Influence of gallium and arsenic deposition rates on the GaAs planar nanowire morphology

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Abstract. Using the Monte Carlo simulation, the dependence of GaAs nanowire morphology on Ga and As\textsubscript{2} flux intensities was analyzed. The self-catalyzed growth of planar GaAs nanowires on GaAs(111)A substrates was considered. Depending on the arsenic and gallium fluxes, three possible scenarios of the GaAs nanowire formation were shown. The regions of gallium and arsenic deposition rates necessary for obtaining a stable planar growth of GaAs nanowires were revealed. The reasons for the transition of planar GaAs nanowire growth to the nonplanar one were analyzed.

1. Introduction
Interest in planar nanowires (PNWs) is due to their compatibility with traditional planar nanoelectronic technology [1, 2]. A targeted search for the conditions of PNW formation is needed. Experimentally, GaAs PNWs were obtained by growth from the gas phase according to the vapor-liquid-solid mechanism using gold as a catalyst [3]. The application of gold-grown nanowires in optoelectronics is undesirable, since gold atoms, when imbedded into a crystal, are the centers of nonradiative recombination centers worsening device characteristics. Currently, the main method of vertical GaAs nanowire formation is self-catalyzed growth, when gallium drops are used as a catalyst [4]. For self-catalyzed NW growth, the presence of a special surface coating (film-mask) is necessary to prevent the growth of GaAs layer on the substrate. To ensure the planar wire growth, a careful selection of the mask-film material is required, which provides the necessary arsenic adhesion coefficient to the substrate and certain diffusion coefficients of gallium and arsenic along the surface. No systematic studies of the self-catalyzed growth of planar GaAs nanowires have been found in the literature. Only in [5] it was experimentally shown that planar nanowires were grown on a Si(111) substrate at certain ranges of temperature and arsenic flux, along with vertical GaAs nanowires.

Earlier, using Monte Carlo simulations, we have analyzed the influence of temperature and substrate orientation on the planar GaAs nanowire morphology [6]. It was shown that a more stable growth of planar GaAs nanowires is observed on GaAs(111)A substrates in the 850–890 K temperature range. The present work is aimed at searching the optimal gallium and arsenic deposition rates for the self-catalyzed growth of GaAs PNs on GaAs(111)A substrates. The influence of gallium and arsenic fluxes on the GaAs wire morphology was studied using the kinetic lattice Monte Carlo model. The kinetics of planar growth failure was shown. The reasons for the breakdown of the planar GaAs nanowire growth to the nonplanar growth were revealed. The optimal range of gallium and arsenic deposition rates was determined for the stable planar growth of GaAs nanowires.
2. Monte Carlo model and simulation results

The simulations were carried out using the program package SilSim3D [7]. In the modeling of GaAs planar nanowire growth, a five-component system was considered: Ga(s), Ga(l), As, As2, M – gallium in solid and liquid states, atomic and molecular arsenic and a film-mask (the substrate surface coating), respectively. The possible elementary events included in the model are: Ga and As2 adsorption, Ga and As2 desorption, As2 dissociation and formation, diffusion of atoms and molecules over the surface, GaAs dissolution and crystallization, As dissolution and diffusion in a liquid metal. A more detailed description of the model and the scheme of planar nanowire growth can be found elsewhere [6]. The procedure for choosing the model energy parameters for the GaAs system is described in [8]. For the PN growth, a special passivation of the substrate surface is required, which is specified in the model by creating a film-mask on the substrate surface. The characteristics of the film-mask should provide both its wetting with liquid gallium and a sufficient arsenic diffusion collection in a droplet. In the model, the binding energy of droplet atoms with GaAs{111}B surfaces is stronger than with the film-mask and GaAs{111}A surfaces. This ratio of the liquid gallium binding energies with solid surfaces turned out to be sufficient for the possibility of the planar nanowire formation.

The planar nanowire growth simulation was carried out on the GaAs substrates with (111)A surface orientation. As the initial model crystal, GaAs(111)A substrates 120 × 20 nm in size with a passivating surface layer were used. A hole 5 nm in diameter was created in the passivating layer into which a Ga droplet was placed. Such a rectangular substrate, due to the cyclic boundary conditions in the lateral directions, is equivalent to the substrate with an infinite number of closely spaced gallium droplets. Such asymmetric droplet location results in the selected direction of the nanocrystal growth along the surface. The crystal mainly grows in the direction of the maximal arsenic supply from the surface.

All calculations in this work were carried out at 890 K. The gallium deposition rate varies from 1 to 6 ML/s; the arsenic deposition rate from 1 to 18 ML/s. Gallium was supplied perpendicular to the substrate and arsenic at arbitrary angles.

Three regions with characteristic development of the GaAs nanowire morphology are distinguished depending on the arsenic and gallium fluxes. With the flux ratio $F_{Ga} : F_{As2} < 1:2$, a noticeable increase in the gallium droplet size is observed already at the initial growth stage. As a result, even before the nanowire starts to grow, the gallium drop contacts the film-mask covering the substrate surface. At the same time, as the droplet grows, the GaAs crystallization and three-dimensional GaAs crystal formation occur under the droplet. The top surface of this 3D crystal is faceted by the (111)A facet; the side surfaces are faceted by three {001} and three {111}B facets. As the GaAs crystal grows under the gallium drop, the droplet in contact with the entire surface of the 3D crystal shifts to the {111}B facets. So, the formation of planar nanowires in the direction of the {111}B facets begins (figure 1). The planar growth is possible due to the contact large area of the droplet with the film-mask, and due to the layer-by-layer GaAs crystallization at the interface because of a low arsenic concentration in the drop. However, under the conditions of a small arsenic flux, its diffusion collection from the surface into the drop is negligible, that is, arsenic enters the droplet directly from the external flux. Therefore, the formation of a new GaAs bilayer at the interface begins in the upper part of the Ga drop, and it can lead to the formation of the following layers until the previous bilayer is completely overgrown. This is schematically shown in figure 2(a). Such crystallization leads to a transition from the planar to nonplanar growth.

**Figure 1.** Top views (top) and cross-sections (bottom) of model GaAs(111)A substrate fragments after the Ga and As2 depositions during 0.1 s (a), 0.2 s (b), 0.4 s (c); $F_{Ga} = F_{As2} = 3$ ML/s.
Three types of planar nanowire growth failures were detected. The prerequisite for all disruptions was the incomplete overgrowth of bilayers at the drop-crystal interface (figure 2(a)). The first type of breakdown is characterized by the complete separation of the droplet from the substrate. In this case, the planar growth completely turns into the tilted one (figure 2(b)). The second type of breakdown is characterized by the simultaneous growth of a tilted and planar wire due to the gallium droplet split (figure 2(c)). In the third case, the drop does not leave the surface, but the growing wire has no connection with the surface (figure 2(d)). Such a nanowire with further growth can again be spliced with the surface. The first type of disruption is typical of relatively small gallium droplet sizes; the second and third ones for large droplets. Since the size of gallium droplets changes during the growth process, the initial planar growth may eventually turn into the nonplanar one.

Figure 2. (a) Scheme of planar growth breakdown ($t_2 > t_1$); side views of planar GaAs nanowires after the breakdown of the first (b), second (c) and third (d) type; (b,d) $F_{Ga} = 3$ ML/s, $F_{As2} = 6$ ML/s, $t = 0.8$ s; c) $F_{Ga} = 6$ ML/s, $F_{As2} = 12$ ML/s, $t = 0.6$ s.

When the flux ratio $F_{Ga}:F_{As2}$ was from 1:3 to 1:18 with the fixed gallium flux $F_{Ga} = 1$ ML/s, the crystal growth rate noticeably increased, and the gallium drop decreased during the growth until it was completely consumed. In such conditions, the formation of tilted and vertical wires was often observed. The formation of vertical nanowires is unstable and usually, even at the initial growth stage, it goes into an inclined mode. At lower absolute values of Ga and As$_2$ fluxes, the vertical nanowire growth is longer. The tilted nanowire (flux ratio 0.33) is shown in figure 3(a). The vertical wire obtained at the flux ratio 0.44 for lower absolute values of Ga and As$_2$ fluxes is shown in figure 3(b).

Figure 3. Side views of model GaAs(111)A substrate fragments after Ga and As$_2$ depositions: 0.2 s, $F_{Ga} = 1$ ML/s, $F_{As2} = 3$ ML/s (a), 1.9 s, $F_{Ga} = 0.2$ ML/s, $F_{As2} = 0.45$ ML/s (b).

A stable planar GaAs nanowire growth was observed with an increase in the gallium flux up to 3 ML/s when changing the flux ratio $F_{Ga}:F_{As2}$ from 1:3 to 1:6, and at $F_{Ga} = 6$ ML/s for $F_{Ga}:F_{As2} = 1:6$ (figure 4). Under such conditions, the gallium flux is sufficient for the droplet increase and wetting the substrate surface, and the arsenic flux is sufficient to provide a noticeable arsenic diffusion collection from the substrate into the droplet. It can be noted that, with a decrease in the arsenic flux, the number of planar nanowires increases (from one to three). This is due to an increase in the gallium drop size and the possibility of the formation of a larger number of the \{111\}B facets on the 3D crystal surface under the droplet.
Figure 4. Side view of GaAs planar nanowire, $F_{Ga} = 3$ ML/s; $F_{As_2} = 12$ ML/s, $t = 0.7$ s.

A diagram in the coordinates $F_{Ga}$ and $F_{As_2}$ is shown in figure 5. It illustrates the nanowire morphology dependence on the Ga and As$_2$ deposition rates. The ranges of gallium and arsenic fluxes are indicated for only nonplanar growth, for the stable PN growth and disruptions of the planar nanowire growth. The boundaries between these regions are not strict because the role of fluctuations in the nanowire growth process is significant, especially at the initial stage of crystal formation. The results presented in figure 5 are averaged over 10 computational experiments.

Figure 5. $F_{Ga} - F_{As_2}$ diagram illustrating the dependence of the GaAs nanowire morphology on the Ga and As$_2$ flux intensities.

3. Conclusions
Using Monte Carlo simulation, the influence of gallium and arsenic deposition rates on the morphology of self-catalyzed planar GaAs nanowires was analyzed. Three possible scenarios of the GaAs nanowire formation on GaAs(111)A substrates were shown, depending on the absolute values and the ratio of gallium and arsenic fluxes: the nonplanar growth, the planar nanowire growth with a subsequent transition to the nonplanar growth, and the stable planar growth. The analysis of the simulation results showed that several conditions are necessary for the planar nanowire formation. The first one is the droplet contact with the film-mask. To fulfill the first condition, a surface wettability and a large enough droplet size are needed. The second factor is the sufficient supply of arsenic to the droplet from the substrate by diffusion collection for the formation of islands connected with the mask surface at the drop-nanowire interface. The kinetics of the transition of the GaAs nanowire planar growth to the nonplanar one was discussed.

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