

On the size dependence of semiconductor nanowires growth rate

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Abstract: The results of studies on the growth kinetics of semiconductor nanowires are considered in the paper. It is proved that the physical mechanisms governing the growth rate of such crystals are insufficiently studied in modern research papers, and information on the kinetics of their growth is still ambiguous and contradictory. The existing ideas about the diffusion character of the decreasing dependence of the growth rate of nanowires Si, Ge, GaAs, GaN, InAs, etc. on their radius are analyzed. New results obtained for the growth kinetics of silicon nanowires are presented. It is shown that an increase in the growth rate of nanocrystals with a decrease in their transverse dimensions is not associated with the influence of diffusion, but with a thermodynamic factor, which causes a decrease in the equilibrium solubility of the crystallizing substance in liquid-phase drops of the catalyst metal with an increase in the dispersion of the catalyst. In this case the stage of crystallization at the solid/liquid interface under a drop of a liquid-phase catalyst metal acts as a limiting stage. The equation is obtained that describes the dependence of the length of a nanowire on the radius under the influence of a thermodynamic factor. Recommendations are given for the intensification of the growth processes of semiconductor nanowires in the exothermic process of the crystallization reaction.

Keywords: nanowires; growth rate; radius; semiconductors; droplet; solubility; kinetics; size effect.

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О размерной зависимости скорости роста нитевидных нанокристаллов полупроводников

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Аннотация: Рассмотрены результаты исследований кинетики роста нитевидных нанокристаллов полупроводников. Показано, что в современных исследованиях недостаточно изучены физические механизмы, управляющие скоростью роста таких кристаллов, а сведения о кинетике их роста остаются неопределенными и противоречивыми. Проанализированы существующие представления о диффузионном характере убывающей зависимости скорости роста нитевидных нанокристаллов Si, Ge, GaAs, GaN, InAs и др. от их радиуса. Приведены новые полученные результаты для кинетики роста нитевидных нанокристаллов кремния. Показано, что увеличение скорости роста нанокристаллов с уменьшением их поперечных размеров связано с влиянием не диффузионного, а термодинамического фактора, обуславливающего снижение равновесной растворимости кристаллизующего вещества в жидкофазных каплях металла-катализатора с увеличением дисперсности катализатора. При этом в качестве лимитирующей стадии выступает стадия кристаллизации на границе кристалл / жидкость под каплей жидкофазного металла-катализатора. Получено уравнение, описывающее зависимость длины нитевидного нанокристалла от радиуса в условиях влияния термодинамического фактора. Даны рекомендации по интенсификации процессов роста нитевидных нанокристаллов полупроводниковых материалов в экзотермическом процессе реакции кристаллизации.

Ключевые слова: нитевидные нанокристаллы; скорость роста; радиус; полупроводники; капля; растворимость; кинетика; размерный эффект.

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1. Introduction

Quasi-one-dimensional nanostructures (nanorods, nanoribbons, nanotubes, nanofibers) with unique electrical and mechanical properties can make a technical revolution in such diverse areas as electronics, catalysis, sensors, composite materials, etc. [1]. Despite the obvious progress in studies on semiconductor nanowires (NWs) observed in recent years, the mechanism of the vapor-liquid-solid (VLS) growth, which is currently used to synthesize most NWs, is still far from being fully understood. In particular, the answer to the question about the stage that controls the growth rate of NWs is the most important in the formation of correct ideas about the VLS growth mechanism. However, data on the growth kinetics of NWs remain ambiguous and contradictory. So Givargizov E.I. [2] considered the stage of crystallization at the solid/liquid interface to be the limiting growth of NWs. Weier J. for Si NWs [3], Debnach R.K. with co-authors [4], Schubert L. et al. [5], as well as Dubrovsky V.G. et al. [6] described models of the diffusion-stimulated growth for GaAs NWs. Bootsma G.A. and Gassin H.J. [7], Kozenkov O.D. [8] singled out a chemical reaction on the liquid/vapor surface as the limiting one in the growth of Si and Ge NWs. In recent years, a number of experimental and theoretical studies have been carried out to investigate the growth rate of NWs using the methods of molecular beam epitaxy (MBE) and metal-organic vapor phase epitaxy (MOVPE) [9–15]. It was found that the growth rate increases hyperbolically with a decrease in the transverse dimensions of NWs, and the absolute values of the rates are several orders of magnitude lower than in the case of synthesis using chemical vapor deposition methods ($1\text{--}25\text{ nm}\cdot\text{s}^{-1}$ versus $1\text{--}2\text{ }\mu\text{m}\cdot\text{s}^{-1}$). However, these studies have not focused on the physical mechanisms that control the rate of crystal growth thoroughly. The fundamental reasons for the very low growth rates in case of MBE are still not understood and are being discussed. Some kinetic characteristics of NWs measured by several researchers differ; they are even contradictory. In this case the dependences of the NW growth rate on the crystal diameter $V=f(d)$ and the growth process time $V=f(t)$ are universal characteristics that can be used to judge the stability of crystallization conditions and the influencing factors. Therefore, there is a need to

analyze the research of other scientists to find out the main reasons underlying the lack of convergence of views on this issue.

Therefore, the purpose of this paper is to carry out a critical analysis of modern ideas about the effect of the transverse size of NWs on the kinetics of crystal growth and to show that in the processes of NW growth the decreasing dependence of the growth rate on the diameter is due to the influence of the thermodynamic factor, and the crystallization stage at the solid/liquid interface acts as a limiting one.

2. Materials and Methods

Si NWs were grown by crystallization from the gas phase in a chloride–hydrogen process using Ni and Au particles with sizes of 200–500 nm or less as catalysts. The temperature range of NW growth was 1273–1373 K. H_2 used for NW growth was purified by modern methods and had a dew point of 215 K. A vapor-gas mixture of H_2 and SiCl_4 was prepared in standard bubble-type liquid sources. The mole ratio of the components $M_{\text{SiCl}_4}/M_{\text{H}_2}$ was maintained in the range from 0.005 to 0.01. The growth substrates were polished single-crystal silicon wafers with the {111} orientation. The growth rate of NWs was determined by the method of “time markers” [2]. To obtain reproducible results and exclude the influence of NWs on each other, it is important that the crystals are isolated, i.e. located on the substrate at a sufficient distance ($\sim 1\text{ }\mu\text{m}$). The dependence of the Si and Ge NW length on the process temperature in the range from 773 to 1273 K was studied by growing crystals on the VAK-501 setup using molecular-beam epitaxy (MBE). The grown NWs were studied by transmission (EMW 100-BR) and scanning electron microscopy (JSM-6380LV, JEOL), the resolution of which is less than 1–2 nm, which is sufficient to determine the growth rate of NWs with the required accuracy.

The kinetic characteristics of Si, Ge, GaAs, etc. NWs were also analyzed based on research papers.

3. Results and Discussion

The current views in research papers on the growth kinetics of semiconductor NWs are based on the concept of diffusion-stimulated crystal growth

[13, 14]. Without going into details of the very term “diffusion-stimulated growth”, we will assume that the process is controlled by a diffusion stage, which, in the authors’ opinion, is mass transfer of atoms or molecules of the crystallized material adsorbed on the surface of the growth substrate and the side surface NWs by means of diffusion.

For Si NWs grown by MBE on an Au-activated Si(111) surface, the experimental data show that thinner crystals are longer than thick ones, and that the observed dependence of the NW length L on their diameter d fits well with the curve $L = H + \text{const} / d$, where $H = \text{const}$ [5]. Experimental results [13] for GaAs NWs grown on GaAs(111)B substrates with the participation of Au also demonstrate a decreasing dependence $L = f(d)$. The maximum length of thin NWs in both cases exceeds the deposition thickness (by the factor of 3 for Si and 7 times for GaAs). The experimental dependence of the length on the diameter for GaN NWs described by the diffusion model is given in [4]. GaN NWs were grown on Si(111) substrates at the temperature of 1073 K. Fig. 1 shows a similar typical empirical dependence of the length on the diameter for Si NWs grown with the participation of Ni that we obtained.

Similar to Fig. 1, the experimental and theoretical dependences of the growth rate of InAs NWs on the diameter (growth temperature $T = 713$ K) were obtained in [15], and the theoretical decreasing dependences of the growth rate of Si NWs on the radius for temperatures in the range from 573 to 1023 K were obtained in [14].

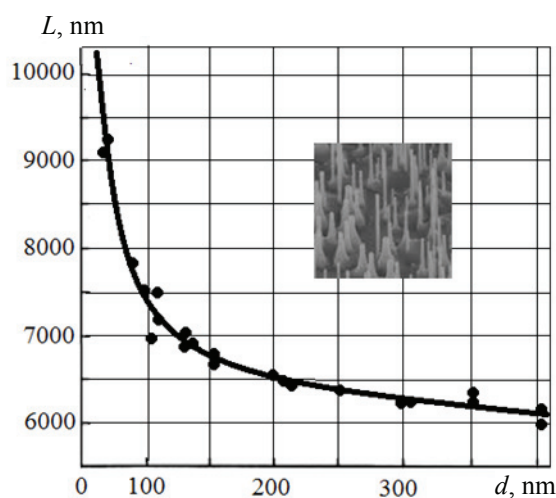


Fig. 1. Experimental dependence of length on diameter for Si NWs grown on a Si(111) substrate at the temperature of 1273 K. Ni is a catalyst. The inset shows SEM images of NWs

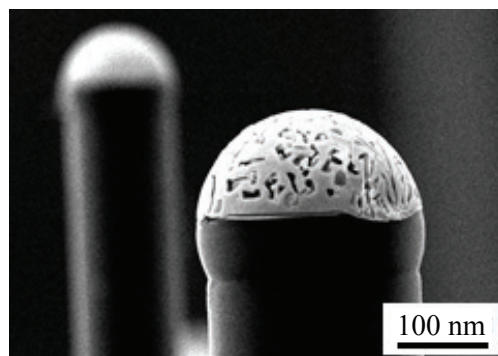


Fig. 2. SEM image of Si NWs grown in the Au-Si system

Figure 2 shows the SEM image of Si NWs grown with the participation of Au catalytic particles. The above image illustrates that thinner NWs grow faster than thicker ones.

The decrease in the NW length with the increasing radius in most studies is explained by the diffusion nature of growth, for which the diffusion of adatoms over the substrate surface and NW side walls is the key growth parameter, which has a significant effect on the rate of crystal elongation. Since there is a sink at the top of the NW, the adatoms diffuse from the side walls to the top under the action of the chemical potential difference. The size effect associated with the ratio of the areas of the feeding lateral and consuming NW end surfaces underlies the explanation of the increase in the growth rate with a decrease in the transverse dimensions of crystals. Thus, the experimental curve $L = f(r)$ in [4] is mathematically described by the dependence $L = H(1 + \lambda/r)$, where r is the NW radius, and the parameters $H = 470$ nm and $\lambda = 40$ nm.

The arguments in favor of the diffusion regime of the NW growth are the decreasing nature of the dependences of the NW growth rate experimentally obtained in MBE processes on the transverse dimensions of the latter, the small (nanoscopic) dimensions of the active surface of the catalyst droplets compared to the sizes of the crystalline surface of the substrate and crystals, low vapor pressure, high condensation coefficients, long lifetime of adatoms on the surface, large diffusion lengths of adsorbed atoms in a rarefied atmosphere.

The theoretical model of the diffusion-stimulated growth was constructed in [6]. In the simplest case, when the growth delays caused by size effects such as the Gibbs–Thomson effect, monocentric nucleation, and the intensity of two-dimensional nucleation on the surface are not taken into account, the NW growth rate is determined by the expression

$$\frac{\pi R^2}{\Omega_S} \frac{dL}{dt} = \left(\frac{V - V_S}{\Omega_S} - \frac{2C_i}{\tau_i} \right) \pi R^2 + j_{\text{diff}}(L), \quad (1)$$

where R is the radius of the catalyst drop, V is the rate of deposition of the material being crystallized, V_S is the rate of the vertical growth of the non-activated surface, C_i is the volume concentration of the drop solution, r_i is the intermolecular distance in the liquid, τ_i is the lifetime of the adatom in the near-surface layer of the drop, Ω_S is the volume occupied by one atom (molecule) of the substance being crystallized in the solid phase.

The first member on the right side of the equation (1) is proportional to the difference between the number of adsorption and desorption events on the droplet surface per time unit. The last member in (1) characterizes the diffusion flow of adsorbed atoms from the surface to the top of the NW.

It is believed that in case of MBE the direct supply of atoms from the gaseous phase to the droplet and to the side surface of vertical NWs is small; therefore, only the diffusion and adsorption-desorption contributions from the substrate surface and the NW side walls can be taken into account in the equation for the adatom concentration. According to the authors' estimates, for the thinnest NWs with the radius of $r \sim 10$ nm, diffusion of adatoms from the substrate surface to the top of NWs can increase their growth rate.

However, in our opinion, despite the various experimental data and the diffusion growth models available in research papers, the formalism of which is applicable to the VLS process, the above facts and arguments do not confirm the conclusions of the authors [4–6] on the diffusion control of the growth process of NWs in modern growth technologies, but, on the contrary, indicate the thermally activated nature of the crystallization regime. Indeed, the dimensional characteristics of NWs are so small, and the temperatures of the processes are high enough, that it is not needed to speak of diffusion processes as the slowest stages that determine the growth rate of NWs.

It can be said that the conclusions of the authors about the diffusion regime of the NW growth using MBE methods are practically based only on the decreasing dependence of the NW growth rate on the radius established in many experiments. Although, it should be noted that there are enough scientific works in which the increasing dependence $V=f(r)$ is observed [1, 14]. It follows that the evaluation of the limiting stage must be considered cautiously.

The frequently observed dependence $V=f(r)$, which shows that thin crystals grow faster than thick ones, cannot be the basis for an unambiguous assertion that the NW growth process is limited by the surface diffusion stage. Let us analyze this in detail.

The surface diffusion on the substrate and side surface of NWs cannot control the crystal growth rate due to the fact that under conditions of a rarefied atmosphere and long free paths of adatoms $\bar{\lambda}_a$ during the residence time τ_a on the growth Si-substrate $\bar{\lambda}_a \approx (D_a^c \tau_a)^{1/2} \sim (3-10) \mu\text{m}$, relatively large values of the effective surface diffusion coefficient D_a^c and small transport routes for the delivery of the feed material due to the small size of NWs (diameter $d \sim (10-100)$ nm and length $L \sim 1 \mu\text{m}$), diffusion, on the contrary, proceeds very quickly ($< \bar{\lambda}_a$). Thus, in the case of growth of GaAs NWs at $T = 853$ K $\bar{\lambda}_a$ the Ga atom on the GaAs surface $(\bar{1}\bar{1}\bar{1})$ B is $\sim 6 \mu\text{m}$, and on the side surface of GaAs NWs $\{110\}$, according to calculations, is from 2–3 to 8–10 μm [6]. Similarly, with typical Si NW lengths $L \sim 1 \mu\text{m}$ and typical surface diffusion coefficients (for Si(111) at $T = 1000$ K, estimated to be $D_a^c \sim 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$), the surface diffusion rate is

$V_{DS} \sim D_a^c / L \sim 10^{-5} \text{ m} \cdot \text{s}^{-1}$. Such a value could be reached in the limit of the growth rate of Si NWs when the process is limited by the stage of surface diffusion. However, the observed NW growth rates ($1-10 \text{ nm} \cdot \text{s}^{-1}$) are three to four orders of magnitude lower than the estimated values obtained.

At the same time, the conclusions about the diffusion regime of the NW growth also contradict the observed exponential, that is, strong temperature dependences $V=f(T)$ (a typical form of such dependences is shown in Fig. 3), indicating the activation nature of the process (the activation energy is usually 40–200 $\text{kJ} \cdot \text{mol}^{-1}$). A strong exponential dependence of the growth rate on the temperature of the growth process for Si and Ge NWs was also obtained in [7] and described in [2]. It was found that the growth rate of Si NWs is higher than that of Ge NWs. But it is known that the temperature dependence of diffusion is weak, power-law (with an exponent of no more than 1.5–2.0), and the diffusion activation energy does not usually exceed 4–20 $\text{kJ} \cdot \text{mol}^{-1}$ [1].

Since the dependences of the growth rate of NWs on the diameter of crystals and the time of the growth process are universal characteristics that can

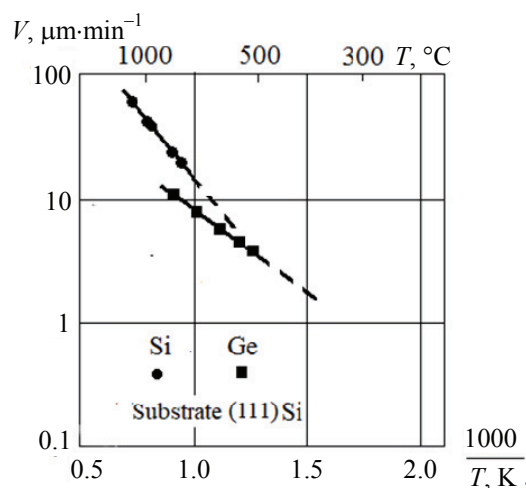


Fig. 3. Comparison of the Axial Growth Rate of Silicon and Germanium NWs

be used to judge the stability of crystallization conditions and the influencing factors, we studied the character of elongation of Si NWs of constant diameter over time $L = f(t)$ (Fig. 4).

As can be seen from Fig. 4, the function $L = f(t)$ is linear with a constant slope. With a change in the growing temperature, the angle of inclination changes slightly: with an increase in the temperature, the angle increases. The linear nature of the dependence $L = f(t)$ indicates stable kinetic conditions for the growth of NWs at an almost constant rate during the studied period of time. The described dependence $L = f(t)$ is observed for different types of catalyst metals (in our case, Au, Cu, Ni) and for various technological conditions (for any temperature ranges, impurity concentrations, gas flow rates, etc.). From the linear nature of the function $L = f(t)$ (Fig. 4) it follows that $V = dL/dt = \text{const}$ and, practically, does not depend on the concentration of the crystallized substance. This is possible only for a zero-order surface process in terms of the volume concentration of the reagent, the rate of which is lower than the rate of delivery of the reactants, since the reaction order in the diffusion region is always the first. In this case, the droplet composition near the solid/liquid interface differs little from the NW composition, and the process does not require diffusion.

Taking into account the above results, we can say that only at first glance it seems that the process of the NW growth, characterized by decreasing dependences $V = f(r)$, is in the diffusion mode [4–6, 10, 13]. In fact, during the crystallization of Si, Ge, GaAs, GaAs and other semiconductor materials under given temperature conditions, the dependence $V = f(r)$ is determined by thermodynamic reasons. Indeed, with an increase in the NW diameter, due to the size dependence of the solubility on the dispersity

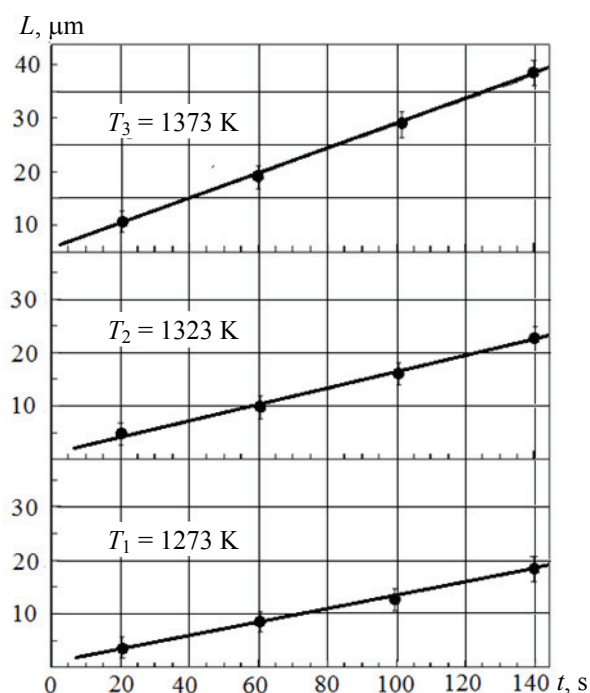


Fig. 4. Dependence of the growth rate of Si NWs of constant radius on the growth time. Ni is a catalyst

of the solvent [16], the equilibrium of the process of crystallization of substance A at the solid/liquid interface ($A_{\text{liq}} \rightleftharpoons A_{\text{cr}}$) shifts towards the dissolution reaction of the crystalline substance, the equilibrium solubility of the crystallized material in the catalyst drop increases, and the rate growth of NWs falls. This fact, along with the exponential functional dependence of the NW growth rate on temperature (Fig. 3), is a strong argument in favor of the growth regime with the limiting thermally activated [2, 7], rather than diffusion stage.

It should be noted that a decrease in the solubility of the solid phase in a small catalyst drop at $R \rightarrow 0$ is a size effect due to the large negative curvature of the solid surface at the boundary with a nano-sized droplet, and is a powerful source of a decrease in surface tension (Fig. 5) [16].

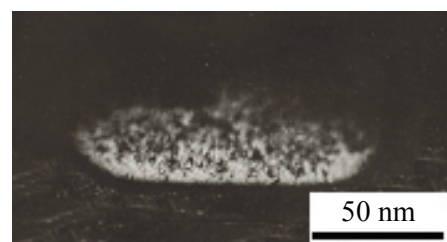


Fig. 5. SEM image of an Au catalyst droplet on a (111) Si substrate, illustrating the negative curvature (the center of curvature is in the liquid) of the crystal at the interface with a small-volume equilibrium liquid phase

Table 1. The decrease in the equilibrium solubility of Si C_{eq} with a decrease in the radius of the metal catalyst drop (C_0 is the solubility of bulk samples at $R \rightarrow \infty$)[16]

Radius of the drop R , nm	Ratio C_{eq} / C_0 , %	
	Cu-Si	Au-Si
10000	99.98	99.99
1000	99.86	99.90
100	98.67	99.00
10	87.5	90.48
1	26.44	36.78

Therefore, the decreasing dependence of the NW growth rate on the diameter is most noticeable for nanosized crystals, and at $R > (75-100)$ nm, the effect practically disappears (Table 1).

Let us combine all stages of the NW growth and assume that the growth rate is determined only by bulk (surface) diffusion and reactions at the interface. Let us represent in a very simplified way the process of the NW growth from two successive stages: diffusion of the crystallized substance in the solution of a catalyst drop and crystallization at the solid/liquid interface. Assuming that equilibrium at the interfaces is established quickly and that adsorption-chemical processes do not limit the growth rate of NWs, we assume that the latter is determined by diffusion, the rate of which is described by Fick's first law. Let us use $\Delta C = C_{surf} - C_{real}$ to indicate the difference between the concentrations of the crystallized substance in the volume of the drop near its surface and at the crystallization front ($\text{kg} \cdot \text{mol} \cdot \text{cm}^{-3}$), where C_{surf} is the concentration of the crystallized substance in the volume of the drop, C_{real} is the concentration of the substance in the drop solution on the edge of the crystal. Then we can use the expression

$$\frac{dm}{dt} = \frac{D\pi r^2}{R}(C_{surf} - C_{real}), \quad (2)$$

where dm/dt is the diffusion increment of the mass m of the growing NW per time unit t ($\text{kg} \cdot \text{mol} \cdot \text{s}^{-1}$), D is the diffusion coefficient in the liquid phase ($\text{m}^2 \cdot \text{s}^{-1}$), πr^2 is the area of the growing end face of the NW of radius r (m).

Using v_D ($\text{m} \cdot \text{mol} \cdot \text{s}^{-1}$) to indicate the linear speed of the diffusion flow of the crystallized substance (internal diffusion) in the drop and taking into account that

$$\frac{dm}{dt} = v_D \pi r^2 \rho, \quad (3)$$

where ρ is the bulk density of NWs ($\text{kg} \cdot \text{m}^{-3}$), we can rewrite the equation (2) in the following way

$$v_D = \frac{D}{\rho R}(C_{surf} - C_{real}). \quad (4)$$

Here the diffusion flow into the droplet is considered as the sum of particle flows adsorbed directly on the droplet surface, on the NW side walls, and migrated from the substrate surface.

If we assume that the crystallization rate at the solid/liquid interface near the triple line limits the NW growth process, and assume that the crystallization reaction is of the first order, then its rate is determined as

$$\frac{dm}{dt} = k_k \pi r^2 (C_{real} - C_{eq}), \quad (5)$$

where k_k is the crystallization reaction rate constant, C_{eq} is the equilibrium concentration of Si in the solution of the drop at the temperature T (the ratio of the number of Si atoms to the volume of the drop).

Passing to the linear rate of crystallization in the kinetic process v_k , from (5) we can obtain

$$v_k = \frac{k_k}{\rho}(C_{real} - C_{eq}). \quad (6)$$

In this case, the constant k_k will depend on the crystallographic direction of growth and the structure of the growth surface. The equation (6) will also be valid for the case when the diffusion rate is comparable to the crystallization rate. If the diffusion rate significantly exceeds the crystallization rate, then $C_{real} \approx C_{surf}$.

In the steady state the rates of successive stages and the rate of the NW growth process are generally equal to each other ($dL/dt = v_D = v_k$). This means that the capabilities of the system as a whole are determined by the bandwidth of the link with the highest resistance or with the lowest value of the rate constant. Excluding from the equations (2) and (3) the intermediate concentration C_{real} , which is not amenable to direct measurement, we will obtain

$$\frac{dL}{dt} = \frac{k_k}{\rho} \left(C_{surf} - \frac{\rho R}{D} \frac{dL}{dt} - C_{eq} \right). \quad (7)$$

Separating variables in (7), we find

$$\frac{dL}{dt} + \frac{k_k R}{D} \frac{dL}{dt} = \frac{k_k}{\rho} (C_{\text{surf}} - C_{\text{eq}}). \quad (8)$$

At the initial moment of time ($t = 0$), the NW has not yet grown and $L = 0$. Integration (8) under these boundary conditions leads to

$$L + \frac{k_k R}{D} L = \frac{k_k}{\rho} (C_{\text{surf}} - C_{\text{eq}}) t. \quad (9)$$

For metal catalysts with high values of the diffusion coefficient of the material being crystallized and with small droplet sizes, i.e. when $\frac{D}{R} \gg k_k$, one

can neglect the second member in comparison with the first member on the left side of the equation (9), which results in

$$L = \frac{k_k}{\rho} (C_{\text{surf}} - C_{\text{eq}}) t. \quad (10)$$

From the expression (10) it follows:

a) the growth rate of NWs does not depend on the radius of the catalyst drop;

b) the NW length is directly proportional to the process time, i.e. crystallization proceeds at a constant rate;

c) the NW growth rate is limited by the crystallization stage (k_k), and the process is in the kinetic region, i.e. the observed speed obeys the laws inherent in chemical interactions.

For large droplet sizes or a small diffusion coefficient of the material being crystallized ($\frac{D}{R} \ll k_k$), the first member on the left side of the equation (9) can be neglected. Then we get

$$\frac{k_k R}{D} L = \frac{k_k}{\rho} (C_{\text{surf}} - C_{\text{eq}}) t$$

or

$$L = \frac{D}{\rho R} (C_{\text{surf}} - C_{\text{eq}}) t, \quad (11)$$

from which we conclude:

a) the growth rate of NWs is inversely proportional to the radius of the catalyst drop;

b) the process is in the diffusion region (D), and the rate of the total transformation obeys the laws characteristic of mass transfer (bulk or surface diffusion).

Thus, from the obtained expressions (10) and (11) we see that for thick NWs ($d \gg 100$ nm) the process is in the diffusion region and the growth rate

should increase with the decreasing radius. With a significant decrease in the NW radius ($d < 100$ nm), the length L grows linearly with the time, and the process mode becomes kinetic. Between these extreme cases the transition region lies, where L and t are related by the equation (9), which takes into account the features of both the crystal chemical stage and diffusion.

As mentioned above however, with the thermodynamic control of the process, with an increase in the dispersion (R^{-1}) of the catalyst, the equilibrium solubility of the solid phase in it decreases [16]

$$C_{\text{eq}} = \bar{C}_0 \exp\left(-\frac{2\alpha_L \Omega}{kTR}\right), \quad (12)$$

where α_L is specific free surface energy of the liquid phase, Ω is the specific volume occupied by one atom in the melt, k is the Boltzmann constant.

Then, substituting (12) into (10), we obtain

$$L = \frac{k_k}{\rho} \left(C_{\text{surf}} - \bar{C}_0 \exp\left(-\frac{2\alpha_L \Omega}{kTR}\right) \right) t. \quad (13)$$

It follows from the equation (13) that at low temperatures during the growth of NWs, the smaller the radius of the catalyst drop is, the lower the equilibrium solubility of the crystallized substance in it is and the higher the supersaturation of the solution is, and, consequently, the higher the growth rate is (the NW length per time unit) (Figs. 1 and 2). In case of the constant radius of the $C_{\text{real}} \approx C_{\text{surf}}$ droplet, the process does not require diffusion and $dL/dt \approx \text{const}$, which we observe experimentally (see Fig. 4).

It also follows from the expressions (10), (11) and (13) that the growth rate of NWs depends on the bulk density of the crystallized material ρ . As ρ increases, the growth rate should decrease. The comparison of the axial growth rates of Si ($\rho = 2.33 \text{ g}\cdot\text{cm}^{-3}$) and Ge ($\rho = 5.33 \text{ g}\cdot\text{cm}^{-3}$) NWs on substrates made of these materials using SiH_4 and GeH_4 as precursors and various metals (Au, Ag, Cu, Ni, Pd) as catalysts shows that the growth rate of Si NWs is higher than that of Ge NWs [1, 7].

Thus, based on the critical analysis of research papers, the linear dependence of the growth rate of Si NWs on the process time, which was experimentally established in the paper, and relying on the results of mathematical calculations, it can be stated that an increase in the growth rate of NWs with a decrease in the crystal radius occurs due to a decrease in the solubility of the solid in liquid-phase drops of the

metal-catalyst with an increase in their dispersity. In other words, a decrease in the equilibrium concentration of the substance being crystallized in liquid catalyst metal droplets with a decrease in their size is equivalent to an increase in the concentration of the substance being crystallized in equilibrium, as a result of which the equilibrium shifts towards the consumption of this substance. The tendency of the system to shift the equilibrium towards the consumption of the substance is expressed in an increase in supercooling (or supersaturation) in the catalyst drop and, as a consequence, in an increase in the growth rate of NWs. In case of constant linear dimensions of the drop and crystal, the equilibrium concentration does not change and $V = \text{const}$, which is confirmed by the experimentally established linear dependence of the Si NW rate on the growth process time at $R = \text{const}$.

To intensify the growth of NWs in an exothermic process, we can recommend lowering the temperature and pressure in the reaction zone.

4. Conclusions

A critical analysis of modern ideas about the effect of the transverse size of NWs on the kinetics of crystal growth was carried out, the linear dependence $L = f(t)$ was experimentally established, and it was shown that the observed decreasing dependence of the growth rate of NWs on their radius is due to the influence of the thermodynamic rather than diffusion factor. In this case, the stage of crystallization at the solid/liquid interface acts as the limiting stage of the NW growth.

It was established that the thermodynamic size effect of a decrease in the solubility of the substance being crystallized in a small-volume liquid phase with a decrease in its size leads to an increase in supercooling (or supersaturation) in a catalyst drop, and, as a consequence, to an increase in the NW growth rate. A decrease in the solubility of the substance being crystallized in liquid-phase drops with a decrease in their size (increase in dispersion) is due to the effect of surface curvature on the thermodynamic potential of the system.

The equation is obtained that describes the dependence of the length of a NW on the radius under the influence of a thermodynamic factor.

Thus, the theoretical significance of this study is to establish the prevailing role of the thermodynamic factor for predicting the course of the size dependence of the growth rate of semiconductor NWs. The practical significance of the results of the research lies in the recommendations for intensifying the growth of NWs by lowering the temperature and pressure in the reaction growth zone.

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6. Conflict of interests

The authors declare no conflict of interest.

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