The model for in-plane and out-of-plane growth regimes of semiconductor nanowires

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Abstract. In this work we present the model capable of prediction whether the vapor-liquid-solid growth would preferably result in the formation of in-plane (horizontal) or out-of-plane (vertical or inclined) nanowires. Within the model, we analyze the particular case of gold-catalyzed germanium nanowire growth on Ge(111), Ge(110) and Si(100) substrates. We focus on two aspects of the growth process: detachment of the catalyst from the substrate and stabilization of horizontal growth by nucleation at the nanowire-substrate-liquid line.

1. Introduction

III-V semiconductor nanowires (NWs) and heterojunctions on their base are widely considered as the promising building blocks for novel photonic and optoelectronic applications [1–4]. However, their use in the device applications usually requires control of the direction of NW growth, which strongly depends on the growth mechanism. Nowadays, one of the most common approaches to the synthesis of III-V and group IV NWs is the epitaxial growth via the vapor-liquid-solid (VLS) mechanism[5,6]. VLS growth may result in different shapes and forms of NWs. Mainly, two types of possible NW growth: in-plane (horizontal) and out-of-plane (vertical or inclined) were observed for different III-V [7–11], II–VI[12] and group IV[13–17] materials. In planar growth, liquid catalyst remains in contact with the substrate, while in vertical or inclined growth the droplet detaches from the substrate and stabilizes on the top of NW. Although this feature of VLS epitaxial growth is not entirely understood. In this work, we discuss two aspects of VLS process, which directly impacts the growth direction: the droplet detachment at the initial stage of NW formation and stabilization of in-plane growth due to nucleation at the nanowire-substrate-liquid line. We present the model which describes two aspects of the growth process and consider the specific cases of germanium NWs on Ge(111), Ge(110) and Si(100) substrates. We use our modeling results to explain the experimentally observed in-plane and out-of-plane Au-catalyzed Ge NW and discuss the factors which determine the growth direction.

2. Model and results

2.1 Droplet detachment

In the studies of droplet detachment or contacting the substrate, we rely on previous considerations of the droplet stability [18–20] to discuss the condition for droplet detachment from the substrate. The equilibrium state of the system, consisting of the droplet on top of the NW stem of length L and radius R is given by the minimum of the surface energy $G_{\text{drop}}$ [18–20]:

$$G_{\text{drop}} = \frac{2\pi R^2}{1 + \cos \beta} y_{\text{L}-V} + \pi R^2 y_{\text{TIP}-L} + 2\pi R y y_{S-L} + 2\pi R (L - y) y_{S-V}, \quad (1)$$

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where $y$ is the length of the sidewall wetted by the droplet, $\beta$ – droplet contact angle, $\gamma_{L-V}$, $\gamma_{TIP-L}$, $\gamma_{S-L}$, $\gamma_{S-V}$ are surface energies of liquid-vapor, NW tip – liquid, NW sidewalls – liquid and NW sidewalls-vapor interfaces. Previously it was demonstrated that under the constrain of constant volume the derivative of $G_{\text{drop}}$ as the function of contact angle $\beta$ can be written as:

$$\frac{dG_{\text{drop}}}{d\beta} = \frac{2\pi R^2}{(\cos \beta)^2} \left( \gamma_{L-V} \sin \beta + \gamma_{S-L} - \gamma_{S-V} \right).$$

One can notice that $G_{\text{drop}}$ has the extremum, which corresponds to the Young’s equation on the sidewalls

$$\gamma_{L-V} \cos \psi + \gamma_{S-L} = \gamma_{S-V}.$$  

(3)

Here $\psi$ is contact angle of droplet lying on NW sidewalls. Thus extremum condition $dG_{\text{drop}}/d\beta = 0$ is equivalent to $\sin \beta = \cos \psi$. The corresponding extremum is maximum when $\beta > \pi/2$ and minimum when $\beta < \pi/2$.

Figure 1. Schematics of the droplet on the substrate and after detachment from the substrate.

Meanwhile, it is widely considered in previous works [18,20] that the droplet does not wet the sidewalls when the condition $\gamma_{L-V} \sin \beta + \gamma_{S-L} > \gamma_{S-V}$ is satisfied. Which, in view of Eq. (7), is equivalent to $\sin \beta > \cos \psi$. In the opposite case, the droplets is unstable and slides down when $\gamma_{L-V} \sin \beta + \gamma_{S-L} < \gamma_{S-V}$ or $\sin \beta < \cos \psi$.

The initial value of $\beta$ is given by the substrate contact angle, which we denote $\theta$. If $\sin \theta > \cos \psi$ ($\theta < \psi + \pi/2$) the minimization of $G_{\text{drop}}$ after the formation of the first monolayer will require the droplet detachment from the substrate and further increase of the contact angle. Otherwise, if $\sin \theta < \cos \psi$ ($\theta > \psi + \pi/2$) the minimization of $G_{\text{drop}}$ corresponds to the decrease of the contact angle and droplet spreading.

2.2 Nucleus position in in-plane nanowire

VLS growth is generally considered to proceed in layer-by-layer regime [19–23]: the formation of each monolayer depletes the droplet and thus makes the nucleation of a new monolayer (ML) less improbable. Subsequent droplet refilling increases the concentration of the growth species and thus induces the nucleation of new ML. The 2D nucleus of size $i$ is described by formation energy [21,22,24]:

$$G_{\text{nucl}} = -\Delta \mu i + A i + B i^{1/2}$$

where $\Delta \mu$ is the chemical potential difference per atom (or pair of atoms for binary materials). In the second term, $A$ is proportional to the nucleus surface energy. The third term in Eq. (4) gives the energy of the side facets, which is proportional to the square root of the size $i$.

The nucleation barrier is given by the maximum of the formation energy:

$$G_{\text{nucl}}^* = B^2/4(\Delta \mu - A).$$

(5)
The nucleation probability \( p \sim \exp(-G_{\text{nuc}}^*/T) \) decreases exponentially with \( G_* \) and thus the preferable growth regime supposed to has the lowest nucleation barrier \( G_* \).

Liquid catalyst allows larger supersaturation in comparison to the vapor phase and thus increases \( \Delta \mu \) and typically facilitate the nucleation [25]. The formation of 2D nucleus inside the droplet on top of substrate requires the formation of top and bottom interfaces as well as the elimination of the liquid-substrate interface, thus

\[
A = \alpha (\gamma_{\text{top}} + \gamma_{\text{bot}} - \gamma_{\text{sub}}),
\]

where \( \gamma_{\text{top}}, \gamma_{\text{bot}} \) and \( \gamma_{\text{sub}} \) are energies of the top, bottom and substrate-liquid interfaces respectively, as shown in Figure 1. The coefficient \( \alpha \) here depends on the geometry of the nucleus. One can notice that \( A = 0 \) in the case of homoepitaxy or nucleation of new ML on top of the previous one. Thus, according to Eq. (2), the nucleation barrier in layer-by-layer regime is controlled by the energies of nucleus side interfaces which contribute to \( B \).

The side facet of the nucleus may contact liquid, vapor or the substrate and form the interfaces with the energies \( \gamma_{S-L}, \gamma_{S-V} \) or \( \gamma_{S-Sub} \) respectively. Thus

\[
B = \kappa_{S-L} \gamma_{S-L} + \kappa_{S-V} (\gamma_{S-V} - \gamma_{L-V}) + \kappa_{S-Sub} (\gamma_{S-Sub} - \gamma_{Sub-L}),
\]

where different \( \kappa \) correspond to fractions of nucleus side facets contacted to liquid, solid or substrate.

![Figure 2. Schematic of the 2D nucleus and corresponding surface energies.](image)

Next, we consider three possible positions of the nucleus on the previous ML: at the center of the droplet (C) or the triple line contacted either to vapor phase (VTPL) or the substrate (STPL). In general, (C) and (VTPL) positions are relevant both for planar and non-planar NWs, while the realization of (STPL) nucleation is possible in horizontal NWs only. We assume that the lowest formation energy defines the preferred growth mode. In calculations, for simplicity, we assume the triangle shape of the nucleus and, thus, \( \kappa_{S-L} = \kappa_{S-V} = \kappa_{S-Sub} = 1/3 \).

Table 1 summarizes the values of \( B \) in each regime of ML nucleation for germanium NWs on Ge(110), Ge(111) and Si(100) substrates grown with golden catalyst. In the growth on Ge(110) and Si(100) substrates NW are typically observed to grow in \{110\} direction with \{111\} sidewall facets. Thus, in this case \( \gamma_{S-L} = 0.542 \text{ J/m}^2 \) [26], while \( \gamma_{S-V} = 1.149 \text{ J/m}^2 \) [26] and \( \gamma_{L-V} = 1.15 \text{ J/m}^2 \) [27]. \( \gamma_{S-Sub} = 0 \) in the case of homoepitaxy and approximated to \( \gamma_{S-Sub} = 0.64 \text{ J/m}^2 \) in the growth of germanium on silicon substrate [28]. In the growth on Ge(111) we assume \( \gamma_{S-L} = 0.626 \text{ J/m}^2 \) and \( \gamma_{S-V} = 1.1 \text{ J/m}^2 \) [26].
Table 1. Expressions and calculated values (in J/m²) of $B$ for nucleation of a new ML at the central position (C), at the contact with vapor phase (VTPL) or at the contact with the substrate (STPL).

|        | $B$  | $\gamma_{S-L}$ | $\gamma_{S-L}(1 - \kappa_{S-V}) + \kappa_{S-V}(\gamma_{S-V} - \gamma_{L-V})$ | $\gamma_{S-L}(1 - \kappa_{S-Sub}) + \kappa_{S-Sub}(\gamma_{S-Sub} - \gamma_{Sub-L})$ |
|--------|------|----------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Ge (110) substrate | 0.542 | 0.411 | 0.153 |
| Ge (111) substrate | 0.626 | 0.575 | 0.209 |
| Si (100) substrate | 0.542 | 0.411 | 0.441 |

3. Conclusions

We consider two factors which impact the character of NW growth: (i) the detachment of the droplet from the substrate at the initial stage of NW growth and (ii) preferred nucleation position during the regular layer-by-layer growth.

On the one hand, the use of Young’s equation (Eq. (7)) and surface energies in the previous section gives $\sin \theta > \cos \psi$ for both Ge (110) and Ge (111) substrates. Experimentally inclined and vertical Ge NWs were observed in the growth on deoxidized substrates[15,29].

On the other hand, in both considered examples of homoepitaxy the minimal $B$ (and minimal $G_{nucl}^*$) corresponds to nucleation next to the substrate (STPL). Assuming that the preferred STPL nucleation insures the horizontal (in-plane) NW growth, one expect Ge NWs on Ge (110) and Ge (111) substrates to grow horizontally. Indeed, Ge NWs were systematically observed on clean and especially smooth substrates together with the decrease of droplet contact angle [30]. In contrast, the etching of the germanium substrate by gold droplet together with intensive surface passivation results in the increase of contact angle and droplet detachment from the substrate[31].

In the case of Si substrate, the minimal $B$ and nucleation barrier corresponds to VTPL nucleation, which, in principle, does not guarantee that NWs will growth horizontally. Meanwhile, the Au droplet is usually observed to detach from the Si (001) [26,32] and Si(111) [33,34] substrates.

In general, large contact angles correspond to droplet detachment from the substrate and formation of vertical or inclined NW. At the same time, the detachment of the catalyst droplet at the initial stage of NW can be avoided in the case small contact angles of the droplet on the bare substrate. In the case of Ge NWs, the horizontal growth is stable due to the preferred nucleation next to the substrate. Meanwhile, it can be realized when the substrate preparation allows reduction of the contact angle of the catalyst droplet.

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