Effect of Radius on Crystal Structure Selection in III–V Nanowire Growth

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**ABSTRACT:** The radius of III–V nanowires is known to have an effect on the resulting crystal structure during particle-assisted growth; however, the causes behind this effect remain under debate. In this work, we use stochastic simulations of nanowire growth to evaluate how the radius (R) affects the growth dynamics and how this in turn affects the crystal structure selection. This is due to the geometry of the growing nanowire: the number of atoms in the seed particle scales with \( R^3 \), and the number of III–V pairs per layer scales with \( R^2 \). The influx of growth species to the seed can, for instance, scale with the surface area of the seed particle for direct impingement (\( \alpha R^2 \)) or the perimeter of the nanowire for sidewall diffusion (\( \alpha R^3 \)) or be radius-independent for substrate diffusion in some cases (\( \alpha R^0 \)). These differences in radius dependencies cause the particle composition to change more rapidly for thinner nanowires, which in turn leads to nucleation at higher supersaturations and promotion of the wurtzite structure. In addition, the geometry can also make the influx V/III ratio dependent on the nanowire radius, which can influence the selection of crystal structure in different ways depending on the materials system and growth regime.

**INTRODUCTION**

The low-dimensional nature of semiconducting III–V nanowires makes them highly interesting, for instance, in device fabrication because of the radial confinement of charge carriers and in growth of lattice mismatched heterostructures because of the radial strain relaxation. However, the small dimensionality also makes the growth of nanowires sensitive to the radius of the catalytic seed particle used, which has been shown to greatly affect, for example, the average axial growth rate and the length distribution of nanowire ensembles.

A key aspect of III–V nanowire growth is the ability to adopt either the zinc blende (ZB) structure, which is the stable crystal structure for non-nitride III–V materials, or the typically metastable wurtzite (WZ) structure. The radius of the nanowire is well-known to affect the crystal structure selection from an experimental point of view, but from a theoretical point of view the role of the nanowire radius is still debated. Johansson et al. presented a theoretical model where the observed WZ predominance in thin nanowires was explained by means of the Gibbs–Thomson (GT) effect. These results differ from the work of Dubrovskii, who takes both the solid and the liquid phases into consideration when calculating the GT effect and concludes that the GT effect does not influence the choice of crystal structure. Meanwhile, different thermodynamic stability studies show that the WZ structure can become energetically favorable compared to ZB for a sufficiently small radius (with transition radii ranging from a few to a few tens of nanometers), while a pure ZB nanowire with a radius as small as 5 nm has been grown. This emphasizes that the radius dependence of crystal structure is still not fully understood.

In this work, we use our previously developed stochastic simulation model to analyze the effect of nanowire radius on the crystal structure selection of growing GaAs nanowires. To gain a more complete picture of the potential effects of a varying nanowire radius, we simulate the growth at different As supply rates (As flows) and expand the model to include two additional aspects of nanowire growth. One is that the GT effect results in a size-dependent effective supersaturation due to the change in the surface area of the seed particle upon nucleation. The second aspect is that the incorporation of Ga can occur via surface diffusion instead of direct impingement, which gives rise to the radius-dependent growth rate of nanowires.

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We find that in the simulated nanowires, the WZ fraction increases with decreasing radius in all cases. We conclude that this is due to the influence of the geometry of the system on the dynamics of the composition throughout the growth, which directly controls the supersaturation. As the radius decreases, nucleation occurs at higher supersaturations, which is known to promote the formation of the WZ structure.\textsuperscript{17,19} We also see that when the group V species is supplied by direct impingement while the group III material enters the seed via surface diffusion, then the V/III ratio becomes radius-dependent. This means that nanowires with smaller radii typically grow with lower V/III ratios, and the V/III ratio is known to affect the crystal structure selection.\textsuperscript{21}

**METHOD**

The model used in this work is based on GaAs nanowires, with Au as the seed material. Growth occurs in cycles, which start with growth species being supplied to the seed particle, either from the vapor or from adatom states on the substrate, as shown in Figure 1. This supply of growth species supersaturates the seed particle, which at some point leads to nucleation at the interface between the seed particle and the nanowire. After nucleation, a complete bilayer forms (either instantly or during a period of time\textsuperscript{20,21}), and then the next cycle begins. Crystal structure selection is determined by the nucleation, which will depend on the momentary state (most notably the supersaturation) of the seed particle at the moment of nucleation, which is determined by the composition. The composition of the seed particle in turn depends on the mass transport of growth species to and from its surroundings, but also on the growth of the previous bilayers. In the model, we iteratively calculate the mass transport based on the current composition of the seed particle, use Monte Carlo sampling to decide if a new bilayer is formed, and then update the composition. This provides a way to track the temporal evolution of the seed particle as the nanowire grows.

In the simulations, initialization occurs by first choosing the growth temperature, radius of the nanowire (which also determines the number of Au atoms in the seed), an initial Ga concentration, and flows of the growth species. Then, in time steps of 10 μs, the evolution of the seed particle and nanowire are calculated. First in each 10 μs cycle, the numbers of Ga and As atoms which have been incorporated into to the seed particle during this period are calculated, and the composition of the seed particle is updated accordingly. Next, the solidification process is considered. In each time step, nucleation rates for the two crystal structures are calculated, using the composition of the seed particle, classical nucleation theory, and nucleation at the triple phase line (TPL).\textsuperscript{19} Given these nucleation rates, Monte Carlo sampling is used to decide whether a bilayer nucleates during the current time step, and if so, whether it has WZ or ZB structure. When a successful nucleation event occurs, Ga and As atoms corresponding to a complete layer are immediately removed from the seed particle. This allows for a direct observation of how the different input parameters (flows, radius, and temperature) affect the dynamics of the seed particle and how the dynamics in turn affect the crystal structure selection. For more details regarding the framework of the simulation, the reader is referred to our previous work.\textsuperscript{18}

Here we focus on two of the input parameters for the model, namely, the nanowire radius and the flows of the growth species. To cover a wide range of possible radius-dependent effects, we consider three distinct cases in our simulations. The first case, hereinafter termed the impingement case, uses the original model.\textsuperscript{18} Here the source of As and Ga is direct impingement on the seed particle. The impingement rate is given by

$$
\dot{n}_{\text{imp}} = \frac{F_i 2 \pi R^2}{1 + \cos \beta}
$$

where $F_i$ is the relative flow of species $i$, $j_0$ is a reference impingement rate, set to $10^{19}$ s$^{-1}$ m$^{-2}$, and $2 \pi R^2/(1+\cos \beta)$ is the surface area of the particle,\textsuperscript{18} with $R$ as the nanowire radius and $\beta$ as the contact angle. In this case, the impingement and evaporation rates (proportional to $R^2$), the initial number of Au atoms in the seed (proportional to $R^3$), and the pre-exponential factor of the nucleation rate (proportional to $R$ for nucleation at the TPL) directly use the nanowire radius as a variable in the simulation. The impingement rates used here are considered to be the effective rates which reach the seed particle. This means steps such as the pyrolysis of precursors in metalorganic vapor phase epitaxy are not modeled, and as a result of this, the flows used here do not have a one-to-one correspondence with experimental flows. However, this does not affect the trends observed when varying the nanowire radius.

The second case, hereinafter termed the GT case, is based on the impingement case but includes a GT-correction term when calculating the effective supersaturation of the liquid particle with respect to the solid phase in the ZB structure. Following the motivation of Dubrovskii et al.,\textsuperscript{17} we replace the supersaturation ($\Delta \mu$) with an effective supersaturation ($\Delta \mu_{\text{GTE}}$):

$$
\Delta \mu_{\text{GTE}} = \Delta \mu - \frac{2 \gamma_{LV} (\Omega_\text{V} - \Omega_\text{L}) \sin \beta}{R}
$$

This introduces an additional radius dependence, by considering the change in surface area of the seed particle when nucleation occurs. Here, $\Delta \mu_{\text{GTE}}$ becomes the effective supersaturation between the liquid and solid phases, while $\Delta \mu$ is the bulk supersaturation. Whether the effective supersaturation is lower or higher than the bulk supersaturation depends on the difference between the volumes of III–V pairs in the solid phase ($\Omega_\text{L}$) and in the liquid phase ($\Omega_\text{V}$), and it scales with the surface energy of the particle ($\gamma_{LV}$), the contact angle

![Figure 1. Schematic figure of the material flows considered in the simulations. The radius of the nanowire is denoted by R, the substrate diffusion length by λ, and the contact angle of the seed particle as β. The blue circle indicates the collection area for Ga adatoms which can diffuse to the nanowire. “Ev” refers to direct impingement of growth species, “Ev” to the evaporation of the volatile As species, and “Diff” to the substrate diffusion of Ga atoms.](https://dx.doi.org/10.1021/acs.cgd.0c00575)
(β), and most importantly the nanowire radius (R). For GaAs, this leads to a reduction in the supersaturation.

The third case, hereinafter termed the diffusion case, is based on the impingement case. However, the influx of Ga is changed from direct impingement to diffusion induced. We use the following expression, based on the work of Dubrovskii et al.:7

$$\pi \lambda = - \frac{\Omega - \Delta}{\mu_{Ga} \mu_{L} - \mu_{Ga}}$$

The diffusion flux depends on the difference in chemical potential between Ga in the liquid phase (consisting of a bulk chemical potential term, $\mu_{Ga,L}$, and a GT correction term) and the chemical potential of Ga atoms in the adatom phase ($\mu_{Ga,A}$). The diffusion length of Ga on GaAs ($\lambda$) has been estimated from several hundred nanometers22 to several micrometers23, and in our simulation, we use a value of 1 μm. Furthermore, $\Omega_{Ga}$, is the volume of a Ga atom in the liquid, and $K_0$ and $K_1$ are the modified Bessel functions of the second kind. We estimate the chemical potential of Ga in the liquid analogously as done for As in ref18, and the chemical potential of the adatom phase is calculated using the ratio between the adatom coverage and the equilibrium adatom coverage, $\mu_{Ga,A} = kT \ln(\theta/\theta_{eq})$.

The adatom coverage during the simulation, $\theta$, is estimated from

$$\frac{1}{\theta} = 1 + \frac{1}{r_{Ga} F_{Ga} \mu_{Ga}}$$

with $r_{Ga}$ as the effective lifetime of a Ga adatom on the surface, which is reported to be on the order of seconds26 and here taken as 1 s. This expression is based on the equilibrium that arises as a result of each empty adatom site being filled at a rate of $F_{Ga} \mu_{Ga}$, with the site area $a_s = a_Z^2 \sqrt{3}/4$ and each occupied site becoming empty after the time $r_{Ga}$.

## RESULTS AND DISCUSSION

To evaluate how the radius of the nanowire affects the crystal structure selection, we used the described framework to perform three sets of simulations. Each set of simulations corresponded to one of the three cases described previously, and within each set, the flows of the growth species were kept constant at $F_{As} = 64$ and $F_{Ga} = 0.88$ (impingement case and GT case) or $F_{Ga} = 0.03$ (diffusion case). The flow of Ga for the diffusion case was chosen such that the growth rates for impingement and diffusion were equal at a radius of 100 nm. The As flow was chosen to be relatively high, which, according to our previous work,18 placed the growth in the high V/III ratio regime where ZB is predominantly formed for nanowires with a large radius. The radius was varied between 10 and 100 nm, in steps of 10 nm, and each simulation covered 60 s of growth time. The temperature of the system was set to 500 °C.

The initial Ga concentration in each simulation run was determined by first performing a trial simulation. The average Ga concentration from the trial simulation was then used as the input value for the real simulation. From each of these simulations, the following values were recorded: the WZ fraction of the simulated wire, the average growth rate of the wire, the average Ga concentration throughout the entire simulation, and the average supersaturation at the moments of nucleation.
conclusions by Dubrovskii et al.7 The Ga concentration in the reference impingement case, which is in line with previous studies, does not have a notable effect on the WZ fraction, compared to the reference impingement case, which is in line with previous studies. The Ga concentration in the GT case and diffusion case deviate from the impingement case, which will be discussed later. The largest difference in composition with varying radius in all the simulations is less than 1.5 percentage points (between the maximum and minimum value in the diffusion case). Comparing this small change in Ga to the results of our simulations is less than 1.5 percentage points (between the maximum and minimum value in the diffusion case). Comparing this small change in Ga to the results of our previous study which discussed the effect of Ga concentration on the WZ formation18 suggests that this shift in composition is not responsible for the change in crystal structure with radius. This can also be seen in Figure 2a,b, as there is no direct correlation between the composition and the WZ fraction in the graphs. For all simulations in the impingement and GT cases, the average axial growth rate, shown in Figure 2c, remained constant around 1 nm/s. For the diffusion case, the growth rate was found to decrease with an increasing nanowire radius approximately as $R^{-2}$, which is expected for growth that is limited by substrate diffusion of the Ga species with a large diffusion length. This change in growth rate is also responsible for the slight deviation in composition (shown in Figure 2b) for the diffusion case compared to the impingement cases.

The supersaturation in Figure 2d was found to decrease with increasing nanowire radius for all cases and is higher for the diffusion case than for the direct impingement and GT cases. Comparing values of supersaturation and WZ fraction in Figure 2a,d, it can be seen that these values show a clear correlation. When nucleation occurs with a high supersaturation, the WZ structure was promoted, which is generally expected in the framework of TPL nucleation.27 The effective supersaturation in the GT case and the impingement case are the same, which explains the slight deviation in the average composition between the two. Because of the GT effect, the GT case will experience a lower effective supersaturation at the same composition. For the GT case to maintain the same nucleation rate as the impingement case (which was required to maintain the balance between the impingement rate of Ga and the average rate at which GaAs pairs solidify), the Ga concentration needs to be slightly higher for the GT case. In the presented simulations, the GT effect was not found to affect the growth in any significant way. For this reason, it will not be discussed further.

To understand why the supersaturation at the moments of nucleation is affected by the radius and the route of the Ga supply, the temporal evolution of some variables, namely the Ga and As concentration as well as the supersaturation, was recorded during the simulation. In Figure 3, these are shown for three simulations: for the impingement case with a 100 nm radius or a 20 nm radius and for the diffusion case with a 20 nm radius. In Figure 3a–c, the Ga concentration for the different cases is shown. In each growth cycle, there is an incubation period where the Ga concentration increases until a nucleation occurs. This depletes the seed particle of Ga corresponding to a drop in the graphs, after which the drop in concentration following the formation of a new bilayer can be written as $\Delta c_{Ga}/dL = dN_{Ga}/dN_{Ga} \times dN_{Ga}/dL$. The first factor, the change in Ga concentration when adding or removing Ga atoms, can be found by differentiating the definition of the molar fraction, $dN_{Ga}/dN_{Ga} = (1 - c_{Ga})/N_{seed}$. Here, $N_{seed}$ is the number of atoms in the seed particle, which scales with the volume of the seed particle making $dN_{Ga}/dN_{Ga}$ proportional to $R^{-3}$. The second factor, the number of Ga atoms ($N_{Ga}$) per layer, $dN_{Ga}/dL$, scales with the liquid–solid interface.
interface area and is proportional to $R^2$. This gives a combined radius dependence of the drop in concentration, $d_c/dt$, which is proportional to $R^{-3}$. This means that as the radius of the nanowire decreases, the drop in concentration following a nucleation becomes larger.

During the incubation periods, the Ga concentration increases at different rates for the different cases. This rate, $dc_{Ga}/dt$, also relates to the geometry of the system and can be expressed as $dc_{Ga}/dt = dc_{Ga}/dN_{Ga} \times dN_{Ga}/dt$. As discussed previously, $dc_{Ga}/dN_{Ga}$ is proportional to $R^{-3}$, and $dN_{Ga}/dt$ is the influx of Ga. The radius dependence of the influx depends on whether the Ga comes from direct impingement or diffusion. For direct impingement, the influx of Ga scales with the surface area of the seed particle ($j_{Ga,Imp} = dN_{Ga,Imp}/dt \propto R^2$), and the radius dependence for substrate diffusion can vary (roughly between $R^1$ and $R^0$ depending on the relation between the radius and diffusion length). In our simulations, the growth rate indicated that the Ga flux was close to radius-independent ($j_{Ga,Diff} \propto R^0$). This means that for the impingement case, $dc_{Ga}/dt$ is proportional to $R^{-2}$, while for the diffusion case, it is proportional to $R^{-3}$.

From Figure 3d–f, it can be seen that $c_{As}$ rapidly reaches a steady-state concentration after each nucleation event for the two simulations using the impingement case. Once $c_{As}$ has stabilized at the constant steady-state concentration, As no longer assists in increasing $\Delta\mu$ and thus it does not influence when the nucleation events occur in the simulations. This means that for our impingement simulations, Ga is the only species that affects the nucleation time. For the diffusion case, Figure 3f, this starts to become less true as the As concentration does not always reach the constant steady-state value. This is due to the different dependencies of the influx of the diffusing Ga and impinging As, which leads to a higher flow of Ga relative to that of As and a lower effective V/III ratio ($j_{As,Imp}/j_{Ga,Diff}$) for smaller nanowires. This relative increase in the Ga flow is reflected in the increasing growth rate for smaller nanowires. Values for the effective V/III ratio could be extracted from the simulations for the diffusion case. The particle for the nanowire with a radius of 100 nm experienced a V/III ratio of 77.5, while the seed particle corresponding to the 20 nm wire experienced a ratio of 5.1. In this simulation, despite the reduction in effective V/III ratio, the 20 nm growth still proceeded in the Ga-limited nucleation regime. As a result, the reduction in the effective V/III ratio had little effect on the steady-state composition of the seed particle. However, this can play a larger role when the flow of As is lower.

The variations seen in the composition are important, because they are clearly reflected in the variations in the supersaturations in Figure 3g–i. When the Ga increases rapidly so does the supersaturation, and when the supersaturation increases rapidly then nucleation on average occurs at a higher supersaturation. This outcome can be understood intuitively, by comparing a dynamically changing seed particle and a static seed particle growing at the same average rate. If the supersaturation is completely static (analogous to a very large particle), then the momentary nucleation rate will equal the average nucleation rate. If the dynamic particle (meaning a thin nanowire) starts at the same supersaturation as the static case, then the Ga will continue to increase over time and further increase the supersaturation. The momentary nucleation rate will increase because of this increasing supersaturation, and nucleation will on average happen sooner, and at a higher supersaturation, compared to the static case. Afterward, the dynamic supersaturation drops as a result of the nucleation and the momentary supersaturation is reduced below the static supersaturation. This leads to a momentary lower nucleation rate for the dynamic seed particle, until enough Ga has accumulated to reach the initial composition, and a full cycle has been completed. For group V atoms, this type of depletion has been discussed in relation to the nucleation antibunching, which affects the length distributions of nanowire ensembles. However, here we clearly see the effect also for the more abundant group III species.

To evaluate the effects beyond the purely Ga-limited nucleation regime, we performed two additional simulations in the diffusion case where the relative flow of As was lowered to $F_{As} = 12$. The temporal evolution of $c_{As}$, $\Delta\mu$, and $\Delta\mu_{ZB=WZ}$ during 0.5 s of growth is shown in Figure 4 for two simulations, one with a radius of 100 nm and one with a radius of 20 nm.

At this lower As flow, the differences in the composition between the 100 nm and the 20 nm simulations become more dramatic, which can be seen in Figure 4a–d. For the 20 nm nanowire, the nucleation is no longer limited only by Ga, as shown by the As concentration in Figure 4d which does not reach its constant steady-state concentration. This affects the character of the supersaturation in panels e and f of Figure 4.
which are dramatically different from each other. Because the As concentration no longer reaches its steady-state value, it continues to increase during the incubation periods and will have a large effect on the supersaturation. The supersaturation increases more rapidly than in the other simulations which, following the same logic as before, leads to nucleation at higher supersaturation for the As-limited nucleation. This effect helps to promote the WZ structure. Second, the average Ga concentration is significantly higher in the 20 nm simulation compared to the 100 nm one, which is expected when the effective V/III ratio decreases. This shift in effective V/III ratio (and the resulting shift in Ga concentration) can affect the crystal structure selection in different ways, depending on the growth regime. At conditions where the experimental V/III ratio is high and thick nanowires typically grow in the ZB regime, this effect will push thin nanowires toward the WZ regime found at intermediate V/III ratios. For experimental parameters where thick nanowires grow in the WZ regime found at intermediate V/III ratios, then using thinner nanowires could lead to the promotion of ZB, as has been observed experimentally. Growth would then occur in the ZB regime, which is found at very low V/III ratios.

Here it is important to note that this effect on the V/III ratio follows the radius-dependent diffusion rate of the Ga species. While we do not reach this regime in the simulations, it is well-known that below some critical radius the diffusion rate can decrease with decreasing radius because of the GT term in eq. In this regime, the presented V/III ratio trend would become the reverse, and a thinner nanowire would experience a higher V/III ratio.

**CONCLUSION**

We have analyzed how the radius of the nanowire can affect the crystal structure selection during growth. On the basis of our simulations, we find that the radius of the nanowire affects the crystal structure selection based on geometrical considerations, namely, the differences in the radius dependence between the volume ($\alpha R^3$), the surface areas ($\alpha R^2$), and the material fluxes (here ranging from $\alpha R^3$ to $\alpha R^6$).

These differences in radius dependencies led to two separate effects. First, the composition of the seed particle varied more rapidly as the seed particles became smaller. This led to nucleation on average happening at a higher supersaturation for nanowires with a smaller radius which, for nucleation at the TPL, is known to promote the formation of WZ.

Second, we see an additional effect for growth when one of the growth species originates from surface diffusion and the other originates from impingement. In this case the effective V/III ratio will change based on the radius of the nanowire, with smaller nanowires typically experiencing a lower V/III ratio. If this reduction of V/III ratio moves the growth out of the Ga-limited nucleation regime, this can have a large effect on the steady-state composition of the seed particle. This can result in the promotion of either the WZ or the ZB structure, depending on where in the parameter space the growth takes place.

The effects discussed here originate from the geometry of the growing nanowire, its seed particle, and the supply pathways of the growth species. Different metal-seeded III–V nanowire materials systems may be very different from the Au-seeded GaAs system in the sense that properties which are significant for crystal structure selection, such as diffusion lengths, surface energies, and differences in cohesive energies between the ZB and WZ structures, are very different. Still, the geometry of the nanowire and its seed particle remain the same. For this reason, we believe that our results can be generalized to nanowire growth in all materials systems and growth reactors, provided that one knows the pathways through which the growth species reach the seed particle.

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**Author Contributions**

E.K.M. carried out the simulations and took the lead in writing the manuscript. All authors discussed and interpreted the results, contributed to writing the manuscript, and approved the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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