Modeling the formation of InP/Ga$_x$In$_{1-x}$P axial nanowire heterostructures

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Abstract. A model is developed to depict the formation of InP/Ga$_x$In$_{1-x}$P axial heterostructures in self-catalyzed Ga$_x$In$_{1-x}$P nanowires. The composition profiles of the InP/Ga$_x$In$_{1-x}$P axial heterostructure are calculated taking into account elastic stresses. It is shown that the InP/Ga$_x$In$_{1-x}$P axial heterojunction width at the growth temperature of 450°C is larger than 12 monolayers for nanowires with the radius larger than 10 nm. Also, the comparison with Ga$_x$In$_{1-x}$As system is performed and reveals that the InP/Ga$_x$In$_{1-x}$P axial heterojunction width is approximately two times smaller than the InAs/Ga$_x$In$_{1-x}$As axial heterojunction width.

1. Introduction

Semiconductor nanowires (NW) are often used as building blocks for nanodevices due to their unique geometry and physical properties [1]. The formation of axial and radial heterostructures in ternary III-V NW particularly allows the combination of materials with large lattice mismatch without generating defects. The modeling of heterostructure formation in NW synthesized via catalytic growth methods is usually performed within the framework of the following approaches [2,3]. The first approach is based on the binary nucleation theory and allows the finding of composition of the critical nucleus forming on the NW-catalyst interface. This composition is then used as an approximation of the monolayer composition. The second approach is based on the assumption that the dependence of the monolayer composition on the catalyst droplet composition during the NW growth is the same as in case of thermodynamic equilibrium between NW and droplet. Within the third approach (the irreversible growth model), the axial heterostructure formation is described in terms of large supersaturations when the size of the critical nucleus is close to unity. The second approach was developed in the paper [4] to describe the axial NW heterostructure formation in case of materials with large lattice mismatch. The model [4] accounts for elastic stresses produced by the lattice mismatch between consecutive monolayers in NW. In this paper, we use the model [4] to calculate the width of InP/Ga$_x$In$_{1-x}$P axial heterojunction in self-catalyzed Ga$_x$In$_{1-x}$P NW. Note, the advantage of the self-catalyzed NW growth is that there is no incorporation of foreign catalyst atoms into NW crystal lattice.

2. Theoretical model

We consider a cylindrical Ga$_x$In$_{1-x}$P NW with the radius $R$ which grows along the [111] direction. The InP/Ga$_x$In$_{1-x}$P axial heterostructure is formed by switching the group III fluxes. In order to take into...
account elastic stresses, the NW is considered as a set of adjacent monolayers. The dependence of monolayer composition on the droplet composition can be found by using the equality of chemical potentials for species in the droplet and monolayer. In such a case, the monolayer composition depends on the composition of underlying monolayers and can be written in the following form [3,4]:

\[ x_i = x_i(y_i, c_{\text{tot},i}, x_{i-1}, x_{i-2}, \ldots), \]

where \( x_i \) is the fraction of GaP pair in the \( i \) monolayer, \( y_i = c_{\text{Ga},i}/c_{\text{tot},i} \), \( c_{\text{tot},i} = c_{\text{Ga},i} + c_{\text{In},i} + c_{\text{P},i} \), and \( c_{\text{Ga},i}, c_{\text{In},i}, c_{\text{P},i} \) are the concentrations of Ga, In and P atoms in the droplet such that \( c_{\text{Ga},i} + c_{\text{In},i} + c_{\text{P},i} = 1 \). Following the paper [2], the catalyst droplet and monolayer materials are considered as regular liquid and solid solutions, respectively. The elastic stress terms to the chemical potentials of GaP and InP pairs are calculated by the following equations [4]:

\[ \mu_{\text{GaP},i}^{\text{elas}} = W_i + (1 - x_i) \partial W_i / \partial x_i \]

\[ \mu_{\text{InP},i}^{\text{elas}} = W_i - x_i \partial W_i / \partial x_i, \]

where \( W_i \) is the average elastic energy per one III-V pair in the \( i \) monolayer.

The elastic energy \( W_i \) as a function of \( x_i \) is calculated by the finite element method [5] and then fitted by the quadratic function. The details of the calculation of the function \( x_i = x_i(y_i, c_{\text{tot},i}, x_{i-1}, x_{i-2}, \ldots) \) can be found in the paper [4].

To obtain a simplified material balance equation for the species in droplet, we introduce the following assumption [2-4]. Firstly, the concentrations of Ga and P atoms in droplet are much less than the concentration of In atoms. Secondly, the group V flux is constant and determines the NW growth rate. Thirdly, we neglect the change in the NW radius during heterostructure formation. Within the assumptions made above, the material balance equation for Ga species can be only considered to calculate the composition profile of the InP/GaIn\(_{1-x}\)P axial heterostructure:

\[ y_i(c_{\text{tot},i}, x_i, x_{i-1}, \ldots) - y_{i-1}(c_{\text{tot},i-1}, x_{i-1}, x_{i-2}, \ldots) = p(q - x_i), \]

here \( p = N_{\text{ML}}/\mathcal{N}, \) \( q = J/N_{\text{ML}}V, \) \( N_{\text{ML}} \) is the number of III-V pairs in monolayer, \( \mathcal{N} \) is the total number of atoms in the droplet, \( J \) is the Ga flux entering the droplet (in s\(^{-1}\)), \( V \) is the NW growth rate (in monolayers per second) and \( y_i(c_{\text{tot},i}, x_i, x_{i-1}, \ldots) \) is the inverse function of \( x_i(y_i, c_{\text{tot},i}, x_{i-1}, x_{i-2}, \ldots) \).

### 3. Results and discussion

The modeling of the InP/GaIn\(_{1-x}\)P axial heterostructure formation is performed by using the reference data [2,6-8]. The interaction coefficients in the droplet equal [6]:

\[ \alpha_{\text{Ga-In}} = 4450.0 + 1.19185 T \text{ J/mol}, \]

\[ \alpha_{\text{Ga-P}} = -9862 J/\text{mol}, \]

\[ \alpha_{\text{In-P}} = 14124.08 - 10.17931 T \text{ J/mol}. \]

The interaction coefficient of GaP and InP pairs in solid is estimated in the paper [7]:

\[ w = 15187.9 J/\text{mol}. \]

The chemical potentials of pure components can be found as functions of temperature in [6]. The values of the model parameters \( p \) and \( q \) are taken from the paper [2] where the Ga,In\(_{1-x}\)As system was considered. The elastic constants and the lattice parameter of Ga\(_x\)In\(_{1-x}\)P are calculated by using the Vegard’s law and the data for bulk GaP and InP [8]:

\[ C_{11}^{\text{GaP}} = 140.5 \text{ GPa, } C_{12}^{\text{GaP}} = 62.0 \text{ GPa, } C_{44}^{\text{GaP}} = 70.3 \text{ GPa, } C_{11}^{\text{InP}} = 101.1 \text{ GPa, } C_{12}^{\text{InP}} = 56.1 \text{ GPa, } C_{44}^{\text{InP}} = 45.6 \text{ GPa, } \]

\[ a_{\text{GaP}} = 0.54505 \text{ nm and } a_{\text{InP}} = 0.58687 \text{ nm}. \]

Figure 1 shows the composition diagrams calculated for the case of \( R = 10 \text{ nm} \) and the growth temperature of 450°C. The monolayers of the Ga\(_x\)In\(_{1-x}\)P section of NW are numbered from \( i = 1 \). It is seen from Figure 1 that there is no miscibility gap as opposed to the case without elastic stresses (the dashed region on the gray line, \( x_i = 0.138 - 0.862 \)).

The composition profiles of InP/GaIn\(_{1-x}\)P axial heterostructure are shown in Figure 2. As for the GaIn\(_{1-x}\)As system [4], the formation of atomically sharp heterojunction is hardly achieved due to elastic stresses. Even if the NW radius is very small (\( R = 5 \text{ nm} \)) the heterojunction width is about of 8 monolayers. It is seen that the heterojunction width in the case of GaIn\(_{1-x}\)P system is shorter compared to the GaIn\(_{1-x}\)As system. This is because the ratio of the reaction rate constants for the self-catalyzed growth of GaIn\(_{1-x}\)P NW is higher than for the self-catalyzed growth of GaIn\(_{1-x}\)As NW:
Figure 1. Composition diagrams for several monolayers of Ga$_x$In$_{1-x}$P NW ($i = 1, 4, 7, 10, 13$). The monolayer compositions obtained as a result of the self-consistent modeling are marked by dots. The composition diagram calculated without taking into account elastic stresses is shown by the gray line.

Figure 2. Composition profiles of InP/Ga$_x$In$_{1-x}$P axial heterostructure (the red lines and symbols) and InAs/Ga$_x$In$_{1-x}$As axial heterostructure [4] (the blue lines and symbols) at the growth temperature of 450°C. The rectangular and quadratic symbols correspond to the NW radius of 10 nm and 5 nm, respectively. The composition profiles are also plotted by using the formula for the dependence $y(x)$ derived in the paper [2], where elastic stresses were neglected (the lines without symbols). The insert shows the model geometry of the system.
\[ \ln K_{\text{InP}} / K_{\text{GaP}} \approx 6.3 \quad \text{and} \quad \ln K_{\text{InAs}} / K_{\text{GaAs}} \approx 4.4 , \]

where \( K_{AB} \) is the reaction rate constant for the reaction \( A + B \rightarrow AB \). Although, the values of elastic constants of \( \text{Ga}_x\text{In}_{1-x}\text{P} \) are larger than those of \( \text{Ga}_x\text{In}_{1-x}\text{As} \) [8]. It is important to note that the elastic constants used in our computation correspond to bulk materials. Elastic properties of monolayers can differ significantly from elastic properties of bulk materials. Thus, the monolayer elastic constants can be smaller or larger than those of bulk materials [9]. Therefore, the theory presented in our paper should be considered only as a first attempt to understand the role of elastic stresses in the formation of \( \text{Ga}_x\text{In}_{1-x}\text{P} \) axial nanowire heterostructures.

To summarize, the estimates of the InP/Ga\(_x\)In\(_{1-x}\)P axial heterojunction width in the self-catalyzed \( \text{Ga}_x\text{In}_{1-x}\text{P} \) NW were presented. The dependence of the monolayer composition on the droplet composition was obtained within the framework of the thermodynamic equilibrium model. The elastic energy terms in the chemical potentials of species in monolayers were calculated by using the finite element method. It was found that the InP/Ga\(_x\)In\(_{1-x}\)P axial heterojunction width at the growth temperature of 450\(^\circ\)C is larger than 12 monolayers if the NW radius is larger than 10 nm. Also, it was shown that the axial heterojunction width in case of \( \text{Ga}_x\text{In}_{1-x}\text{P} \) NW is approximately two times smaller than that in case of \( \text{Ga}_x\text{In}_{1-x}\text{As} \) system.

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