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Opportunities to rule the growth direction of nanocrawlers

© *N.V. Sibirev*[1,2], *I.V. Shtrom*[1]

[1] Institute for Analytical Instrumentation, Russian Academy of Sciences,
198095 St. Petersburg, Russia
St. Petersburg State University,
199034 St. Petersburg, Russia
E-mail: n.sibirev@mail.spbu.ru

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A model of nanocrawler or planar wire growth through the vapor–liquid–solid process is proposed. The conditions for changing the growth direction of nanowcrawler in the substrate plane are identified. The process of wire detachment from the substrate is described. It is shown that the direction of planar nanowire growth can be controlled by varying the fluxes of groups V and III.

Keywords: vapor–liquid–solid mechanism, planar nanowire, planar wire, nanocrawlers.

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Group III-V planar semiconductor nanowires (NW) are often considered as promising active components for new optoelectronic and nanoelectronic devices [1–7]. NW growth and doping nanolevel-control during formation of nanostructures is one of the key device fabrication problems.

When creating NW-based integrated optical and electrical circuits on silicon, nanolevel control of position, shape, number of defects, doping type and level is critical. Due to a number of unique properties, modern NW development makes it possible to use NW as virtually any micro/nanocomponents of integrated circuits. For example, NWs are widely used as waveguides where NW waveguide geometry needed for effective propagation of the desired wave is set directly in the growth process. In photonic circuits, NW are used as nanolasers and single-photon sources.

When making switching components of integrated circuits, NW doping must be strictly controlled. Since, most of these components are based on the *p*–*n*-junction formed during the NW synthesis where switching is initiated by applying an electric field or mechanical stress that induces piezoeffect. The latest success achieved in this area for NW synthesized through the vapor–liquid–solid (VLS) bottom-up process face big difficulties in transferring NW from a substrate to a planar integrated circuit. Therefore, a controlled planar NW (p-NW) synthesis and doping process is addressed in this work. Such p-NWs may be synthesized as ready-made integrated circuit components provided that parameters are chosen properly.

Growth direction and doping variation processes are generally addressed separately [8,9]. On the other hand, there are many facts showing that a change of the p-NW doping level may cause a change of the p-NW growth direction [1–3,9]. Figure 1 shows such changes of the p-NW growth direction: p-NW rotations in the substrate plane and p-NW separation from the substrate. Growth of this NW is described in [2].

Synthesis conditions leading to controlled change of p-NW growth direction in the substrate plane an synthesis conditions leading to p-NW separation from the substrate are discussed in this work. It is shown that the p-NW growth direction may be changed by controlling group V and III fluxes.

Focus was made on the following aspects of p-NW growth: rotation in the substrate plane marked as *R* in Figure 1, and separation from the NW substrate marked as *D* in Figure 1.

It was shown in [5,6] that the p-NW growth is defined by location of a new layer nucleus. If the new layer nucleus evolves at the droplet–NW–substrate interface, then the planar growth continues. If the new layer nucleus evolves in some other location, then NW is separated from the substrate and grows at an angle (see Figure 2).

Thus, the planar NW growth condition may be written as:

$$\gamma_{n\mathrm{Sub}} - \gamma_{\mathrm{Sub}L} < \min\left(\gamma_{nL},\ \gamma_{nV} - \gamma_{LV}\right). \tag{1}$$

Here, $\gamma_{n\mathrm{Sub}}$, $\gamma_{\mathrm{Sub}L}$, γ_{nL}, γ_{nV}, γ_{LV} are surface energies of the nucleus–substrate, substrate–droplet, nucleus–droplet,

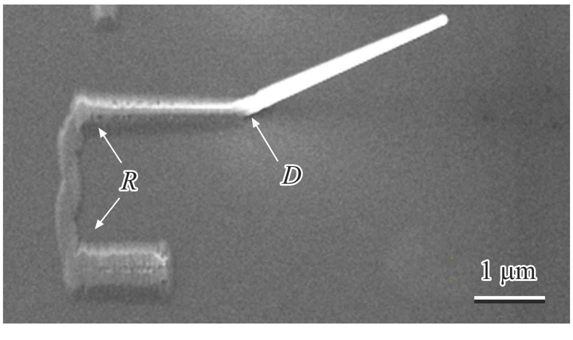

Figure 1. Change of the p-NW growth direction caused by a change of the doping level: rotation in plane — *R*, separation of p-NW — *D*.

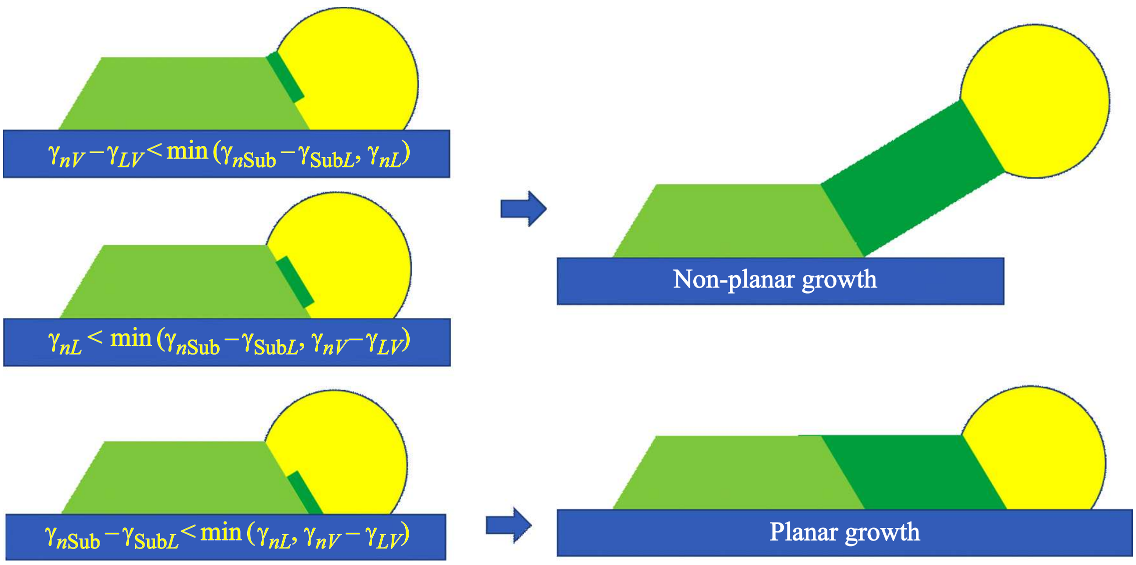

Figure 2. p-NW growth condition.

nucleus–vapor, droplet–vapor interfaces. Nucleus position is defined by the minimum of three values: γ_{nL}, $\gamma_{nV} - \gamma_{LV}$ and $\gamma_{n\mathrm{Sub}} - \gamma_{\mathrm{Sub}L}$. If $\gamma_{nSub} - \gamma_{SubL}$ is minimum, then the nucleus occurs at the substrate–droplet–NW triple line. NW continues growing in the substrate plane. If γ_{nL} is minimal, then the nucleus occurs under the droplet. If the droplet continues wetting the substrate and $\gamma_{n\mathrm{Sub}} < \gamma_{\mathrm{Sub}L} + \gamma_{nL}$, then growth may continue along the substrate surface for some time, though in an unstable mode. A p-NW facet in contact with the substrate will expand gradually and at some time the droplet will not be able to wet simultaneously the growing facet and the substrate. If $\gamma_{nV} - \gamma_{LV}$ is minimum, then the nucleus occurs at the vapor–droplet–NW triple line. All nucleus facets will be perpendicular to the growing facet in the [111]B direction [2,7,10,11] as in the inclined NWs. This direction is usually not in the substrate plane. p-NW thickness will be increasing, growing facet area will be growing and at some time the droplet will separate from the substrate. If the new layer nucleus occurs not on the triple line, then NW separates from the substrate [5,6].

In [5], conditions leading to p-NW rotation on the substrate were formulated. It was shown that, when p-NW comes across the barrier or a high step bunch, four fundamentally different scenarios are possible: p-NW grows along a step, p-NW is reflected from a step, p-NW continues growing forward or deviates upwards. Figure 3 shows all these scenarios and corresponding p-NW images made by scanning microscopy.

By introducing γ_{nB}, γ_{BL} — the surface energies between the barrier and nucleus (NW) and the barrier and droplet, then requirements for each of the scenarios may be formulated: reflection — $\gamma_{nB} - \gamma_{BL} > \gamma_{nL}$ and $\gamma_{n\mathrm{Sub}} - \gamma_{\mathrm{Sub}L} < \gamma_{nL}$, growth along the barrier — $\gamma_{nB} - \gamma_{BL} < \gamma_{nL}$ and $\gamma_{n\mathrm{Sub}} - \gamma_{\mathrm{Sub}L} < \gamma_{nL}$, inclined growth — $\gamma_{nB} - \gamma_{BL} > \gamma_{nL}$ and $\gamma_{n\mathrm{Sub}} - \gamma_{\mathrm{Sub}L} > \gamma_{nL}$, continued growth — $\gamma_{nB} - \gamma_{BL} < \gamma_{nL}$ and $\gamma_{n\mathrm{Sub}} - \gamma_{\mathrm{Sub}L} < \gamma_{nL}$ [5]. It was also shown there that these ratios might be changed by changing the droplet composition (fraction of gallium) and, consequently, the NW growth direction might be changed. However, it was assumed in the work that the barriers should be formed in advance at the substrate preparation stage.

In [2], p-NWs were found to be able to rotate also when coming in contact with natural irregularities on the substrate. Ordering along a particular direction is a major advantage of using natural irregularities [12]. Thus, a natural grid of two directions occurs — along and across the steps. However, when p-NW is grown using only a gold-gallium catalyst, the growth conditions cannot be broken. Growth with a gold catalyst goes in one of two modes — near the $\mathrm{Au_2Ga}$ eutectic or with a highly gallium-enriched droplet ($> 70\,\%$). During the near-eutectic growth, the droplet surface energy turns out to be quite high and the growth becomes inclined. During the growth with a gallium droplet, it is very difficult to change surface energies.

A more interesting situation is observed when the droplet composition may be changed in a wide range. Growth of antimonides is the simplest option. Antimony is easily soluble in the catalyst material [11,13]. This is also possible, though more rarely, during arsenide growth with catalysts from the carbon group — tin and lead [14]. In this case, the triple diagram contains several eutectic points with much different properties (see Figure 4).

$\mathrm{A^{III}B^{V}}$ NW may grow at least in three fundamentally different modes: catalyst and group III metal eutectic, catalyst and nitrogen group element eutectic, and with pure catalyst. Growth with pure catalyst depleted in both elements is used quite rarely because the catalyst itself may start being spent during NW growth. Two other modes are quite practical. GaSb HNW growth with a In droplet is possible near $\mathrm{InGa_7}$ eutectic and $\mathrm{InSb_2}$ eutectic.

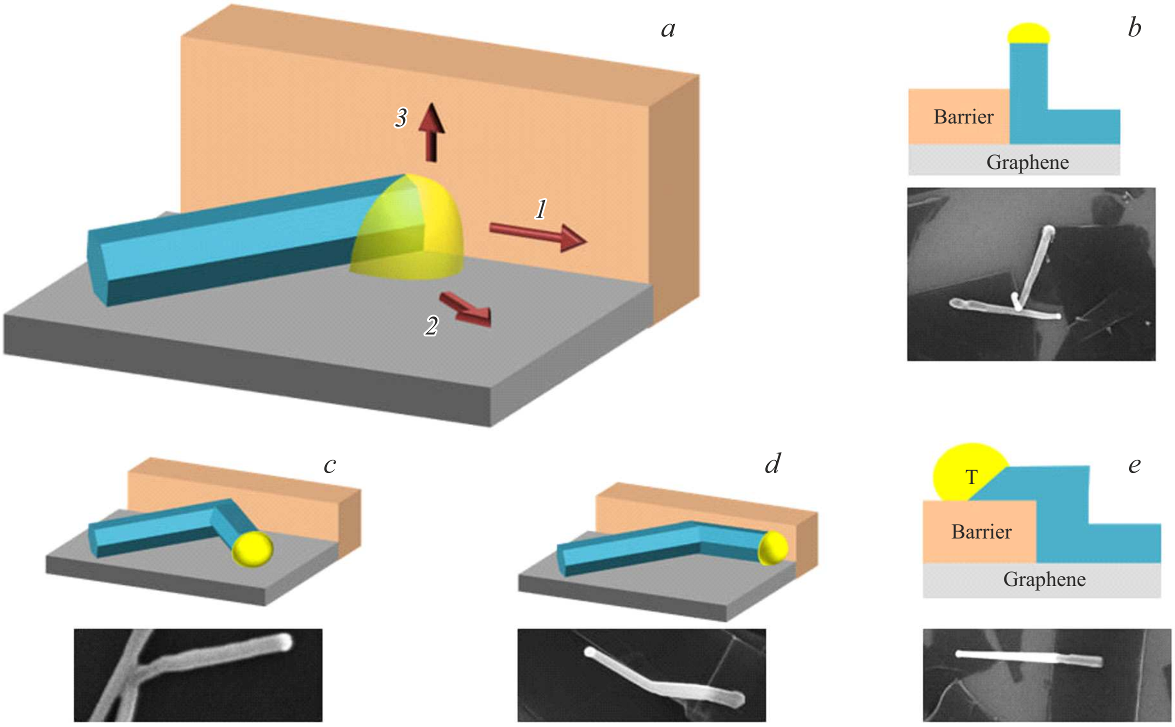

Figure 3. *a* — possible p-NW growth directions after coming in contact with the barrier; *b* — p-NW reflection from the barrier; *c* — continued NW growth along the barrier; *d* — inclined growth; *e* — continued growth through the barrier.

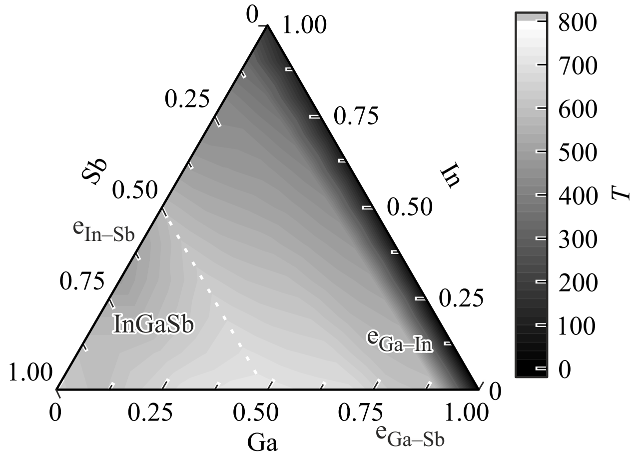

Figure 4. Triple phase diagram in the Ga–In–Sb system on the basis of [13,15].

GaSb NW growth with a Sn-droplet, despite that there is no Sn–Sb eutectic, is also possible in different modes with a gallium-enriched droplet and antimony-enriched droplet [16]. Switching between two growth modes makes it possible to change the p-NW growth direction, though in papers, where this phenomenon was observed, it is treated rather as a negative effect [16,17]. Authors usually wanted to modify p-NW composition or doping and tried to avoid a change of growth direction. For p-NW growth, singular surfaces were chosen where a turn to the left or to the right was equally probable when the droplet composition was modified.

Adding zinc [2,3], tin [2,9,16] or lead [9], materials that can be embedded and dope p-NW, increases controllability. GaAs NW growth with a Sn droplet is possible near — As_3Sn_2 eutectic [18] and near $Ga_{12}Sn$ eutectic [19]. Thus, not only a group III element, for example, Ga or In, but also a group V element, for example, As or P, are very soluble in tin and lead. This property was usually treated as a key factor in changing the p-NW growth direction [9].

Triple diagrams of states for the Ga–As–Sn and Ga–As–Pb systems given in Landolt–Bornstein [20], and binary diagrams show that tin and lead easily dissolve any of these elements at typical growth temperatures. And the catalyst droplet composition may be changed from Sn–Ga to Sn–As and vice versa by short-term turning off one of the element flows. However, while p-NWs with the Sn–Ga catalyst droplet tend to grow along the steps, then p-NWs with the Sn–As tend to grow across the steps.

This work develops a p-NW growth model, proposes a new method to control the arsenide and phosphide p-NW growth direction with tin or lead catalyst.

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Conflict of interest

The authors declare that they have no conflict of interest.

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