Kinetics of growth of nanowhiskers (nanowires and nanotubes)

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Abstract The kinetics of nanowhiskers growth is studied theoretically taking into account the adatom diffusion from the surface to the top of needle. An exponential growth with time is expected for the initial stages of the process, when the length l of the whisker is smaller than the average diffusion length λ of adatoms. It transforms to linear growth rate for $l > \lambda$. The formation of nanotubes with a hollow core dislocation is explained by accounting for the role of the stress in the middle of screw dislocations. When the magnitude of the Burgers vector exceeds a critical value, it is energetically more favorable to remove the highly strained material around the dislocation line and to create a tube with an additional free surface. Additionally, there is an important size effect, due to the small radius R of the nanowhisker. The interplay, between the contributions from the size effects and from the diffusion, explains why for the very thin nanowhiskers the length l is proportional to the radius R while, otherwise the length is inversely proportional to it, i.e., $l \sim 1/R$.

Keywords Nanotubes · Nanowires · Nanowhiskers

Introduction

The kinetics of formation of nanowires and of nanotubes (both known earlier as whiskers) is of special interest for the theory and practice of crystal growth. The theory has to elucidate two important questions: The first problem is why

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nanowhiskers have unlimited size in one direction while the size in the other directions is of the order of nanometers. The second one is why the growth rate exceeds considerably velocity expected from the direct deposition of atoms on the top of the needle. Evidently, the contribution of the diffusion of adatoms plays an important role.

The growth of whiskers is strongly anisotropic, i.e., the growth rate U of length of the whisker is several orders higher than the rate of thickening. Therefore it is assumed that the walls of whiskers are perfect, with no growing places (kinks) on them. On the other hand, a relatively large part, ω_{top}, of the atoms on the top, are at a kink position. According to the so called vapor-liquid-solid (*VLS*) [1–4] mechanism of growth, a small droplet is formed on the top of the whisker (see Fig. 1B). The crystal/droplet interface energy is relatively low so that the interface is rough, i.e., $\omega_{\text{top}} \approx 0.5$ and growth proceeds according to the ''normal'' mechanism. In the same time, the crystal/vapors interface energy is high so that the side surfaces are smooth and $\omega_{\text{side}} \rightarrow 0$.

An alternative reason for high ω_{top} value is the presence of a screw dislocation on the top (see Fig. 1A). It seems that first Sears [5, 6] discusses the possible mechanisms of whiskers growth. Gomer [7] derived as a limiting case the exponential law of initial stages of the process. Kinetics of whiskers growth was studied in details by Dittmar and Neumann [8, 9] under the assumption that a screw dislocation is formed on the top. It can be easily generalized for the case of a droplet on the top (*VLS* mechanism).

The model

Here we consider nanotube of length l and radius R, as illustrated in Fig. 1A. In the core of the screw dislocation,
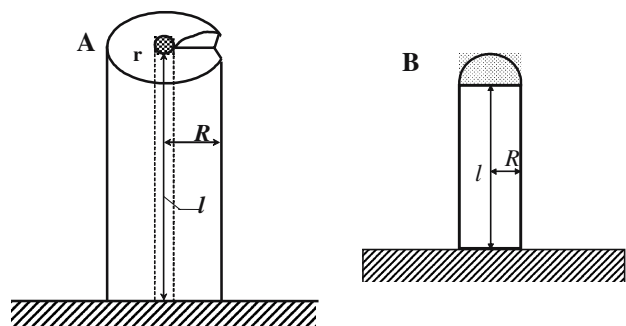
Fig. 1 Models of growing nanowhiskers: Fig.1A—growing nanotube. The length is l, the inner radius of the pipe is r; the radius of the nanotube is R. The growth is secured by a screw dislocation. Fig1B—growing nanowires by VLS mechanism

stress energy is created proportional to the product of the Burgers vector B and the shear modulus E. Therefore, from the thermodynamic view point, it is favorable to remove a given amount of substance from the dislocation core. So, a pipe is formed, the radius r of which is determined by the interplay of the stress energy gained, $-l\frac{EB^2}{4\pi}\ln r$, and the interface energy, $2\pi r\sigma l$, created in the inner side. The minimum free energy condition determines the famous [10, 11] Frank's radius r of the pore as:

$$r = \frac{B^2 E}{8\pi^2 \sigma} \tag{1}$$

In general, the crystals growth rate U depends on the supersaturation in the following way:

$$U = \omega_{\text{top}} d_{\text{o}} W \tag{2}$$

where W is the net flux of atoms, *per unit place* on the top of the nanowhisker, d_{o} is the mean interatomic distance and k_{B} is the Boltzmann constant. The net flux W depends on supersaturation $\Delta\mu$ according to

$$W = W_\infty\left(1 - e^{-\frac{\Delta\mu}{k_{\text{B}}T}}\right) \approx W_\infty \frac{\Delta\mu}{k_{\text{B}}T} \tag{3}$$

where W_∞ is a constant. As compared to the supersaturation of infinitely large phase $\Delta\mu_\infty$, in the case of nanotube the supersaturation $\Delta\mu$ is lowered due to the size effect.

$$\Delta\mu = \Delta\mu_\infty - \Delta\mu(R, r) \tag{4}$$

For a cylindrical nanotube with inner radius r and outer radius R the lowering of supersaturation is

$$\Delta\mu(R, r) = \frac{\sigma d_{\text{o}}^3}{R\left(1 - \frac{r}{R}\right)} \approx \frac{\sigma d_{\text{o}}^3}{R}\left(1 + \frac{r}{R}\right) \quad, \tag{5}$$

under the assumption that both inner and outer sides of the walls have equal interface energy σ.

The supersaturation $\Delta\mu_\infty$ can be expressed through the temperature T_{dep}, responsible for the direct deposition rate from the ambient phase W_{dep}, and through the enthalpy h of sublimation (*per atom*) as:

$$\Delta\mu_\infty = h\left(1 - \frac{T}{T_{\text{dep}}}\right) \tag{6}$$

The crystal/gas interface energy can be expressed using the Scapski-Turnbull equation (see [12, 13]) in the following way:

$$\sigma \approx a\frac{h}{d_{\text{o}}^2} \tag{7}$$

where a is a dimensionless constant [14], which varies in the limits $0.30 < a < 0.55$. Finally, the supersaturation becomes

$$\Delta\mu = h\left(1 - \frac{T}{T_{\text{dep}}}\right)\left[1 - a\frac{d_{\text{o}}}{R}\frac{\left(1 + \frac{r}{R}\right)}{\left(1 - \frac{T}{T_{\text{dep}}}\right)}\right] \tag{8}$$

In Eq. (2), the flux

$$W_\infty = W_{\text{dep}} + W_{\text{side}} \tag{9}$$

accounts for two processes. The first one, W_{dep}, accounts for the flow of atoms arriving from the ambient phase directly on the top. The second term, W_{side}, accounts for the diffusion flux of adatoms from the side surfaces. It depends on the diffusion coefficient D as well as on the gradient $\frac{dc}{dx}\big|_{x=l}$ of adatoms on the side surfaces of the nanotubes. The overall flux is proportional to the periphery $2\pi R$ of the whisker and is deposited on the peak area $\pi(R^2 - r^2)$, so that:

$$W_{\text{side}} = -\frac{2R}{R^2 - r^2}D\frac{dc}{dx}\bigg|_{x=l} \tag{10}$$

To determine the gradient $\frac{dc}{dx}\big|_{x=l}$, Dittmar and Neumann [8, 9] solve the balance equation, based on the second Fick law:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + W_{\text{dep}}\left(1 - \frac{c}{c_{\text{side}}}\right) \tag{11}$$

where c_{side} is determined by the adsorption/desorption equilibrium established on the side surface, in the middle of a large $l \to \infty$ nanotube, far from both the top and the substrate. The term $W_{\text{dep}}\left(1 - \frac{c}{c_{\text{side}}}\right)$ accounts for the local adsorption/desorption balance on the side surfaces. Near the top of the nanowhisker, the concentration c_l is kept constant, controlled by the incorporation to the peak. Under

stationary conditions, $\frac{\partial c}{\partial t} = 0$, Eq. (11) transforms to an ordinary second order differential equation

$$D\frac{\partial^2 c}{\partial x^2} + W_{\text{dep}}\left(1 - \frac{c}{c_{\text{side}}}\right) = 0 \qquad (12)$$

Solving the diffusion Eq. (12) under the boundary conditions: for $x = l$; $c = c_l$ and for $x < < l$; $c = c_{\text{side}}$ Dittmar and Neumann [8, 9] find

$$c - c_{\text{side}} = (c_l - c_{\text{side}})\frac{ch\left(\frac{x}{\lambda}\right)}{ch\left(\frac{l}{\lambda}\right)} \qquad (13)$$

where

$$\lambda = \sqrt{\frac{Dc_{\text{side}}}{W_{\text{dep}}}} \qquad (14)$$

is the average diffusion length of adatoms. The gradient of concentration is given by the derivative of Eq. (13)

$$\left.\frac{dc}{dx}\right|_{x=l} = \frac{(c_l - c_{\text{side}})}{\lambda} th\left(\frac{l}{\lambda}\right) \qquad (15)$$

Introducing Eqs. (14,15) into Eq. (10) for W_{side} is obtained:

$$W_{\text{side}} = W_{\text{dep}}\frac{2}{1 - \left(\frac{r}{R}\right)^2}\frac{\lambda}{R}\left(1 - \frac{c_l}{c_{\text{side}}}\right)th\left(\frac{l}{\lambda}\right) \qquad (16)$$

So, the net flux becomes

$$W = W_{\text{dep}}\frac{\Delta\mu}{k_B T}\left(1 + \frac{2}{1 - \left(\frac{r}{R}\right)^2}\frac{\lambda}{R}\left(1 - \frac{c_l}{c_{\text{side}}}\right)th\left(\frac{l}{\lambda}\right)\right) \qquad (17)$$

By means of Eq. (17) the growth rates becomes

$$U = U_\infty\left[1 - a\frac{d_o}{R}\frac{\left(1 + \frac{r}{R}\right)}{\left(1 - \frac{T}{T_{\text{dep}}}\right)}\right]\left[1 + 2\frac{\lambda}{R}\frac{\left(1 - \frac{c_l}{c_{\text{side}}}\right)}{1 - \left(\frac{r}{R}\right)^2}th\left(\frac{l}{\lambda}\right)\right] \qquad (18)$$

where

$$U_\infty = \omega_{\text{top}}d_o\frac{h}{k_B T}\left(1 - \frac{T}{T_{\text{dep}}}\right)W_{\text{dep}} \qquad (18a)$$

is the isotropic growth rate of large crystals.

At initial stages of growth, the length of the nanowhisker is small, $l < \lambda$, so that $th\left(\frac{l}{\lambda}\right) \approx \frac{l}{\lambda}$.

$$\frac{dl}{dt} \approx 2U_\infty\left[1 - a\frac{d_o}{R}\frac{\left(1 + \frac{r}{R}\right)}{\left(1 - \frac{T}{T_{\text{dep}}}\right)}\right]\frac{l}{R}\frac{\left(1 - \frac{c_l}{c_{\text{side}}}\right)}{1 - \left(\frac{r}{R}\right)^2} \qquad (19)$$

Here we take into account that $2l > > R$. With this approximation, under the initial condition, for $t = 0$, $l = l_{\text{in}} > > R$, the solution of Eq. (18) is leading to exponential growth law.

$$l = l_{\text{in}}\exp\left(\left[1 - a\frac{d_o}{R}\frac{\left(1 + \frac{r}{R}\right)}{\left(1 - \frac{T}{T_{\text{dep}}}\right)}\right]\frac{2G_\infty}{R}\frac{\left(1 - \frac{c_l}{c_{\text{side}}}\right)}{1 - \left(\frac{r}{R}\right)^2}t\right) \qquad (20)$$

For large nanotubes, $l > > \lambda$, $th\frac{l}{\lambda} \approx 1$ so that Eq. (18) transforms to

$$U = 2\frac{\lambda}{R}U_\infty\left[1 - a\frac{d_o}{R}\frac{\left(1 + \frac{r}{R}\right)}{\left(1 - \frac{T}{T_{\text{dep}}}\right)}\right]\frac{\left(1 - \frac{c_l}{c_{\text{side}}}\right)}{1 - \left(\frac{r}{R}\right)^2}, \qquad (21)$$

resulting to a linear dependence of the length l on time.

VLS grown nanowires

Figure 1B represents a nanowire growing according to the *VLS* mechanism. The main difference between Fig. 1B and A is that there is a liquid droplet on the top of the nanowire. The droplet plays a role of mediator, providing for the easy attachment of atoms (molecules) to the top of the whisker. In this case, the growth does not require the presence of screw dislocation (although it does not forbid it). As soon as the exchange of atoms (molecules) between the droplet and the whisker's top is faster, then the supply of new atoms, the expressions given above continue to be valid. Moreover, Eqs. (18–20) could be simplified, because, in the absence of screw dislocation, $r = 0$. Eqs. (18–20) are generalization of the model of Dittmar and Neumann (see [8, 9, 15]). Moreover, they are in agreement with the interpretations on *VLS* growth kinetics given in [16].

Discussion

Why whiskers start to grow so fast? At first site, the contact between the crystal and the substrate would provide continuous source of kink positions. Therefore, the crystal should start to grow laterally, unless these kinks are blocked. The same reason that hampers radial growth could prevent transitions of adatoms from the substrate on the side walls of the crystal. The possible contribution to the
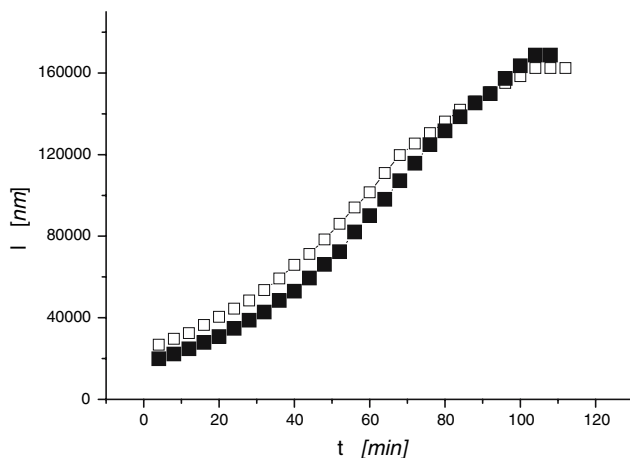
Fig. 2 The time t dependence [15] of the length l of two Rb whiskers grown by vapor deposition on Ag substrate. In both cases, the initial exponential growth transfers to linear growth. Although grown under the same conditions, the two whiskers (open points and black points) slightly differ in radius R
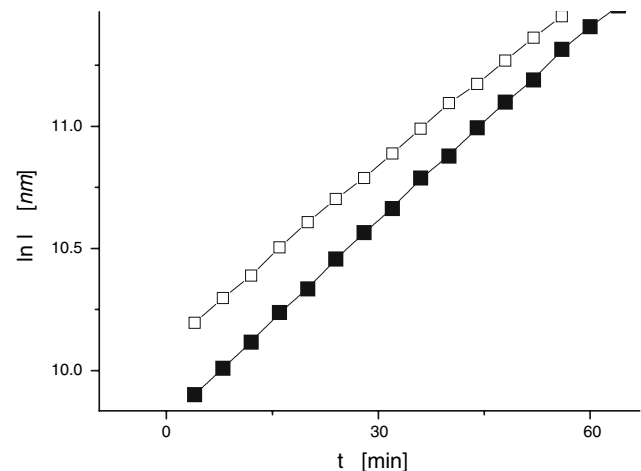

Fig. 3 Results on initial stages of growth from Fig.2 in semi logarithmic scale. The straight line dependencies are indications for exponential growth

growth rate of adatoms, arriving from the substrate, was discussed by Ruth and Hirth [17]. Their conclusions are that the initial stage of exponential growth should disappear if the substrate has important contribution to the adatoms flux. The result is logical: exponential growth appears because the area, that contributes for the adatoms flux, increases when the whisker elongates. However, further elongation has minor contribution to the flux, when the length l is becoming comparable to the average diffusion distance λ. If the flux from the substrate is important, the area that is a source of adatoms, should be sufficiently large from the very beginning. Figure 2 gives [15] the temporal dependence of the length l of two Rb whiskers grown on silver substrate from a gas phase. The initial stages of growth give perfect straight lines in semi-logarithmic plot (Fig. 3) as required by Eq. (19). This is an indication, that substrate plays minor role during the growth.

Many authors report that the thicker whiskers are the higher is the grow rate (see for instance [16]). The Givargizov–Chernov theory [1, 18] gives for the growth rate the expression $G = (A–B/R)^2$. An interesting experimental prove of the size effect was find in [19] for the growth in glassforming matrix. After growing very fast in one direction, the growth stops, due to changes in concentration, and turns into dissolution. Along the other directions (along which the size of the crystal is sufficiently large) the growth rate was initially lower, it also slows down but never becomes negative.

It is frequently found that thinner whiskers grow faster, an observation apparently contradicting the statement in the paragraph above. Still, both observations are in line with the present model. Due to the Thomson–Gibbs size effect the growth rate of extremely thin whiskers is

reduced. In this size range, growth rate increases with radius. The size effect is weakening fast with the R increase. On the other hand the ratio of periphery to area on the top of the whiskers requires the growth rate to be inverse proportional to R. Indeed, according to Eqs. (18–20), the growth rate against R dependence has a maximum. Figure 4 represents the experimental data from [20] on the length l against the radius R of $GaAs$ nanowhiskers grown by molecular beam epitaxy. The solid line is according to Eq. (20). with $r = 0$ and $d_o = 0.563$ [nm]. According to the data published in [20–23] the rate G_L of $GaAs$ nanowhiskers, grown by VLS mechanism at $T = 823$ K, increases
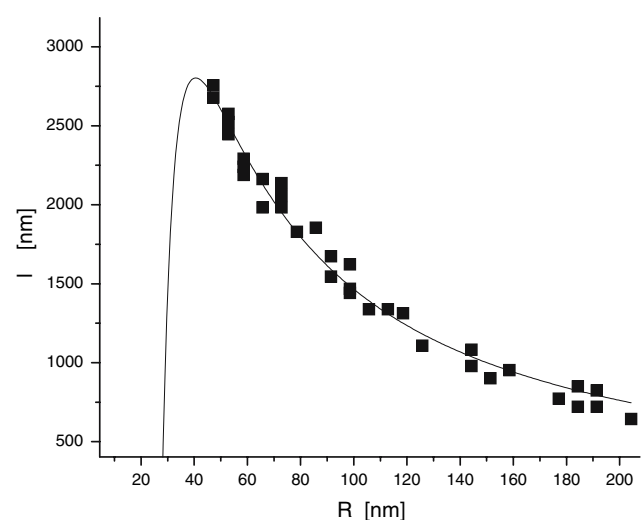

Fig. 4 Experimental data from [16] on the length l against the radius R of $GaAs$ nanowhiskers grown by molecular beam epitaxy. The solid line is according to Eq. (18). with $r = 0$, and $d_o = 0.563$ [nm]

when R varies in the range $15 < R < 55$ [nm], a result in agreement with the prediction given in Fig. 4.

The lateral growth (thickening) depends on the formation of new nucleus. This is most likely to happen when the concentration of adatoms is high. This is the case, for $l > \lambda$, on the side surfaces, far from the top of the nanowhisker. As soon as a new nucleus is formed the radius R increases with a jump. According to Eq. (20) this corresponds to a break of the slope of linear growth rate as observed experimentally for both nanowhiskers presented in Fig. 2.

Conclusions

The deformation stress energy in the core of screw dislocation is reason for the formation of hollow in nanotubes. The hollow is formed when the magnitude of the Burgers vector exceeds a critical value. Extremely short nanotubes grow exponentially with time. The mode of growth transforms to linear when the nanotube length l exceeds the average diffusion length of adatoms λ.

The linear growth rate increases when the radius decreases just as does the ratio of the periphery to the area of the top of the whisker. However, for extremely tiny nanowhiskers, the growth rate decreases with radius because of the Thomson–Gibbs effect.

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