Kinetics and mechanism of planar nanowire growth

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Surface-guided growth of planar nanowires offers the possibility to control their position, direction, length, and crystallographic orientation and to enable their large-scale integration into practical devices. However, understanding of and control over planar nanowire growth are still limited. Here, we study theoretically and experimentally the growth kinetics of surface-guided planar nanowires. We present a model that considers different kinetic pathways of material transport into the planar nanowires. Two limiting regimes are established by the Gibbs–Thomson effect for thinner nanowires and by surface diffusion for thicker nanowires. By fitting the experimental data for the length–diameter dependence to the kinetic model, we determine the power exponent, which represents the dimensionality of surface diffusion, and results to be different for planar vs. nonplanar nanowires. Excellent correlation between the model predictions and the data is obtained for surface-guided Au-catalyzed ZnSe and ZnS nanowires growing on both flat and faceted sapphire surfaces. These data are compared with those of nonplanar nanowire growth under similar conditions. The results indicate that, whereas nonplanar growth is usually dominated by surface diffusion of precursor adatoms over the nanowire walls, planar growth is dominated by surface diffusion over the substrate. This mechanism of planar nanowire growth can be extended to a broad range of material–substrate combinations for higher control toward large-scale integration into practical devices.

nanowires | Gibbs–Thompson | surface diffusion | guided growth

Semiconductor nanowires (NWs) have been extensively studied as promising building blocks for next generation optoelectronics (1, 2), logic circuits (3, 4), quantum computing (5, 6), and other potential applications in nanoscience and nanotechnology (7). Assembling the NWs into ordered arrays, however, remains a challenging step toward device fabrication. One promising pathway to overcome this technological barrier is the surface-guided growth of planar (also referred as “horizontal,” “in-plane,” or “lateral”) NWs. This approach uses the epitaxial and graphoepitaxial relations between the material and the substrate surface to guide and align the NWs as they grow (8, 9). Integration processing of the surface-guided planar NW structures becomes much easier with respect to that of nonplanar ones, which requires harvesting, dispersion, and postgrowth assembly into planar arrays. Despite the technological potential of planar NW growth, the growth kinetics and structural characteristics of planar NWs are much less known than those of the more usual nonplanar NWs. Understanding the kinetics and mechanism of planar NWs growth would significantly contribute to their controlled assembly into ordered arrays and integration into practical devices.

One of the most common methods for the growth of NWs is the vapor–liquid–solid (VLS) process introduced in 1964 by Wagner and Ellis for Au-catalyzed Si NWs that grow vertically on Si(111) substrates (10). In the VLS growth, a metal catalyst forms a liquid alloy droplet with a semiconductor material and promotes 1-dimensional growth under the droplet. A significant contribution to the fundamental understanding of the NW growth mechanisms was made in the 1970s by Givargizov (11), in particular by showing the importance of the Gibbs–Thomson (GT) effect for Si NWs. Givargizov (11) showed that whiskers

with smaller diameters grow more slowly because the supersaturation of semiconductor material in them decreases. This effect originates from the surface curvature, originally thought to be the surface of the cylindrical NW (11). Later, however, it was shown that deposition should originate from the liquid droplets catalyzing the VLS growth, the chemical potential of which increases with respect to planar surface (ref. 12 has a detailed discussion and the relevance of the GT effect for Si, Ge, and different III to V NWs). Therefore, surface energy of the liquid droplet is the one that should be used in modeling, with the geometrical coefficient corresponding to its spherical cap shape (13). Overall, material incorporation into smaller droplets becomes more difficult due to enhanced desorption from their surface. As a result of the GT effect, the growth rate of thinner NWs is reduced and becomes 0 below a minimum diameter (11, 13).

One attractive approach to integrate NWs into circuits and other planar devices is the guided growth of planar NWs. Within this approach introduced in the first paragraph, the NW growth is directed by the substrate surface by 3 main modes (9, 14): epitaxy, graphoepitaxy, and artificial epitaxy. In the epitaxial growth mode, the NWs grow along a specific crystallographic direction dictated by the epitaxial relations between the NW material and the substrate, which is usually a flat single crystal. In the graphoepitaxial growth mode, the NWs grow on a faceted substrate surface, usually along nanoscale features, such as steps or grooves. In the artificial epitaxy mode, the NWs grow along artificially created guides, such as trenches and ridges that are lithographically patterned on an amorphous substrate (9, 14). Compared with other NW assembly approaches, guided growth eliminates the

Significance

Surface-guided growth of planar nanowires is an attractive way of creating aligned arrays of nanowires to enable their large-scale integration into practical devices, but the kinetics and mechanism of planar vs. regular nonplanar growth are poorly controlled and understood. We present kinetic data for planar nanowire growth supported by a theoretical model. Planar vs. nonplanar nanowire growth rates show different power dependence on nanowire diameter attributed to the dimensionality of precursor material diffusion. Whereas the regular nonplanar growth is dominated by surface diffusion over the nanowire sidewalls, planar growth is found to be dominated by surface diffusion over the substrate. This knowledge enables much higher control over the diameter and length distribution of surface-guided nanowires in different material systems.

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requirement of postgrowth assembly processes (15–18) and enables control over the NW position, direction, crystallographic orientation, and length. Guided horizontal NWs were first demonstrated by Nikoobakht et al. (8) and Li and coworkers (19) for ZnO on A-plane sapphire and for GaAs on GaAs, respectively. Following these pioneering works on surface-guided growth of NWs, Joselevich and coworkers (9) generalized this approach from epitaxial to graphoepitaxial growth, including millimeter-long GaN NWs with controlled orientations on different planes of sapphire. Such controlled guided growth of planar NWs was then extended beyond GaN (9, 20, 21) to other semiconductor materials, such as ZnO (4, 22), ZnSe (23), ZnTe (24), CdSe (25), CdS (26), and ZnS (27). Core-shell NW and nanowall heterostructures were also demonstrated and integrated into efficient photodetectors and photovoltaic cells (28, 29). Guided and nonguided planar growth of Si NWs has also been reported (30, 31). Surface-guided growth by non-VLS mechanisms has also gained ground in recent years: for instance, using soft semiconductor materials, like CsPbBr₃ perovskite (32–35), and selective area growth of NW networks on patterned single-crystal substrates (36, 37). Despite the successful VLS growth of surface-guided NWs, device fabrication is still challenging because the planar NWs have different lengths. The broad lengths distribution constitutes a morphological obstacle when trying to make an optimal array with required performance. Control over the lengths of the guided NWs could overcome this challenge, greatly facilitating their integration into devices. Yet, extensive research on surface-guided NWs is mainly focused on synthesis, characterizations, and fabrication of devices, while controlling these relationships is still unresolved. In order to control the guided growth of planar NWs, understanding the guided growth mechanism is mandatory.

Over the last 15 years, the VLS growth mechanism has been studied in great detail for nonplanar NWs of elemental and III to V compound semiconductors, including the transport-limited growth models (38–42). However, there have been relatively few attempts to adapt these models to planar NWs (43). Based on a revised GT equation, Zi et al. (44) presented a thermodynamic model for planar growth of InAs NWs, which predicted the conditions to promote nonplanar or planar NW growth depending on the partial pressures of the group III and V precursors. Although the preferred NW orientations were described for different growth conditions, a relationship between the dimensions of the planar NWs and their growth rate was not elaborated. Shen et al. (45) also described the growth kinetics of planar InSnO NWs by a modified version of the GT equation. Assuming negligible surface diffusion, the results confirmed the presence of the GT effect and revealed the impact of doping and the substrate surface orientation on the NW morphology. However, the kinetic data for different substrate orientations could not be fitted to a single quadratic function as in the Givargizov theory (11, 12, 46), suggesting that the growth kinetics is different on different substrates and may be influenced by the growth mechanism.

A nontrivial interplay between the GT effect and surface diffusion from the NW sidewalls and/or the substrate surface is well known for nonplanar VLS Si and III to V semiconductor NWs (47–54). The first one suppresses and the second enhances the axial growth rate of thinner NWs, which is why the resulting length–radius [$L(R)$] dependence starts from the minimum radius, increases for smaller radii, reaches a maximum at a certain radius, and decreases for larger radii (48, 49, 51). In the diffusion-induced mode, the typical radius dependence of the NW growth rate or the resulting length after a given growth time is inversely proportional to R or R^2 depending on the mechanism of diffusion transport as described by Dubrovskii and coworkers (39, 48, 49, 51). Zhang et al. (54) used these findings for correlating the axial growth rates to the radius of planar and nonplanar GaAs NWs. The

results showed negligible diffusion for those particular growth conditions. It seems, however, that surface diffusion from the substrate toward the sidewalls of planar NWs laying on the substrate should generally have a strong impact on the growth rate and morphology as we will demonstrate in this work.

Here, we report the kinetics of planar NW growth supported by a theoretical model. The model includes the GT effect, the direct impingement and subsequent diffusion of the growth species along the NW sidewalls to the tip, and the material collection from the substrate surface. These kinetic pathways are compared with the case of nonplanar NWs, with the main difference manifesting in the power law dependence of the diffusion flux on the NW radius, which represents the effective dimensionality of the surface diffusion. We present kinetic data for planar Au-catalyzed ZnSe and ZnS NWs grown on flat and faceted sapphire surfaces at different growth temperatures. The results clearly reveal a nonmonotonic dependence of the growth rate on the NW radius, which is qualitatively similar to that observed for nonplanar NWs (49, 50, 52, 53) but quantitatively different in terms of the power exponent of the radius dependence, representing the dimensionality surface diffusion. The results, which are well fitted to the model growth equation in all cases, indicate that planar growth is dominated by surface diffusion over the substrate, whereas nonplanar growth is dominated by surface diffusion over the NW sidewalls. These results also show the importance of the GT vs. surface diffusion effects in surface-guided growth of planar NWs and enable precise control over their length, width, and size homogeneity by rationally tuning the catalyst size and growth parameters.

Model

Kinetics of the VLS growth of nonplanar vs. planar NWs is illustrated in Fig. 1. For planar (horizontal) growth, the NW shape is assumed 1/2 of a cylinder with a time-independent radius R , resting on a substrate and growing in the y direction. The droplet guiding its planar growth in a given direction is assumed 1/4 of a sphere of the same radius R . The vapor flux of the element that limits the growth (Zn in our case) is denoted I (nanometers^{−2} second^{−1}). Adatoms of this element are able to diffuse on the substrate surface and along the NW sidewalls. In this case, there are 4 possible contributions into the overall growth rate in the horizontal direction, dL/dt (similarly to refs. 38–42 and 47–52), for nonplanar NWs:

Fig. 1. Schematic representations of the diffusion-induced growth mechanism for (A) nonplanar and (B) planar NW. Nonplanar growth is driven by 1) adsorption–desorption at the droplet surface and diffusion fluxes of adatoms from 2) the NW sidewalls and 3) the substrate surface. Planar growth is driven by 1) adsorption–desorption at the droplet surface, 2) direct diffusion of surface adatoms to the droplet, 3) diffusion of surface adatoms to the NW sidewalls and then to the droplet, and 4) direct impingement of atoms onto the NW sidewalls with subsequent diffusion to the droplet. The x , y , and r in B denote the direction perpendicular to the NW axis, the NW growth direction, and the 2D radius vector in the substrate plane, respectively.

- 1) Direct impingement of atoms onto and their desorption from the droplet surface;
- 2) Diffusion of adatoms from the substrate surface to the droplet;
- 3) Diffusion of adatoms from the substrate surface to the NW sidewalls and then, to the droplet; and
- 4) Direct impingement of atoms onto the NW sidewalls and then, to the droplet.

Clearly, processes 2 to 4 are different for planar NW with respect to nonplanar NW, and hence, the models for nonplanar VLS growth (48–51) should be modified accordingly.

The NW growth rate in this geometry can be written as

$$\frac{dL}{dt} = 2\Omega \left(I - \frac{n_l}{\tau_l} + \frac{j_{diff}^s}{\pi R^2} + \frac{j_{diff}^f}{\pi R^2} \right), \quad [1]$$

where Ω is the elementary volume per pair in solid, n_l/τ_l is the desorption flux from the droplet with the characteristic lifetime in liquid τ_l , and the 2 diffusion currents j_{diff}^s (seconds⁻¹) originating from the surface (labeled “s”) and sidewall or side facet adatoms (labeled “f”) coming to the droplet.

The 2-dimensional (2D) growth picture shown in Fig. 1B cannot be resolved analytically in the general case and requires numerical analysis. We can, however, simplify it by roughly dividing the total diffusion flux into the 2 one-dimensional fluxes of different origin, one coming from the top half-plane directly to the droplet along the radius vector r and the other going first along the x axis perpendicular to the growth direction y and then along y to the droplet. Then, the 2 diffusion fluxes j_{diff}^s and j_{diff}^f entering Eq. 1 can be obtained in the closed analytical form. This requires long calculations based on the stationary diffusion equations for different adatom populations connected with each other by the boundary conditions. The calculation scheme seems quite different from that used for nonplanar NWs (49–51). The details of the calculation are given in *SI Appendix, Details of the Growth Model*.

To account for the GT effect, the n_l in Eq. 1 should be written in the form (51)

$$n_l = n_l^\infty \exp\left(\frac{R_{GT}}{R}\right), \quad [2]$$

describing the elevation of chemical potential (or activity) in the droplet of radius R with respect to its value n_l^∞ at $R \rightarrow \infty$. The $R_{GT} = 2\Omega\gamma/(k_B T)$ is the characteristic GT radius, which is proportional to the droplet surface energy γ , with T as the absolute temperature and k_B as the Boltzmann constant (51).

Collecting all of the contributions in Eq. 1 and using Eq. 2, the final result for the growth rate of surface-guided planar NW at a time-independent radius R is obtained in the form

$$\frac{dL}{dt} = 2\Omega I \left\{ 1 - \frac{n_l^\infty}{I\tau_l} e^{R_{GT}/R} + \left(1 - \frac{n_l^\infty}{I\tau_s} e^{R_{GT}/R} \right) \left[\frac{\lambda_s}{R} \frac{K_1(R/\lambda_s)}{K_0(R/\lambda_s)} + \frac{\lambda_f}{R} \sqrt{1 + \frac{2\lambda_s}{\pi R}} \text{cth}\left(\frac{L}{\Lambda}\right) \right] \right\}. \quad [3]$$

The first term in the curly bracket stands for the adsorption-desorption processes at the droplet surface, with the desorption rate being enhanced for thinner NWs due to the GT effect. The second GT term directs the diffusion flux of surface adatoms either toward or away from the catalyst droplet, with $I\tau_s$ as the surface concentration of adatoms and τ_s as their characteristic lifetime on the substrate surface. The first diffusion-induced contribution to the NW growth rate in the brackets stands for the flux of surface adatoms directly

entering the droplet, with $\lambda_s = \sqrt{D_s \tau_s}$ as the adatom diffusion length and D_s as the diffusion coefficient on the substrate surface. The $K_m(\xi)$ denotes the modified Bessel function of the second type of the order m in standard notations. The second bracket term describes the diffusion flux entering the droplet from the NW side facets, including the populations directly impinging the facets or diffusing to the facets from the substrate surface. The $\lambda_f = \sqrt{D_f \tau_f} \cong \sqrt{D_f \tau_s}$ is the effective adatom diffusion length on the NW side facets, with D_f as the diffusion coefficient and τ_f as the characteristic lifetime on the side facets assumed close to τ_s (*SI Appendix, Details of the Growth Model*). The Λ originates from a competition between the 2 populations of adatoms brought to the NW side facets either directly from the vapor or from the substrate surface and is given by

$$\Lambda = \frac{\lambda_f}{\sqrt{1 + 2\lambda_s/(\pi R)}}. \quad [4]$$

Compared with the general growth equation for nonplanar VLS NWs (49–51), this equation 1) contains the surface diffusion term described by the K_1/K_0 factor in Eq. 3, which does not vanish for long NWs because this diffusion flux enters the droplet directly catalyzing the VLS growth of planar NWs, and 2) presents the radius-dependent $\sqrt{1 + 2\lambda_s/(\pi R)}$ modification of the sidewall diffusion flux and the effective diffusion length Λ due to planar geometry. Analysis of Eq. 3 leads to the following conclusions.

1) The GT effect leads to suppression of the VLS growth of thin NWs because the vapor flux to the droplet is positive only for the droplet radii greater than $R_{l,min} = R_{GT}/\ln(I\tau_l/n_l^\infty)$ and the adatom diffusion flux is positive for radii greater than $R_{s,min} = R_{GT}/\ln(I\tau_s/n_l^\infty)$.

2) Time dependence of the NW length is generally nonlinear due to the presence of $\text{cth}(L/\Lambda)$ in the right-hand side of Eq. 3. To find explicitly the NW length vs. time, we put Eq. 3 in the form

$$\frac{dt}{\tau} = \frac{dz}{a + b \text{cth}(z)}, \quad [5]$$

with $z = L/\Lambda$ as the dimensionless length, and other parameters are given by

$$\begin{aligned} \tau &= \frac{\Lambda}{2\Omega I}, \\ a &= 1 - \frac{n_l^\infty}{I\tau_l} e^{R_{GT}/R} + \left(1 - \frac{n_l^\infty}{I\tau_s} e^{R_{GT}/R} \right) \frac{\lambda_s}{R} \frac{K_1(R/\lambda_s)}{K_0(R/\lambda_s)}, \\ b &= \left(1 - \frac{n_l^\infty}{I\tau_s} e^{R_{GT}/R} \right) \frac{\lambda_f}{R} \sqrt{1 + \frac{2\lambda_s}{\pi R}}. \end{aligned} \quad [6]$$

Integrating Eq. 5 with initial condition $L(t=t_0)=0$, where t_0 is the incubation time for growth of a given NW, we obtain the length-time dependence in the form

$$\frac{t-t_0}{\tau} = \frac{az - b \ln[(a/b) \sinh(z) + \cosh(z)]}{a^2 - b^2}. \quad [7]$$

This is of course reduced to $L = 2\Omega I(a+b)(t-t_0)$ or the time-independent growth rate $dL/dt = 2\Omega I(a+b)$ at $L/\Lambda \gg 1$.

3) For small diffusion lengths on the substrate surface, $\lambda_s/R \ll 1$, we have $K_1(R/\lambda_s)/K_0(R/\lambda_s) \cong 1$ and $\sqrt{1 + 2\lambda_s/(\pi R)} \cong 1$. In this case, the diffusion-induced terms in Eq. 3 are reduced to the

classical $1/R$ radius correlation (38), and the asymptotic NW growth rate at $L/\lambda_f \gg 1$ takes the form

$$\frac{dL}{dt} = 2\Omega I \left\{ 1 - \frac{n_l^\infty}{I\tau_l} e^{R_{GT}/R} + \left(1 - \frac{n_s^\infty}{I\tau_s} e^{R_{GT}/R} \right) \left(\frac{\lambda_s + \lambda_f}{R} \right) \right\}. \quad [8]$$

In this case, due to $\lambda_s/R \ll 1$, a significant increase of dL/dt with respect to the “nominal” growth rate $2\Omega I$ (given by the vapor flux) can be explained only by a high diffusivity of sidewall adatoms such that $\lambda_f \gg \lambda_s$.

4) In the opposite case of large diffusion lengths on the substrate surface, $\lambda_s/R \gg 1$, we have $K_1(R/\lambda_s)/K_0(R/\lambda_s) \cong \lambda_s/[R \ln(\lambda_s/R)]$, $\sqrt{1 + 2\lambda_s/(\pi R)} \cong \sqrt{2\lambda_s/(\pi R)}$, and hence, the asymptotic growth rate is given by

$$\begin{aligned} \frac{dL}{dt} = 2\Omega I \left\{ 1 - \frac{n_l^\infty}{I\tau_l} e^{R_{GT}/R} + \left(1 - \frac{n_s^\infty}{I\tau_s} e^{R_{GT}/R} \right) \left[\left(\frac{\lambda_s}{R} \right)^2 \frac{1}{\ln(\lambda_s/R)} \right. \right. \\ \left. \left. + \left(\frac{2\lambda_s}{\pi} \right)^{1/2} \frac{\lambda_f}{R^{3/2}} \right] \right\}. \quad [9] \end{aligned}$$

Both diffusion-induced contributions are much larger than unity, and the growth rate should be much higher than nominal. The radius dependence of a decreasing part of dL/dt contains the $1/R^2$ dependence with weak logarithmic correction and the unusual $1/R^{3/2}$ correlation, which has never been observed in nonplanar NWs. The effective diffusion length Λ is much smaller than λ_f according to Eq. 4 at $\lambda_s/R \gg 1$, which is why the asymptotic regime given by Eq. 9 is reached at shorter NW lengths and may apply almost from the very beginning of growth.

As a result of this analysis, the length-independent NW growth rate can be approximated by the simplified expression

$$\frac{dL}{dt} = 2\Omega I \left\{ 1 - \theta_{lv} e^{R_{GT}/R} + \left(1 - \theta_{ls} e^{R_{GT}/R} \right) \left(\frac{\lambda}{R} \right)^m \right\}. \quad [10]$$

Here, $\theta_{lv} = n_l^\infty/(I\tau_l)$ and $\theta_{ls} = n_s^\infty/(I\tau_s)$ are the ratios of liquid to vapor and surface to vapor activities, respectively (51). This formula applies in the case where 1 of the 3 possible diffusion mechanisms is dominant, corresponding to the power exponents $m = 1, 1.5$, or 2 . The power value m represents the dimensionality of the dominant diffusion pathway and is an important parameter to investigate the effect of the surface on the kinetics of the guided NWs as will be shown in the experimental results and discussion. The λ denotes the effective diffusion length of the adatom population with the highest diffusivity under a given set of the growth conditions. Without any surface diffusion ($\lambda \rightarrow 0$), Eq. 10 is reduced to increasing length–radius dependence, starting from 0 at a certain minimum radius as in refs. 11, 13, 44, 46, and 54. For thick NWs with $R_{GT}/R \ll 1$, Eq. 10 gives the inverse radius dependence of the NW length as in refs. 12 and 16. When both GT and surface diffusion effects are present, Eq. 10 gives a nonmonotonic length–radius correlation with a maximum as in refs. 51 and 52. According to Eq. 8, the $1/R$ radius dependence of the NW growth rate (with $m = 1$) is expected when the main diffusion-induced contribution originates from the atoms that impinge directly onto the NW sidewalls from vapor, while the collection of adatoms from the substrate surface is negligible due to their low diffusivity. According to Eq. 9, the $1/R^2$ or $1/R^{3/2}$ radius correlations are expected when the adatoms are mainly collected from the substrate, with $m = 3/2$ corresponding to thicker NWs or $\lambda_f \gg \lambda_s$ and $m = 2$ corresponding to thinner NWs or $\lambda_f \ll \lambda_s$. Measuring the NW growth rate (or length) vs. the radius allows one to analyze the dominant growth mechanism. Eq. 10 can be applied to both nonplanar and planar NWs; however, the power exponents m and other parameters are expected to be different.

Results and Discussion

The growth and analysis of Au-catalyzed ZnSe and ZnS surface-guided NWs were first focused on the NWs grown on flat C-plane sapphire substrates via the chemical vapor deposition (CVD) method using 3-zone furnace (*Materials and Methods*). The Au catalyst was patterned as straight stripes or squared islands by standard lithography including evaporation of a 0.5-nm-thick Au layer and liftoff. Prior to growth, these thin Au films thermally dewet and convert into Au nanoparticles, which serve as the catalyst seeds for the VLS growth. Hence, the catalyst seeds are aligned but randomly dispersed along the pattern edges and randomly size distributed (*Materials and Methods* has details). ZnSe NWs were grown without and with Zn pretreatment of the Au catalyst film at a fixed precursor temperature of 910 °C. These NWs grew along 6 isoperiodic $m < 10\bar{1}0 >$ directions of the sapphire substrate and had the zincblende crystal structure with an axial growth direction of $[11\bar{2}]$ as shown in Fig. 2 A and C. Our previous work (28) provides comprehensive details about the crystal phases, epitaxial relations, and crystallographic orientations for similar ZnSe NWs grown under the exact same conditions. ZnS NWs were grown at 3 different precursor source temperatures—970 °C, 980 °C, and 990 °C. These NWs grew along the same 6 isoperiodic $m < 10\bar{1}0 >$ directions of the sapphire but had the wurtzite crystal structure with an axial growth direction of $m [\bar{1}100]$ as shown in Fig. 3 A–C. Also here, previous study (27) presents full details about the crystal phases, epitaxial relations, and crystallographic orientations for ZnS NWs grown under the exact same conditions. ZnS NWs were also grown on faceted annealed M-plane and miscut C-plane sapphire substrates, presenting graphoeptitaxial growth along the nanogrooves and nanosteps (*SI Appendix, Figs. S2 and S3*). Morphological characterization was performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM) (*Materials and Methods*). At least 50 NWs were randomly selected in each sample for analysis. As a first approximation, the axial growth rates were calculated by dividing the measured length of each NW by the growth time. This is justified for relatively short diffusion lengths but will require some correction as will be discussed shortly. The NW radii were measured directly using AFM (on flat surfaces) or SEM (on faceted surfaces), and correlated to their measured growth rates. These data are shown in Fig. 2 E and F for ZnSe and Fig. 3 D for ZnS NWs.

We first discuss the data presented in Fig. 2E for ZnSe NWs grown without Zn pretreatment of the Au catalysts. These data show a large dispersion and do not show a clear correlation of the NW growth rate with the radius apart from a general trend of decrease for larger R . The large variance of the NW lengths can in principle be attributed to different factors, including 1) variation of the incubation time before the NWs nucleate, 2) variation of the growth termination time of different NWs caused by the spatial inhomogeneity of the vapor flux, and 3) inherent stochasticity of the growth process. Effect 1 has been recognized as a major source of the broad length distribution (53) and may be expected to be the main reason for the data randomness also in our case. Possible causes for the variation in the incubation time from NW to NW can be a delay in dissolving the precursor atoms in the Au droplet or delay before the NW starts to nucleate (47, 55, 56). Previous kinetic studies attempted to overcome this difficulty by considering only the average growth rate for each radius (49, 53) or only the envelope of the upper points (53), assuming that it represents the longest growth rates (or maximum lengths) of NWs that have emerged earlier than the others. However, studying the NW growth kinetics in the case of synchronized nucleation is always much clearer and truer (48). We, therefore, tried to reduce the incubation time and to synchronize nucleation of ZnSe NWs. Previously, Orrù et al. (57) suggested a pretreatment of the original Au catalyst film to ensure uniform saturation of the Au

Fig. 2. SEM images and kinetic data on surface-guided ZnSe NWs grown on flat sapphire substrates at a ZnSe precursor source temperature of 910 °C. Growth of ZnSe NWs (A and B) with and (C and D) without Zn pretreatment of the Au film. (E) Growth rate vs. radius of ZnSe NWs without (orange dots) and with (black dots) Zn pretreatment of the Au catalyst. (F) Data (dots) and fit by Eq. 10 (line) of the growth rate vs. radius for NWs grown with Zn pretreatment.

droplets for growing ZnTe NWs. We adopted a similar approach in which the Au catalyst film was exposed to Zn vapor before the NW growth (*Materials and Methods*).

Fig. 2 A–D shows no significant difference in the morphology of individual NWs growth with or without Zn pretreatment. However, the statistical properties of the length distribution change drastically as seen from Fig. 2E. This is quantitatively expressed by the R^2 coefficient of determination values for fitting to the model equation, which is $R^2 = 0.419$ without pretreatment and $R^2 = 0.955$ with pretreatment. Clearly, the pretreated sample shows a much narrower length distribution with a clear length–radius correlation (Fig. 2F). The measured NW growth rate does not start from 0, meaning that the initial droplets are larger than the minimum size originating from the GT effect. However, there is a clear trend for increasing the growth rate for the thinnest NWs measured, reaching the maximum growth rate at a certain optimal radius followed by the long decreasing right tail. The kinetic parameters are obtained by fitting the data to Eq. 10. The best fit for surface-guided ZnSe NWs on C-plane sapphire gives $\Omega I = 1.95 \mu\text{m/min}$, $R_{GT} = 7.70 \pm 0.48 \text{ nm}$, $\lambda = 32.94 \pm 2.73 \text{ nm}$, and $m = 1.53 \pm 0.17$. The entire sets of fitting parameters for each experiment are summarized in Table 1. Interestingly, the fitting value m is very close to 1.5, which is specific for planar growth. As follows from our theoretical analysis, the case of $m = 1.5$ corresponds to the diffusion regime in which Zn adatoms are collected from the substrate surface and then quickly transferred to the catalyst droplet (at $\lambda_f \gg \lambda_s$). The fitted values of the diffusion lengths for all of the samples (32 to 91 nm) are 2 orders

of magnitude lower than the distance between the NWs (0.4 to 2 μm). This suggests that the area around the NW from where the adatoms are collected and diffuse to the NW sidewall or catalyst droplet is relatively short, and hence, the growth kinetics should not be significantly affected by the NW spacing.

The maximum NW growth rate of $\sim 1.4 \mu\text{m/min}$ is obtained for 20-nm-radius NWs.

Zn pretreatment of the Au film was also explored to reduce the length distributions of ZnS NWs, although it did not work as impressively as with ZnSe NWs. The lower points corresponding to short lengths did disappear, but the length dispersions remained quite large (*SI Appendix, Fig. S4*). Therefore, only the envelope points of the length–radius curves were considered, representing the maximum length for a given radius. These data and the corresponding fits are shown in Fig. 3D for 3 different ZnS source temperatures in the range from 970 °C to 990 °C. The maximum NW growth rate increases from ~ 2 to $\sim 5 \mu\text{m/min}$ with rising of the source temperature. The optimal radius corresponding to these maximum growth rates remains around 20 nm in all cases. The fitting values of the diffusion length of Zn increase from $\sim 38 \text{ nm}$ at 970 °C to 91 nm at 990 °C. In principle, raising the source temperature while keeping the substrate temperature unchanged should only increase the precursor concentration in the reactor but not the diffusion length of adatoms on it. One reason for the change in the diffusion length on increasing the source temperature could be that, due to insufficient thermal isolation between the 2 zones of the furnace, the substrate temperature is also slightly increased, thus leading to an increase in the

Fig. 3. SEM images of ZnS NWs grown at different ZnS precursor source temperatures of (A) 970 °C, (B) 980 °C, and (C) 990 °C. D shows the measured NWs growth rates vs. radius (symbols) for different ZnS source temperatures along with their fits by Eq. 10 (lines), with the parameters summarized in Table 1.

surface diffusion coefficient and in the diffusion length. Due to the exponential dependence of the diffusion length with temperature, even a small change in the latter could lead to a significant change in the former. The GT radii remain almost the same, around 8 to 9 nm, which seems plausible because this parameter is determined by the surface energy of the droplet during growth.

The power exponents m are found to be 1.89 ± 0.21 , 1.79 ± 0.16 , and 1.83 ± 0.08 at 970 °C, 980 °C, and 990 °C, respectively. These very close values correspond to Eq. 10 with m between 1.5 and 2, which is specific for planar VLS growth. Unlike the case of ZnSe NWs, where m equals 1.5, growth of ZnS NWs proceeds in an intermediate regime where the main diffusion path is the adatom collection from the substrate, but the λ_f and λ_s values are similar. This is more precisely described by Eq. 9, where both diffusion terms are on the same order. Overall, both ZnSe and ZnS planar NWs exhibit qualitatively similar dependences of the growth rates on the NW radius influenced by the GT and surface diffusion effects. The power exponents of the diffusion-induced growth rate are in the range from 1.5 to ~ 1.8 . Such values are never observed in nonplanar geometry (39–41, 48, 49, 51, 52) and are related to the specific features of material collection from the substrate surface during planar growth of NWs.

After finding the special kinetic characteristics of epitaxially guided growth on flat surfaces, we characterized the kinetics parameters of graphoepitaxial growth along nanogrooves and nanosteps of 2 different types of periodically faceted surfaces: annealed miscut C-plane and annealed M-plane sapphire, respectively (9). Whether the kinetics of planar growth on flat and

faceted surfaces are similar is not a trivial question because a priori, the surface topography and anisotropy could affect the motion of adatoms in a way that affects the dimensionality of surface diffusion. The kinetic data for these experiments are shown in *SI Appendix, Figs. S2 and S3* and summarized in Table 1. The best-fitting values of the power exponent m for annealed M-plane and miscut C-plane sapphire are $m = 1.75$ and $m = 1.88$, respectively, which are both very close to the previously obtained values between 1.79 and 1.89 on flat surfaces. We can thus conclude that the collection mechanisms of the surface Zn adatoms are similar for flat and faceted surfaces, regardless of the different topography.

In order to test the validity of the kinetic model for planar growth of NWs, we also collected the kinetic data for nonplanar NWs for comparison. Data for nonplanar growth of ZnS NWs on flat R-plane sapphire surface are shown in Fig. 4 and compared with the surface-guided planar growth on annealed M-plane sapphire surface at the same source temperature of 980 °C along with the corresponding fits to Eq. 10. The best-fitting parameters for these samples are given in Table 1. The obtained diffusion lengths appear close in both cases (60.44 nm for the planar growth on the faceted surface and 47.31 nm for nonplanar NWs). Furthermore, the diffusion length for surface-guided NWs on faceted surface appears almost identical to the one obtained earlier for planar NWs on the flat surface at 980 °C (65.10 nm). The characteristic GT radius for nonplanar ZnS NWs appears noticeably larger than for the planar ones (22.90 against 9.71 nm), which should be related to a different droplet

Table 1. Parameters of different samples with ZnSe and ZnS NWs

NWs	Sapphire substrate	Source temperature, °C	Fitting parameters						
			Ωl , μm/min	θ_{IV}	θ_{IS}	R_{GT} , nm	λ , nm	m	
ZnSe	C plane	910	1.95 ± 0.02	0.89 ± 0.05	0.38 ± 0.03	7.70 ± 0.48	32.94 ± 2.73	1.53 ± 0.17	
ZnS	C plane	970	2.24 ± 0.48	1.00 ± 0.06	0.43 ± 0.02	7.99 ± 0.42	37.89 ± 0.75	1.89 ± 0.21	
ZnS	C plane	980	1.06 ± 0.35	1.00 ± 0.24	0.41 ± 0.02	8.99 ± 0.51	65.10 ± 0.72	1.79 ± 0.16	
ZnS	C plane	990	1.67 ± 0.12	0.32 ± 0.05	0.53 ± 0.04	8.32 ± 0.14	91.44 ± 0.54	1.83 ± 0.08	
ZnS	Annealed M plane	980	0.91 ± 0.22	0.95 ± 0.04	0.49 ± 0.01	9.71 ± 0.51	60.44 ± 0.74	1.75 ± 0.12	
ZnS	Annealed miscut C plane	980	0.95 ± 0.14	0.13 ± 0.01	0.29 ± 0.03	8.93 ± 0.13	45.99 ± 1.40	1.88 ± 0.10	
ZnS (nonplanar)	R plane	980	1.65 ± 0.24	0.99 ± 0.03	0.04 ± 0.04	22.90 ± 0.68	47.31 ± 1.05	1.16 ± 0.03

Fig. 4. Kinetic data for planar vs. nonplanar ZnS NWs grown at a source temperature of 980 °C on faceted M-plane and flat R-plane sapphire surfaces, respectively. Schematic representation of (A) planar and (B) nonplanar growth. SEM images of (C) planar and (D) nonplanar ZnS NWs. Envelope data (symbols) for the growth rate vs. radius for (E) planar and (F) nonplanar NWs. The lines show the fits obtained from Eq. 10, with the best-fitting values of $m = 1.75$ for planar and 1.16 for nonplanar NWs, $m = 1$ and 2 .

composition and shape in nonplanar growth. Therefore, planar ZnS NWs can be grown much thinner, with a minimum radius of about 10 nm, while all nonplanar NWs are thicker than 20 nm.

Most importantly, the dimensionality of surface diffusion that is determined by applying the model to the kinetic data for nonplanar NWs is $m = 1.16$, which is very different from the m values obtained for planar NW growth. Furthermore, Fig. 4F shows that the growth rate of nonplanar NWs can be well fitted with $m = 1$, corresponding to the adatom collection from the upper part of the NW sidewalls. This is the most usual case in the VLS growth of nonplanar Si (41) III to V (39, 40, 48, 58) and III to N (59) NWs. The graphs in Fig. 4E and F clearly demonstrate the different growth kinetics of planar and nonplanar ZnS NWs. In particular, the data for planar NWs can be reasonably fitted with $m = 2$ but not with $m = 1$, while the data for nonplanar NWs cannot be fitted with $m = 2$. This comparative experiment indicates that planar growth is dominated by surface diffusion over the substrate, whereas nonplanar growth is dominated by surface diffusion over the NW walls.

Summary and Conclusions

To summarize, we have presented a full transport-limited model for planar NW growth and various sets of corresponding experimental data, including surface-guided ZnSe and ZnS NWs grown by Au-catalyzed CVD on both flat and faceted sapphire substrates. The model and the data are in excellent agreement and reveal that

this surface-guided planar growth is in all cases dominated by surface diffusion of precursor adatoms from the substrate surface to the catalyst droplet. The growth of thin NWs is suppressed by the GT effect. The resulting growth rate as a function of radius has a maximum at a certain optimal radius ($R = 20$ nm) for obtaining the longest NWs. The minimum radii of surface-guided ZnSe and ZnS NWs are approximately $R = 10$ nm. This corresponds to the characteristic GT radii in the range of 8 to 9.5 nm. The diffusion-induced contribution to the planar NW elongation rate features a power exponent for the inverse radius dependence, which is $m = 1.5$ for ZnSe NWs and close to $m = 2$ for ZnS NWs, compared with the standard value of $m = 1$ for nonplanar ZnS NWs. The effective diffusion lengths at a source temperature of 980 °C are on the order of 60 to 65 nm. The excellent fitting of the experimental data to the model under all these different conditions, including different semiconductor materials (ZnSe and ZnS), on 2 different substrate morphologies (flat and faceted), and at 3 different growth temperatures, strongly supports the generality of the model. Preliminary results on the growth kinetics of surface-guided GaN NWs by reaction of Ga vapor with NH_3 from Ni catalyst show equally excellent agreement with the same model, further supporting its generality for planar vs. nonplanar NW growth (*SI Appendix*). Understanding the growth mechanism of surface-guided NWs (and planar NWs in general) has a fundamental and practical significance. Introducing the possibility of controlling the NWs size and length uniformity by tuning the catalyst size and

growth parameters may be extended to other material systems for practical electronic and optoelectronic applications.

Materials and Methods

Growth of NWs. Surface-guided NWs were synthesized on C- and M-plane sapphire wafers (Roditi International, Inc.) and miscut (2° toward [1100]) C-plane sapphire wafers (Gavish Ltd.). The M-plane wafer was annealed before the synthesis at $1,600^\circ\text{C}$ in air for 10 h using a high-temperature tube furnace. On thermal treatment at elevated temperature, the M-plane surface undergoes restructuring and presents the more thermodynamically stable S planes ($10\bar{1}1$) and R planes ($1\bar{1}02$) in periodically faceted V-shaped nanogrooves. The miscut C plane was also annealed at the same conditions, producing an array of L-shaped nanosteps due to step bunching of the high-index planes that are exposed. The NWs were grown both from a dispersed Au nanoparticle solution and from patterned Au catalyst to achieve long arrays. The results presented here are for NWs grown from patterned catalyst, while those grown from dispersed Au nanoparticle solution were used as an internal test to verify that the NWs do grow from Au nanoparticles. The patterning was performed using a conventional photolithography faceted (MA/BA6 Karl-Suss mask aligner) with a negative photoresist (NR-9 1000PY) and suitable masks. An Au (Holland Moran; 99.999%) thin film of thickness 5 Å was deposited using an electron-beam physical vapor deposition system (Telemark) followed by liftoff in acetone. Before the synthesis dewetting process was performed, the substrates were heated in a quartz tube to 550°C for 7 min at atmospheric pressure. As a result, Au nanoparticles with a variety of sizes were produced. Zn pretreatment was performed to a part of the samples, and the described dewetting process was performed in a quartz tube with 3 to 5 pellets of zinc (Sigma Aldrich; 99.99%) at a distance of 3 to 4 cm from the sapphire substrates. The temperature was

550°C with a mixture of N_2 (Gordon Gas; 99.999%) and H_2 (Parker Dominic Hunter H_2 generator; 99.9995%) 490 and 12 sccm, respectively, at 400 mbar for 7 min.

The NWs were grown by CVD in a 3-zone tube furnace (Lindberg Blue M; Thermo Scientific). The source materials were ZnS powder (Sigma Aldrich; 99.99%) and ZnSe powder (American Elements; 99.999%). The sapphire substrates were placed downstream on a quartz slide. The tube was purged with a mixture of N_2 and H_2 490 and 12 sccm, respectively, at 400 mbar. The temperature of the source powder was held at 910 to 990°C , and the sapphire substrates were maintained at 735 to 780°C . The typical growth time was 15 min.

Sample Characterization. The synthesized NWs were characterized using optical microscopy (Olympus BX-51) and field-emission SEM (LEO Supra 55 VP and Sigma 500 Zeiss) over the working voltage range 3 to 5 kV. The thickness of the NWs, related to their radius, was measured using AFM (Multimode Nanoscope 7.30; Veeco/Bruker) by applying tapping mode and using 70-kHz etched Si tips (Nanoprobes) as presented in *SI Appendix, Fig. S5*.

Data Availability. All data discussed in the paper are available in the main text and *SI Appendix*.

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