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Influence of the surface energy on the composition and growth of In$_x$Ga$_{1-x}$As nanowires

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The formation of self-catalyzed and Au-catalyzed nanowires is studied theoretically within the nucleation limited regime. Within the model the nanowire composition is obtained as a function of liquid composition in the cases of nucleation at the triple phase line and central nucleation. We study the influence of the nucleus surface energy on the nanowire composition, varying temperature, Au concentration and group V concentration. We show that the compositional independence of the surface energy term is a good approximation comparing the results with exact calculations.

Keywords: modeling, nanowires, chemical composition, In$_x$Ga$_{1-x}$As, surface energy, critical nucleus.

In the background of a slight decline in the annual number of publications devoted to nanowires (NWs) [1], interest in the study of NW ternary compounds is only growing. This is because in addition to the unique properties of these nanostructures (growth on mismatched substrates without dislocation formation [2], the ability to control the solid structure [3], morphology [4] and location [5]), the ability to control the composition [6] and consequently the band gap width [7]) is added. In most cases, NWs are grown by the vapor−liquid−solid (VLS) [8] mechanism using molecular beam [9] or vapor phase epitaxy [10]. In the VLS mechanism, NWs grow as follows: a semiconductor material is deposited on a prepared substrate surface, which is trapped in metallic droplets. As a result, the solution becomes supersaturated and crystallizes on the surface below the droplet. Along with Au-catalyzed growth [11], autocatalyzed growth [12] (without the use of an external catalyst) is the most popular, which avoids unwanted contamination of the NW [13].

Control of the composition of the $A_xB_{1-x}D$ NW is essential in the development of most optoelectronic devices based on NW [14]. However, the task is complicated by the fact that the chemical composition is affected by many factors, including the material system, synthesis method, droplet size [15], NW radius [16], growth temperature [17], flux ratio of the elements A and B [18], and III/V flux ratio [19]. Over the past few decades, a large number of models [1] have been developed by many research groups to describe the composition of the NW as a function of gas phase composition or droplet composition (equilibrium model [20], „nucleation-limited" [21] and kinetic model [22]). However in the vast majority of cases, it was assumed that the surface energy of a critical nucleus (or supercritical nucleus) is independent of its composition

due to surface segregation (those components that make the smallest contribution to the surface energy are concentrated near the solid boundary). In the [23] work, such a dependence was taken into account and the influence of the surface energy of the critical nucleus on the composition of the NW in the case of nucleation at the center was studied. In the present work, we investigate the effect of surface energy on the composition of NW during nucleation at the triple phase line and compare the results with nucleation at the center. The calculations are consistent with the regime of nucleation-limited growth of NWs, which assumes that the composition of the growing monolayer matches the composition of the critical nucleus.

Consider the formation of $A_xB_{1-x}D$ solid solution solid islands from a supersaturated four-component droplet containing the components A, B, D and U and located at the top of the NW (Fig. 1). The component U plays the role of an external catalyst (e.g., Au); in the case of self-catalyzed growth, its concentration is zero. Nucleation can occur either at the triple phase line (TPL) or at the center (C) of an − liquid-solid interface. According to nucleation theory, the size s and composition x of a critical nucleus can be found as a result of solving the following system of differential equations:

$$\frac{\partial F}{\partial x} = -\frac{\partial \Delta \mu}{\partial x}s + \frac{da}{dx}\sqrt{s} = 0, \qquad (1)$$

$$\frac{\partial F}{\partial s} = -\Delta \mu + \frac{a}{2\sqrt{s}} = 0. \qquad (2)$$

Here, $F = -\Delta \mu s + a\sqrt{s}$ — the formation energy of a solid island having surface energy $a = xa_{AD} + (1-x)a_{BD}$, where a_{AD} and a_{BD} — the surface energies of the AD and BD nuclei. In that case, $da/dx = \Delta a \equiv a_{AD} - a_{BD}$. $\Delta \mu$ — the chemical potential difference between the liquid and
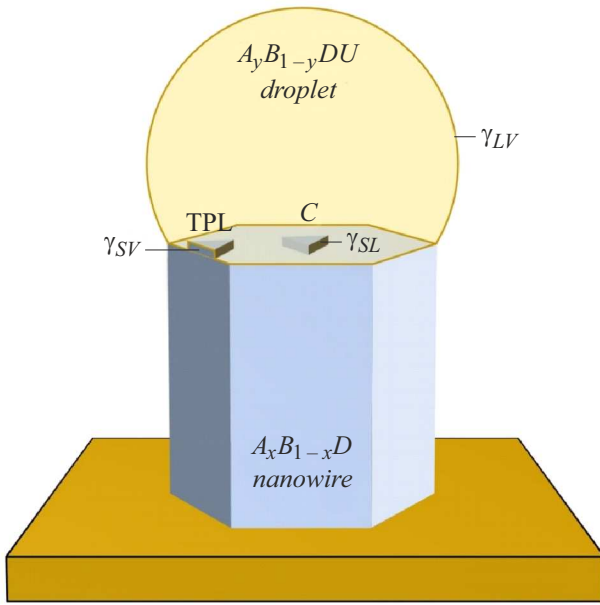
Figure 1. Scheme of nucleation in the center and at the triple phase line during the growth of NW of a ternary compound from a four-component droplet

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the solid. Substituting the critical nucleus size according to $\sqrt{s} = a/(2\Delta\mu)$ into equation (1) and using the ratios $\Delta\mu = x\mu_{AD} + (1 - x)\Delta\mu_{BD}$ and $\partial\Delta\mu/\partial x = \mu_{AD} - \mu_{BD}$, the droplet dependence of the critical nucleus composition can be found from equation

$$\frac{\Delta\mu_{AD}}{\Delta\mu_{BD}} = 1 + \frac{\frac{2\Delta a}{a}}{1 - \frac{2\Delta a}{a}x}. \tag{3}$$

Here, $\Delta\mu_{AD}$ (and $\Delta\mu_{BD}$) — the difference in chemical potentials of the atoms A and D (B and D) in liquid and the pair AD (BD) in crystalline phase. For -calculations, we use the regular solution model, and for -describing the interaction parameters — Ridlich−Kister [24] polynomials.

The surface energy of the critical nucleus of the binary compound $i = (AD, BD)$ has the form [25]:

$$a_i = 2 \cdot 3^{3/4}\Gamma_i\sqrt{\Omega_S h}, \tag{4}$$

where Ω_S — the volume of pair III−V in the solid phase, h — the height of the monolayer. Γ_i is a function of the surface energies at the boundary of solid−vapor (γ_{SV}), solid−liquid (γ_{SL}) and liquid−vapor ($\gamma_{LV} \approx y(1 - c_{Au})\gamma_{LV}^{In} + (1 - y)(1 - c_{Au})\gamma_{LV}^{Ga} + c_{Au}\gamma_{LV}^{Au}$):

$$\Gamma_i = \chi\gamma_{SL} + (1 - \chi)\left(\gamma_{SV} - \gamma_{LV}\frac{\Omega_L}{\Omega_S}\sin\beta\right). \tag{5}$$

Here, Ω_L — the vapor volume in the liquid phase, β — the contact angle. At nucleation in the center $\chi = 1$, whereas in the case of nucleation at the triple phase line $\chi = 2/3$. The following values [26] were used to describe the $In_xGa_{1-x}As$

system (i.e., in the case of $A = In$, $B = Ga$, and $D = As$):

$$\Omega_L^{InAs} = 0.056\,\text{nm}^3 \text{ and } \Omega_L^{GaAs} = 0.04\,\text{nm}^3,$$

$$\Omega_S^{InAs} = 0.0556\,\text{nm}^3 \text{ and } \Omega_S^{GaAs} = 0.045\,\text{nm}^3,$$

$$h^{InAs} = 0.35\,\text{nm}, \quad h^{GaAs} = 0.33\,\text{nm},$$

$$\beta = 90°, \ \gamma_{SV}^{InAs} = 1.1855\,\text{J/m}^2, \ \gamma_{SV}^{GaAs} = 1.3617\,\text{J/m}^2,$$

$$\gamma_{SL}^{InAs} = 0.63\,\text{J/m}^2, \ \gamma_{SL}^{GaAs} = 0.73\,\text{J/m}^2,$$

$$\gamma_{LV}^{Ga} = 0.708 - 6.6 \cdot 10^{-5}(T - 302.8)\,\text{J/m}^2,$$

$$\gamma_{LV}^{In} = 0.568 - 4 \cdot 10^{-5}(T - 273) - 7 \cdot 10^{-8}(T - 273)^2\,\text{J/m}^2,$$

$$\gamma_{LV}^{Au} = 1.15 - 1.64 \cdot 10^{-4}(T - 1337)\,\text{J/m}^2.$$

The values of interaction parameters and chemical potentials were given in [24]. The dependence of the surface energy ratio a_{GaAs}/a_{InAs} on the composition of the droplet during nucleation in the center and on the triple phase line at different values of the concentration of Au is presented in Fig. 2, a. It can be seen that for nucleation at the t, the a_{GaAs}/a_{InAs} ratio decreases with increasing concentration of In in the droplet and decreasing concentration of Au in the droplet.

We begin our analysis by comparing the dependence of the NW composition on that of the droplet in the cases of nucleation at the triple phase line and at the center. The composite dependences at different values of Au concentration are shown in Fig. 2, b. It can be seen that in the case of self-catalyzed growth ($c_{Au} = 0$) the curves are almost identical. Moreover, the results coincide with the case when the approximation of independence of the surface energy of the nucleus from its composition is used. However, in the case of Au-catalyzed growth, a discrepancy between the curves is observed: for a fixed droplet composition, in the case of nucleation at the triple phase line, the In content in the critical nucleus is higher than in the case of nucleation at the center.

We next consider the effect of temperature on the formation of self-catalyzed NWs$In_xGa_{1-x}As$. As evident from Fig. 3, a, an increase in temperature leads to an increase in the In content in the NW at fixed droplet composition, but the compositional dependences of $x(y)$ for nucleation at the triple phase line and at the center are almost identical. Finally, the effect of As concentration on the formation of NW $In_xGa_{1-x}As$ is shown in Fig. 3, b. $T = 440°C$ and $c_{Au} = 0$ were chosen as parameters. It can be seen that the concentration of As has practically no effect on the curve of dependence of the composition NW on the liquid composition, except for the case when nucleation occurs on the triple phase line from a droplet containing a large number of As ($c_{As} = 0.05$) atoms. It should be noted that further reduction of the concentration As ($c_{As} < 0.01$) practically does not change the position of the curve.

The constructed model allows us to describe the composition NW of ternary compounds in the framework of nucleation-limited growth with account for the contribution
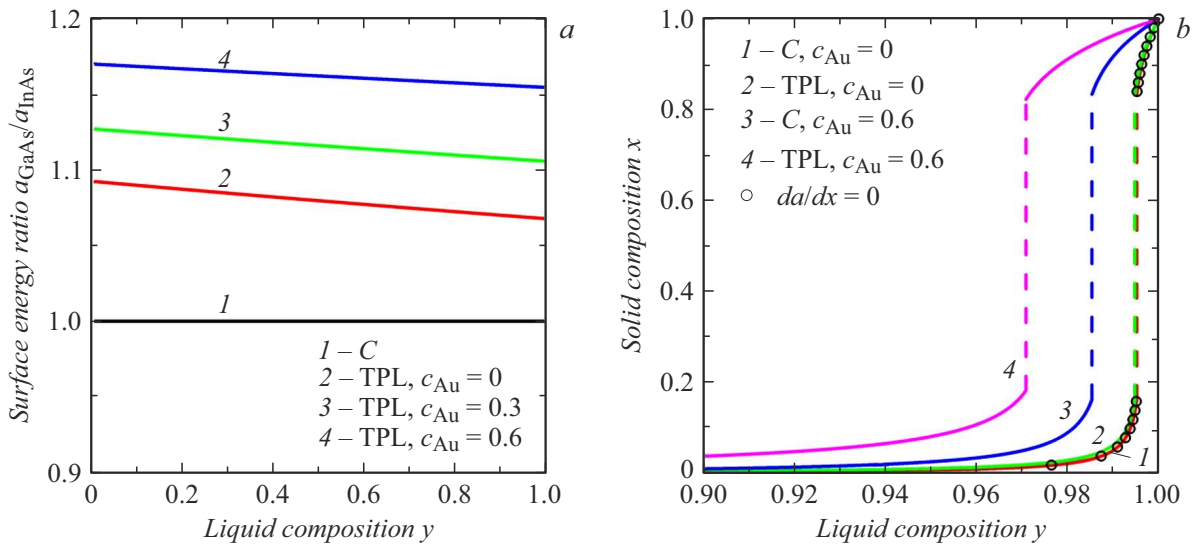
Figure 2. *a* — dependence of the surface energy ratio a_{GaAs}/a_{InAs} on the composition of the droplet at nucleation in the center and on the triple phase line at different values of concentration Au and fixed $T = 440°C$ and $c_{As} = 0.01$. *b* — the dependence of the composition of NW In$_x$Ga$_{1-x}$As on the liquid composition at nucleation in the center and on the triple phase line at different values of Au concentration and fixed $T = 440°C$ and $c_{As} = 0.01$. The dashed line corresponds to immiscibility. Circles — an approximation of the independence of the surface energy of the nucleus from its composition.
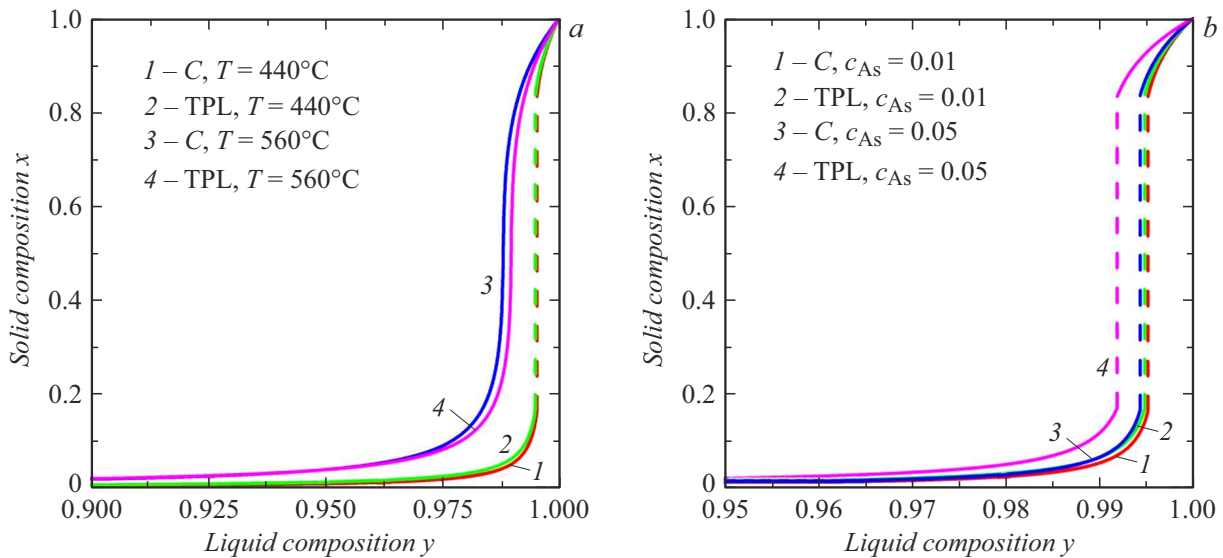

Figure 3. *a* — dependence of the composition NW In$_x$Ga$_{1-x}$As on the composition of the droplet during nucleation in the center and at the triple phase line at different values of temperature and fixed $c_{As} = 0.01$ and $c_{Au} = 0$. The dashed line corresponds to the miscibility gap. *b* — the dependence of the composition of NW In$_x$Ga$_{1-x}$As on the liquid composition at nucleation in the center and on the triple phase line at different values of Au concentration and fixed $T = 440°C$ and $c_{Au} = 0$. The dashed line corresponds to the miscibility gap

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of surface energy. It has been shown that under typical growth conditions ($T < 560°C$ and $c_{As} < 0.01$) of autocatalytic NWIn$_x$Ga$_{1-x}$As, the compositional curves calculated for nucleation at the triple phase line and center and when the $da/dx = 0$ approximation is used coincide. This accounts for the widespread approximation of independence of the surface energy of the nucleus from its composition. However, in the case where Au predominates in the droplet,

the contribution of surface energy to the energy of nucleus formation must be taken into account. The model is applicable to describe the composition NW of any ternary system. The choice of the range of concentration and temperature values for the modelled structure is related to the typical parameter values during the growth of NW In$_x$Ga$_{1-x}$As. The results obtained can be used to optimize the growth parameters of NW with predetermined composition.

Conflict of interest

The authors declare that they have no conflict of interest.

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