1:3)$). Growth temperatures were measured using a pyrometer and a thermocouple calibrated with the temperature of the $Si(111)7 \times 7 \leftrightarrow 1 \times 1$ reconstruction transition and positioned in close proximity to the substrate. Synthesis of epitaxial arrays of InAsP NWs was carried out under identical growth conditions (flux ratio $(As_4 + P_2)/In = 90$, $T = 450-460°C$) and differed only by different ratios of partial pressures As_4/P_2 (1/1 or 1/3). The morphology of the synthesized arrays was investigated by scanning electron microscopy (SEM, Zeiss SUPRA 25-30-63) microscope. Energy dispersive X-ray spectroscopy (EDX) was used to determine the composition of the solid solutions.

3. Results

It has been demonstrated that the formation of SiO_x solid solutions by the NW method on a Si(111) surface coated with a thin layer of $InAs_{1-x}P_x$ oxide by a self-induced

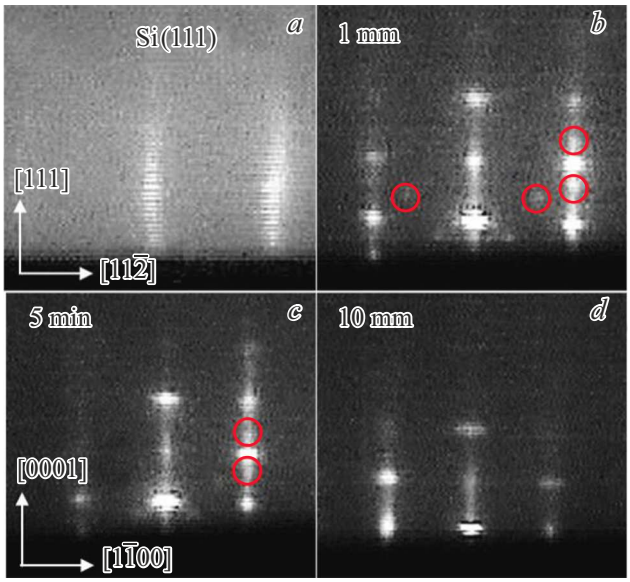

Figure 1. Reflection high-energy electron diffraction (RHEED) patterns taken before the onset of growth (*a*), after 1 (*b*), 5 (*c*), and 10 (*d*) minutes. Red circles mark reflexes of cubic structure of sphalerite type. (The colored version of the figure is available on-line).

mechanism is possible. The defects („holes") of the SiO_x, layer formed in the process of pre-growth thermal annealing of the oxide serve as the centers of NW nucleation.

The evolution of RHEED patterns (Figure 1) shows that at the initial stage of growth two structural phases are formed almost synchronously: cubic structure of sphalerite type and hexagonal structure of wurtzite type. The diffraction pattern shows reflexes of cubic phase twins rotated relative to each other by 180°, and the occurrence of these reflexes is described in detail in [8]. As the NW size increases, the sphalerite reflexes go out and, accordingly, the contribution of the wurtzite phase increases. The low surface energy of the $[11\bar{2}0]$ lateral face and the effective diffusion of In adatoms along it favor the pronounced further unidirectional formation of $InAs_{1-x}P_x$as NWs. It was found that all the formed NWs are epitaxially oriented: the growth axis of NW [0001] is oriented along the crystallographic direction of the Si[111] substrate, and the azimuthal direction $[11\bar{2}0]$ of the NW lattice coincides with the direction $[1\bar{1}0]$ of the substrate Si (see Figure 1).

To study the peculiarities of the formation of self-induced NWs based on solid solutions $InAs_{1-x}P_x$, a series of samples was synthesized in which the flux ratio As_4/P_2 was varied, but the ratio of the total pressure of molecular beams V group to In, i. e., remained unchanged. $P_{(As_4+P_2)}/P_{(In)} = 90$. Thus, at equal partial pressures As_4 and P_2, the content P in the forming NWs is $\sim 10\%$ (Figure 2, *a*). It was found that further decreasing the partial pressure of the As_4 molecular beam decreases the rate of axial and increases the rate of radial growth of NWs. An integrated phosphorus concentration of 40% was achieved with a flux ratio of $As_4/P_2 = 1/3$ (Figure 2, *b*). Thus, the $InAs_{0.6}P_{0.4}$ NWs have 1.5 times larger diameter and 1.3 times smaller height compared to the $InAs_{0.9}P_{0.1}$ NWs (see Figure 2, *a*). In this case, the surface density of NWs in the epitaxial array decreases by an order of magnitude, and the main volume is formed in the form of three-dimensional islands (see Figure 2, *b*). It should be noted that the present study was able to achieve higher concentrations of P in self-induced NWs of InAsP solid solution than previously reported in [9,10]. Thus it was found that the presence of flux P_2 inevitably leads to radial growth, which may prevent the formation of axially heterostructured NWs.

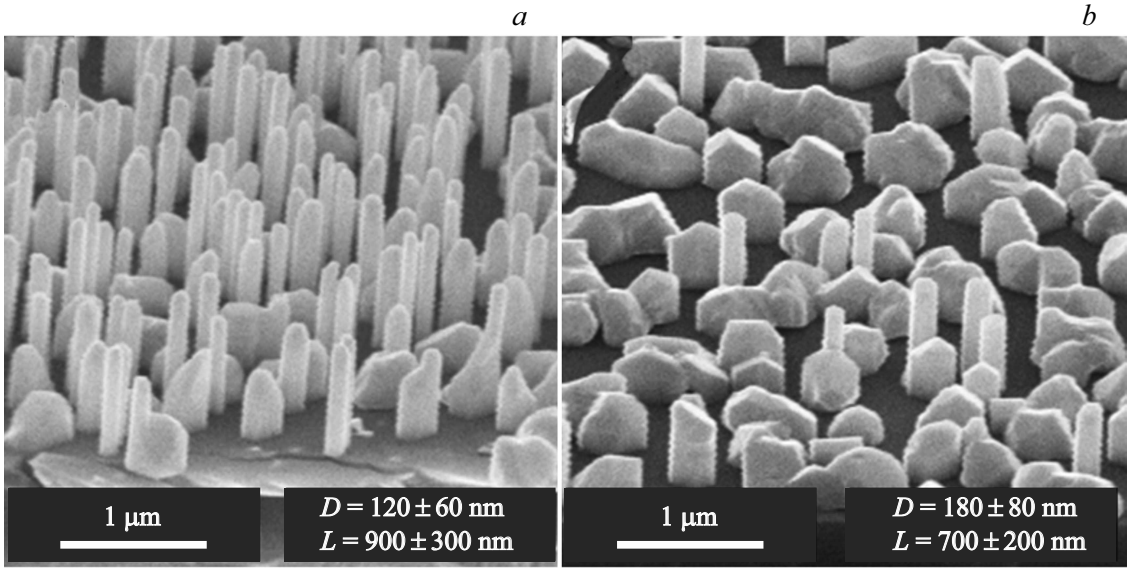

Figure 2. SEM images of InAsP arrays of NWs synthesized at the partial pressure ratios of molecular beamsAs_4/P_2 1/1 (*a*) and 1/3 (*b*).

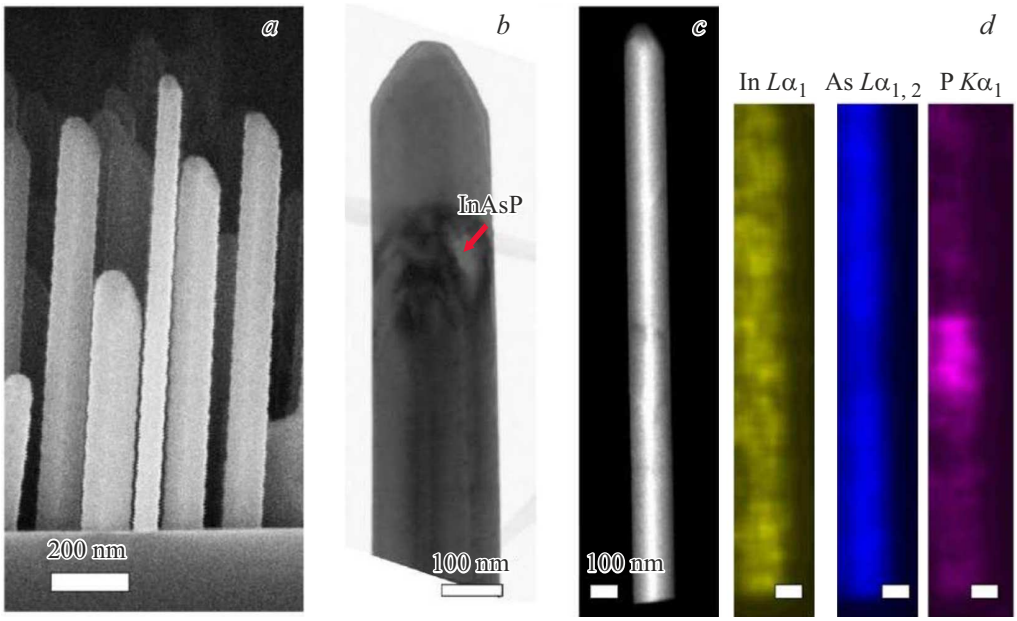

Figure 3. *a* — SEM image of a chipped structure with an array of axially heterostructured NWs; *b* — wide-angle dark-field SEM image, the contrast is related to the excellent atomic density in the InAs–InAsP heterojunction band; *c* and *d* — wide-angle dark-field TEM image and corresponding intensity distribution maps of the characteristic X-ray emission of In, As, and P, illustrating the formation of the InAsP segment.

Axial InAsP/InAs heterostructures were also synthesized (see Figure 3, scanning (SEM) and transmission (TEM) electron microscopy images) and it was found that by forming thin (< 100 nm) segments of solid solution $InAs_{1-x}P_x$ and maintaining a sufficiently high partial pressure of As flow, it is possible to reduce the rate of undesirable radial growth and form an axial heterojunction. In this case, the presence of As flux constrains the maximum achievable concentration of P as $x = 10\%$. It can be assumed that the opposite situation, allowing the formation of more extended axial segments, will be observed in the formation of InAs segments in solid solutions of InAsP NWs with low phosphorus content.

4. Conclusion

It was found that two structural phases are formed during the synthesis of InAsP NW: a cubic sphalerite-type structure and a hexagonal wurtzite structure. The epitaxial ratios were also established: $[0001]_{HHK} \parallel [111]_{Si}$, $[11\bar{2}0]_{HHK} \parallel [\bar{1}10]_{Si}$. Decreasing the partial pressure of the As_4 molecular bundle and increasing the partial pressure of the P_2 molecular bundle during synthesis leads to a decrease in the axial growth rate and an increase in the radial growth rate of NWs, as well as a decrease in the surface density of NWs. InAsP/InAs heterostructured NWs were also synthesized and it was found that by forming thin $InAs_{1-x}P_x$ segments and maintaining a high partial pressure of As, the radial growth rate can be reduced and an axial heterojunction can be formed.

Acknowledgments

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Conflict of interest

The authors declare that they have no conflict of interest.

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