Influence of elastic stresses on the vapor-solid-solid growth mechanism of Au-catalyzed GaAs nanowires

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Abstract. Influence of elastic stresses on the vapor-solid-solid growth mechanism of Au-catalyzed GaAs nanowires is studied. The elastic energy of the triangle-shaped island formed on the catalyst-nanowire interface is calculated. It is shown that the nucleation time of the triangle-shaped island is several times higher than that of the disk-shaped island in the case of nucleation of semi-coherent islands. The contribution to the free energy of island formation from the formation of island side walls is higher for the triangle-shaped island, although, its contribution from the elastic energy is lower when islands nucleate at the catalyst free surface.

1. Introduction
Nanowires (NWs) of III-V semiconductors are widely considered as building blocks for novel devices [1]. The III-V NWs are often synthesized at present by catalytic epitaxial methods. As a catalyst material, various metals (e.g. gold, silver) or group III elements (e.g. indium, gallium) can be used. If the NW growth proceeds at a temperature below the estimated melting point of catalyst particle it is often difficult to determine its phase state [2, 3]. However, most of the theoretical works that study the catalytic NW growth consider only the vapor-liquid-solid growth mechanism. Relatively few works (e.g. [2-4]) are dedicated to the vapor-solid-solid (VSS) growth mechanism.

This report continues the investigation of Au-catalyzed GaAs NW growing in the direction [111] via the VSS mechanism started in [5]. It was shown [5] that the VSS growth can proceed by the As diffusion along the catalyst-NW interface, whereas the volume diffusion flux is insufficient to feed the growing monolayer. In this paper, the estimation of the nucleation time in the case of nucleation of the triangle-shaped island at the catalyst-NW interface is performed.

2. Elastic energy of the triangle-shaped island
The growing NW facet is fed by the material fluxes coming from the vapor phase or side walls. The elements of group III and V dissolved into the catalyst particle that is considered as a solid solution in the case of VSS growth reach the catalyst-NW interface and form islands of monolayer height [6]. Here, we assume that the growth is limited by the As flux because the As concentration in catalyst is usually of the order of one percent or less whereas the concentration of Ga is of the order of tens of percent. Therefore, the As fluxes only should be taken into account. In figure 1, the NW top is schematically shown with two possible ways of As diffusion, interface and volume diffusion [5]. As a result of the lateral growth of island, the monolayer forms and the vertical NW growth proceeds [6].

Consider the free energy of island formation in the following form [7]

\[ \Delta F(i) = \alpha i^{1/2} - (\Delta \mu - w)i \]

(1)
Figure 1. Schematic illustration of the As material fluxes coming into the catalyst particle during the NW growth.

Figure 2. Model geometry of the system used for the calculation of elastic energy of triangle-shaped island formation.

where $\Delta \mu$ is the difference of the chemical potential per the GaAs pair between the catalyst particle and GaAs crystal; $i$ is the number of GaAs pair in the island; $\alpha = 2 \cdot 3^{-1/4}(2\gamma + \gamma_{SV})(h\Omega)^{1/2}$ characterizes the contribution from the formation of island side walls in the case of triangle-shaped island of the monolayer height $h$ and with the side $l = R/3^{1/2}$, $R$ is the island radius; $\gamma$ is the energy of interface of island side walls and catalyst, $\gamma_{SV}$ is the energy of interface of island side walls and vapor phase; $\Omega$ is the volume of the GaAs pair in solid phase; $w$ is the elastic energy per GaAs pair.

In the work [5], the dependence of $w$ on $i$ was found numerically. The function $w(i)$ can be approximated by the equation \[5, 8\]:

$$w(i) = w_0 + b(ln i + d)/i^{1/2}, \tag{2}$$

$w_0$, $b$ and $d$ are constants ($w_0$ and $b$ are expressed in meV below). In present work, the nucleation of the triangle-shaped islands is studied. We consider the formation of the triangle-shaped island at the catalyst free surface to estimate the maximum relaxation of elastic stresses caused by the difference of atomic densities of GaAs and catalyst material (figure 2).

The calculation of elastic stresses is performed by the finite element method [5, 9]. To imitate the phase transition, the effective coefficient of thermal expansion is introduced [9]. For the catalyst material and GaAs island, this coefficient equals to 0 and $\varepsilon$, respectively, where $\varepsilon$ is the free deformation tensor that corresponds to the reconstruction of Ga sublattice in catalyst to the Ga sublattice in GaAs crystal. To find the minimal elastic stresses in the system, we perform the calculation for the different initial deformations of the island such that [5] $\varepsilon_{xx} = 3\varepsilon - 2\varepsilon_{xx}$, where $\varepsilon_{xx}$ changes from 0 to 1.5$\varepsilon$, $\varepsilon_{yy} = \varepsilon_{xx}$, $\varepsilon_{ij} = 0$ for $i \neq j$, $\varepsilon$ is the lattice mismatch between the Au-Ga catalyst and GaAs crystal. For simplicity, we also assume that $\varepsilon_{ij} > 0$ owing to the fact that $\varepsilon > 0$.

We use the following simplified geometry for the estimation. The catalyst is considered in the form of the cuboid with the size $Lx2Lx2L$, where $L = 50$ nm. Taking into account the symmetry of the system, the calculation can be realized for 1/4 part of the system that is schematically shown in figure 2. The boundary conditions for the equation of the elasticity theory are: $U_y(y = 0) = 0$, $U_z(z = 0) = 0$, $\sigma_{ij} = 0$ at the surface $x = 0$, $x = L$, $y = L$, $z = L$, where $U_i$ is the deformation vector, $\sigma_{ij}$ is the stress tensor. The results of the calculation by the finite element method for the case of nucleation in the
AuGa catalyst ($\varepsilon = 0.092$) and AuGa$_2$ catalyst ($\varepsilon = 0.172$) are presented in figure 3. The elastic coefficients of Au-Ga and GaAs can be found in the paper [5]. For comparison, the elastic energies obtained in [5] for the disk-shaped islands are also plotted on figure 3.

![Figure 3](image_url)

**Figure 3.** Dependence of the minimum elastic energy of island formation at $\varepsilon = 0.092$ (AuGa) and $\varepsilon = 0.172$ (AuGa$_2$). The results are shown for the case of formation of the triangle-shaped island at the free catalyst surface (circle symbols), disk-shaped island formed far from the free catalyst surface (triangle symbols) [5] and disk-shaped island at the free catalyst surface (square symbols) [5]. The results of fitting by the equation (2) are shown as solid lines.

The coefficients of the fitting function (3) in the case of the triangle-shaped island equal to: $w_0 = 20.33$, $b = 90.01$, $d = 1.507$ ($\varepsilon = 0.092$) and $w_0 = 71.04$, $b = 314.6$, $d = 1.507$ ($\varepsilon = 0.172$). Thus, it is seen from the figure 2 that the elastic energy per one III-V pair is several tens of percent lower in the case of nucleation of the triangle-shaped island compared to the formation of the disk-shaped island.

3. Results and discussion

Let us calculate the nucleation time of the triangle-shaped island using for a rough estimation the following diffusion equation that accounts for the As flux along the catalyst-NW interface [5]:

$$\frac{\partial C_{As}}{\partial t} = D_{As}\Delta C_{As},$$

(3)

where $\Delta = 1/r \frac{\partial / \partial r}{(r \cdot \partial / \partial r)}$, $r$ is the polar radius, $D_{As}$ is the diffusion coefficient on the catalyst-NW interface, $C_{As}$ is the As concentration. The boundary conditions and initial condition for the equation (3) are as follows [5]:

$$j_{As,r}(D/2,t) = -(j_0 - k_0C_{As}^2(D/2,t)),$$

(4)
\[ j_{\text{As,r}}(0,t) = 0, \]
\[ C_{\text{As}}(r,0) = 0. \]

Here \( j_{\text{As,r}} \) is the As radial flux along the interface; \( j_0 \) is the As flux per unit of the length of the perimeter of the NW top facet; the flux \( j_0 \) includes the direct As flux and the re-adsorption As flux (see figure 1); \( k_0 \sim k_{\text{As}} h \), where \( k_{\text{As}} \) is the coefficient that characterizes the As evaporation flux; \( D \) is the NW diameter. The time required for the first island formation can be estimated by means of equating the nucleation time \( \tau_N \) and growth time [5]:

\[ \tau_N(C_{\text{As}}(r,t)) = t, \tag{5} \]

where \( \tau_N \sim 1/\pi(D/2)^2 l \) [6], \( l = N_0 W^+(i_c) Z \exp(-\Delta F(i_c)/kT) \) is the nucleation intensity, \( N_0 \) is the number of adsorption sites on the catalyst-NW interface; \( W^+(i_c) \) is the rate at which the GaAs pair attach to the island, \( Z \) is the Zeldovich factor, \( i_c \) is the critical size of the island, \( k \) is the Boltzmann constant; \( T \) is the growth temperature. To estimate the order of \( \tau_N \), we use the formula \( W^+(i_c) = 2\pi N_0 D_{\text{As}} C_{\text{As}}^{\infty}/\ln \lambda_{\text{As}}/R_c \) obtained for the case of the disk-shaped island [5], where \( C_{\text{As}}^{\infty} \) is the equilibrium As concentration at \( R = \infty \), \( R_c \) is the critical island radius, \( \lambda_{\text{As}} \sim R \) is the diffusion length of As species at the catalyst-NW interface, and expression for \( Z \) and \( \Delta F(i_c) \) derived in [5]. The results of self-consistent solution of the equations (3)-(5) show that the nucleation time of the semi-coherent triangle-shaped island at the free catalyst surface (when \( \gamma \sim 0.3 \text{ Jm}^{-2} \) and we assume \( \gamma_{SV} = \gamma \) for a simple consideration), \( \tau_N \sim 0.01 \text{ s} \), is several times higher than that of the disk-shaped island. Therefore, the nucleation of the semi-coherent disk-shaped island is energetically more favorable process than the nucleation of the semi-coherent triangle-shaped island. This result can be explained by the fact that the surface energy term to the nucleation barrier is higher for the triangle-shaped island because it has a longer length of the perimeter but the elastic energy term is lower. However, the nucleation of the coherent triangle-shaped island \( (\gamma \sim 0.01 \text{ Jm}^{-2}) \) proceeds at a higher rate than the nucleation of the coherent disk-shaped island, although, the orders of magnitude of nucleation time is the same in both cases \( (\tau_N \sim 10^{-4} \text{ s}) \). This is associated with the decrease of the role of the side wall term to the free energy. The parameters of the model used in the computation are as follows [5]: \( D_{\text{As}} \sim 10^{-12} \text{ m}^2\text{s}^{-1}, \ T = 420 \degree \text{C}, \ R = 50 \text{ nm}, \ k_{\text{As}} = 3.9 \cdot 10^{21} \text{ m}^{-2}\text{s}^{-1}. \) The chemical potential difference \( \Delta \mu \) and desorption coefficient \( k_{\text{As}} \) are calculated by means of the method presented in [10].

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