Suppression of miscibility gaps in vapor-liquid-solid InGaAs and InGaN nanowires

T Jean1,2 and V G Dubrovskii2

1Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut Pascal, F-63000 Clermont-Ferrand, France
2ITMO University, Kronverkskiy pr. 49, 197101 St. Petersburg, Russia

Abstract. Miscibility gaps in ternary III-V and III-N alloys often prevent their compositional tuning required for new generation electronic and optoelectronic devices. Here, we show how the miscibility gaps are suppressed on kinetic grounds at high enough supersaturations in liquid droplets catalyzing the vapor-liquid-solid growth of ternary III-V and III-N nanowires. We give two examples for highly mismatched InGaAs and InGaN material systems in terms of the compositional diagrams describing the solid composition as a function of the indium content in the liquid or vapor phase.

Introduction

III-V and III-N nanowires (NWs) are widely considered as promising building blocks for fundamental nanoscience and nanotechnology [1-3]. NWs allow for almost unlimited bottom-up design and coherent growth on lattice-mismatched substrates without forming misfit dislocations [4-6]. Useful NW structures in most cases comprise ternary III-V NWs and heterostructures within such NWs. Immiscible III-V alloys such as InGaAs and InGaN have enabled new classes of optoelectronic devices, but it is admittedly challenging to tune their operating wavelength. This requires an increased In content x in In$_x$Ga$_{1-x}$As or In$_x$Ga$_{1-x}$N, prevented by the indium segregation within the miscibility gaps. Beyond the advantage of dislocation-free growth on dissimilar substrates, NWs may help to extend the compositional range of such alloys and ultimately to fabricate high quality photonic heterostructures with tunable and well-controlled compositions [7-13]. However, the mechanisms behind the formation of ternary III-V NWs are very different from the thin film case and their comprehensive understanding is beyond reach to this end (see Ref. [3] for a detailed review).

Consequently, here we develop a model that attributes the wide compositional range of VLS III-V NWs to the purely kinetic growth regime without macroscopic nucleation. This requires a high degree of supersaturation in liquid droplets catalyzing the VLS growth, which is accessible in epitaxial techniques with high material inputs such as metal organic vapor phase epitaxy (MOVPE) or hydride vapor phase epitaxy (HVPE).

Model

The composition of ternary III-V NWs grown by the VLS method can be described using four different approaches – (i) equilibrium model [14,15]; (ii) binary nucleation model [15-17], (iii) regular
growth model [7,18] and (iv) kinetic growth model [19,20]. Following the kinetic approach of Refs. [19,20], we define the composition of a ternary $A_xB_{1-x}D=(AD)_{1-x}(BD)_x$ NW as $x = i/(i+j)$, where $i$ is the number of AD pairs, $j$ is the number of BD pairs, and $i+j$ is the total number of III-V pairs in a growing island. Putting $dx/dt$ to zero yields the natural result [19]

$$x = \frac{di/dt}{di/dt + dj/dt},$$

(1)

showing that the kinetically controlled composition is given by the ratio of the growth rate of AD fraction in the island over the total growth rate of the island.

For the growth rates of AD and BD fractions in the island, we take the usual approximations justified earlier in Ref. [21]

$$\frac{di}{dt} = K_{AD} \left( e^{\mu^s_{AD} - \mu^S_{AD}} - e^{\mu^L_{AD} - \mu^L_{AD}} \right),$$

$$\frac{dj}{dt} = K_{BD} \left( e^{\mu^s_{BD} - \mu^S_{BD}} - e^{\mu^L_{BD} - \mu^L_{BD}} \right).$$

(2)

Here, $\mu^s$ are the chemical potentials for atoms A, B and D in solid and $\mu^L$ are the chemical potentials of AD or BD solids in liquid, all measured in thermal units of $k_B T$. The crystallization rates $K_{AD}$ and $K_{BD}$ summarize kinetic growth effects associated with different diffusivities of atoms in the liquid phase and crystallization rates of AD and BD pairs, respectively. Both growth rates in Eq. (2) equal zero when $\mu^s_A + \mu^s_B = \mu^s_{AD}$ and $\mu^s_B + \mu^s_D = \mu^s_{BD}$, by definition of thermodynamic equilibrium in a ternary liquid-solid system [14,15]. Using Eqs. (2) in Eq. (1), it is easy to obtain

$$\frac{1-x}{x} = \frac{K_{BD}}{K_{AD}} e^{(\mu^s_{AD} - \mu^s_{BD})} \left( 1 - e^{-\Delta \mu_{BD}} \right) / \left( 1 - e^{-\Delta \mu_{AD}} \right).$$

(3)

The chemical potential differences $\Delta \mu_{AD}$ and $\Delta \mu_{BD}$ depend on the solid composition $x$ and liquid composition $y = c_A/(c_A + c_B)$ (with $c_A$ and $c_B$ being the atomic concentrations of atoms A and B in liquid) according to

$$\Delta \mu_{AD} = \mu^s_A(y) + \mu^s_B(y) - \mu^s_{AD} - \ln x - \omega_s (1-x)^3,$$

$$\Delta \mu_{BD} = \mu^s_B(y) + \mu^s_D(y) - \mu^s_{BD} - \ln(1-x) - \omega_s x^3.$$  

(4)

Here, $\mu^s_{AD}$ and $\mu^s_{BD}$ are the chemical potentials of pure binary AD and BD solids and $\omega_s$ is the interaction constant in thermal units. The solid state is described within the regular solution model [17], although it is not critical. The factor in the right hand side of Eq. (3) depends only on $y$, while all characteristics of the solid state enter the exponential terms $e^{-(\Delta \mu_{AD})}$ and $e^{-(\Delta \mu_{BD})}$. The kinetic factor $K_{BD}/K_{AD}$ should not depend on $y$ for ternary materials based on the group III intermixing for arsenides, phosphides and nitrides, because both crystallization rates are proportional to the concentration of highly volatile arsenic or nitrogen atoms, which cancels in the ratio of $K_{BD}$ over $K_{AD}$. Any geometrical effect associated with the size dependence of the crystallization rates is proportional to a certain power of the island size $i+j$ depending on the island growth mechanism [22], and cancels in the $K_{BD}/K_{AD}$ ratio.

Despite its simplicity, Eq. (3) clearly shows the main effect - for small $\Delta \mu_{AD}$ and $\Delta \mu_{BD}$, the compositional diagram $x(y)$ contains the miscibility gap described by the quadratic interaction terms in Eqs. (4) at $\omega_s > 2$, while at $\Delta \mu_{AD} >> 1$ and $\Delta \mu_{BD} >> 1$ the dependence on $x$ in the right hand side disappears. Of course, the miscibility gaps can be modified by strain induced by the lattice mismatch (see, for example, Refs. [23] and [24]), the effect which is not taken into account in Eqs. (4). However, Eq. (3) shows that the miscibility gap is fully suppressed on kinetic grounds at high enough supersaturation in the liquid phase even if it is present in bulk thermodynamics. Such high degrees of supersaturation in the catalyst droplets are locally accessible in MOVPE or HVPE VLS techniques with high material inputs [25].
Equation (3) is considerably simplified in the case of ternaries based on the indium (A=In, D=V) and gallium (B=Ga, D=V) intermix due to the known high stability of indium in the liquid phase such that the indium content in the catalyst droplet is very close to unity [16,17]. In the following, we will additionally assume that \( \varepsilon = (K_{InV}/K_{GaV}) \exp(\mu_{InV}^0 - \mu_{GaV}^0) << 1 \). This strong inequality is consistent with \( y \approx 1 \), because indium-rich liquid requires that the crystallization rate of In-V pairs is much lower than that of Ga-V pairs. Using Eqs. (4), we can re-arrange Eq. (3) as

\[
\zeta = e^{-\frac{1-x}{x}} + \alpha(1-x)e^{e^{\alpha(1-x)} - \alpha(1-x)e^{\alpha(1-x)^{1-x}}},
\]

with

\[
\zeta = e^{-\beta - \mu_{InV}^0 - \mu_{GaV}^0},
\]

\[
\varepsilon = (K_{InV}/K_{GaV}) \exp(\mu_{InV}^0 - \mu_{GaV}^0) \text{ and } \alpha = \exp[-(\mu_{InV}^L + \mu_{InV}^L - \mu_{GaV}^0)].
\]

Clearly, the \( \alpha \) parameter changes from unity in the equilibrium case to zero at very high supersaturations in liquid.

Chemical potentials of the indium and gallium atoms in the liquid phase are given by [17]

\[
\mu_{In}^L = \mu_{In}^0 + \ln c_{In} + \varphi_{In} = \mu_{In}^0 + \ln[y(c_{In} + c_{Ga})] + \varphi_{In},
\]

\[
\mu_{Ga}^L = \mu_{Ga}^0 + \ln c_{Ga} + \varphi_{Ga} = \mu_{Ga}^0 + \ln[(1-y)(c_{In} + c_{Ga})] + \varphi_{In},
\]

where the \( \varphi \) terms sum up the terms describing interactions of indium and gallium with all other atoms. At \( y \approx 1 \), we can neglect the \( y \) dependence of all the terms in Eqs. (7) except for the leading logarithmic dependence \( \ln(1-y) \) for gallium. Taking the difference, we obtain

\[
1 - y = \left[ 1 - x \right] e^{-\frac{1-x}{x}} + \alpha(1-x)e^{e^{\alpha(1-x)} - \alpha(1-x)e^{\alpha(1-x)^{1-x}}},
\]

with \( Q = \exp[\mu_{InV}^0 - \mu_{GaV}^0 - (\mu_{InV}^L - \mu_{GaV}^L) + \varphi_{In} - \varphi_{Ga}]. \) At \( \varepsilon << 1 \), the last term in the brackets can be neglected with respect to the second one. Using the notations

\[
a = Q\varepsilon, \quad \delta = \alpha / \varepsilon,
\]

Eq. (8) takes the final form

\[
y = 1 - a \left[ 1 - x \right] e^{\frac{1-x}{x} + \delta(1-x)e^{\alpha(1-x)^{1-x}}}.
\]

This solid-liquid compositional diagram is controlled by three parameters. The thermodynamic parameter \( a \) should be much smaller than unity to ensure that the droplet is indium-rich. The kinetic \( \delta \) factor describes the relative importance of macroscopic nucleation with respect to the growth kinetics and tends to zero in the purely kinetic growth regime when \( \mu_{InV}^L + \mu_{InV}^L >> \mu_{InV}^0 \).

Equation (10) is our final result for the \( x(y) \) dependence. We now want to find the relationship between the liquid composition \( y \) and the indium fraction in vapor in HVPE growth of InGaN NWs at high temperatures, as in Ref. [20]. We consider stationary solutions of the kinetic equations for the total numbers of the indium (\( N_{In} \)) and gallium (\( N_{Ga} \)) atoms in liquid

\[
dN_{In}/dt = -V_{In}/\tau_{In} - dN_{In}/dt,
\]

\[
dN_{Ga}/dt = V_{Ga} - N_{Ga}/\tau_{Ga} - dN_{Ga}/dt,
\]

with \( V_{In} \) and \( V_{Ga} \) as the total atomic influxes of indium and gallium into the droplet, and \( \tau_{In} \) and \( \tau_{Ga} \) as the mean lifetimes of the indium and gallium atoms in liquid.

Neglecting the \( dt/dt \) term for indium corresponds to the case where \( N_{In} \) is controlled by the indium desorption rather than its consumption due to the VLS growth of a NW. This explains the strong inequality \( N_{In} >> N_{Ga} \), which is required for \( y \approx 1 \). Thus, we obtain the stationary solution in the form

\[
N_{In} = \frac{V_{In}}{\tau_{In}^L}.
\]

As for the gallium atoms, nothing can be said about \( N_{Ga} \) from the stationary solution to the kinetic equation. However, since gallium desorbs much less than indium, we can simply assume a temperature independent \( N_{Ga} = const \) in the first approximation. Next, we notice that
\( N_{Ga} / N_{In} = (1 - y)/y \equiv 1 - y \) and \( V_{Ga} / V_{In} = (1 - z)/z \), where \( z = V_{In}/(V_{In} + V_{Ga}) \) is by definition the indium content in vapor. These considerations yield \( 1 - y = (\tau_*/\tau_0)(1 - z)/z \), with \( \tau_* = N_{Ga}/V_{Ga} \).

Comparing this to Eq. (5), we find the \( x(z) \) dependence explicitly in the form

\[
\begin{align*}
\tau = \left[1 + bF(x)^{-1}\right]^{-1},
F(x) &= \frac{1-x}{x} + \delta (1-x)e^{ax^2},
\end{align*}
\]

(11)

with \( b = a(\tau_0/\tau_0) \).

Results and discussion

Let us now see how the obtained expressions change the compositional diagrams of VLS InGaAs and InGaN NWs. We first note that the earlier results of Refs. [16] and [17], obtained within the frame of binary nucleation theory with a saddle point of the island formation energy, predict the presence of the miscibility gaps in ternary VLS NWs whenever \( \omega > 2 \). This is due to the main assumption on the nucleation-limited composition, determined by the composition of the critical island (or nucleus). Our model is different and takes into account that the NW composition may change in the follow-up stage where the island grows to fill the monolayer slice of a NW. This growth can be driven by either thermodynamics or kinetics. In particular, Figure 1 shows the solid-liquid \( [x(y)] \) compositional diagram for VLS InGaAs NWs grown at 450°C. According to the data of Ref. [17], the \( \omega \) value at this temperature equals 2.375, while the \( a \) value should be very small to ensure that \( y \) is close to unity. Choosing \( a = 0.0005 \), we obtain the compositional diagrams shown in Fig. 1. As expected from Eq. (10), large \( \delta \) correspond to the thermodynamically controlled NW compositions with the miscibility gaps, although slightly modified with respect to purely thermodynamic values of Refs. [16], [17]. Decreasing \( \delta \) leads to the kinetically limited VLS growth regime where the miscibility gap disappears.

![Figure 1](image_url)

**Figure 1.** Solid-liquid compositional diagram for InGaAs NWs grown at 450°C (\( \omega = 2.375 \)). The small \( a = 0.0005 \) describes a high stability of indium in liquid such that any appreciable fraction of InAs in solid requires very high indium content in liquid (more than 0.97), as in Refs. [16] and [17]. Large \( \delta > 20 \) yield the miscibility gaps in solid InGaAs, while smaller \( \delta \) correspond to the kinetically controlled VLS growth in which all solid compositions become possible. The dashed line corresponds to \( \delta = 0 \).
These results qualitatively explain the experimental data of Refs. [7] and [28], reporting stationary compositional tuning of gold-catalyzed MOVPE InGaAs NWs throughout the entire compositional range. Most probably, InGaAs NWs described in Refs. [7,28] grew at high supersaturations via regular crystallization without macroscopic nucleation. In this case, the entire range of solid compositions becomes accessible, as described by our model. We note, however, that the solid composition remains very sensitive to the indium content in liquid even at small $\delta$ and requires more indium-rich droplets to access any appreciable InAs content in NWs.

Figures 2 and 3 show the solid-liquid [$x(y)$] and solid-vapor [$x(z)$] compositional diagrams for self-catalyzed InGaN NWs, obtained from Eqs. (10) and (11), respectively. The $\omega_x$ value was set to 3.33 at the growth temperature of 645°C according to the data of Ref. [26], corresponding to the experimental conditions of Ref. [20]. This value yields the miscibility gap of unstrained In$_x$Ga$_{1-x}$N between $x = 0.12$ and $x = 0.88$, described by the wavy regions of both diagrams in the thermodynamically controlled regime at $\delta = 10$. Increasing the chemical potential difference of InN pairs in liquid and solid decreases the $\delta$ values and the miscibility gap starts to shrink, as we saw earlier in Fig. 1 for InGaAs NWs. The gap is completely suppressed at $\delta \approx 1.5$ for these plausible parameters. The dashed curves at $\delta = 0$ correspond to the purely kinetic VLS growth regime. This regime is described by the one-parametric equation for the solid-vapor composition

$$x = \frac{bz}{1 + (b - 1)z},$$

(12)

where the miscibility gap disappears. For any $b$, it becomes possible to cover the entire compositional range of InGaN by simply changing the indium content in vapor. The results of Ref. [20] demonstrate how the solid composition can be tuned even at a fixed $z$ by changing the growth temperature in HVPE process. Indeed, for high enough temperatures typically employed in HVPE, indium desorbs more than gallium and this changes the temperature-dependent $b$ value in favor of more gallium-rich droplets and consequently NWs at higher temperatures. This effect can be described by a simple Arrhenius-like dependence of the factor $\tau^L_{\text{In}} / \tau_{\text{..}}$, as discussed in more detail in Ref. [20].

Figure 2. Solid-vapor compositional diagram for self-catalyzed InGaN NWs grown at 645°C (corresponding to $\omega_x = 3.33$), at $a = 0.002$. 
Figure 3. Solid-vapor compositional diagram for self-catalyzed InGaN NWs grown at 645°C (corresponding to $\omega_r = 3.33$). The $b$ value in was set to 0.5, corresponding to an InN fraction of about 0.4 for the vapor composition $z = 0.6$ in the purely kinetic growth regime (shown by dashed lines at $\delta = 0$). The miscibility gap, described by the wavy regions of the diagrams, is present for large enough $\delta$ but shrinks to zero for $\delta$ smaller than 1.5 for these parameters.

In conclusion, we have shown that the miscibility gap of any ternary material, if present in the bulk thermodynamics at a growth temperature, is completely suppressed under high enough supersaturations of a metastable mother phase. This fundamental property is not specific for NWs. However, ternary VLS NWs give an example of the growth system where supersaturations in a nano-sized catalyst can be extremely high compared to the standard thin film case. For InGaAs and InGaN NWs catalyzed by indium-rich droplets, it is possible to cover the entire compositional range of InV fractions in solid, which is not always accessible in the conventional growth techniques.

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References

[1] Zhang A, Zheng G, Lieber C M 2016 Nanowires: building blocks for nanoscience and nanotechnology, Springer, 2016
[2] Dubrovskii V G 2015 Theory of VLS growth of compound semiconductors, 93 ed Anna Fontcuberta I Morral, Shadi A Dayeh and Chennupati Jagadish (Burlington: Academic Press) pp. 1-78
[3] Dubrovskii V G 2017 J. Phys. D: Appl. Phys. 50 453001.
[4] Glas F 2015 Strain in nanowires and nanowire heterostructures Semiconductors and Semimetals 93 ed Anna Fontcuberta I Morral, Shadi A Dayeh and Chennupati Jagadish (Burlington: Academic Press) pp.79-123
[5] Ng K W, Ko W S, Tran T T D, Chen R, Nazarenko M V, Lu F, Dubrovskii V G, Kamp M, Forchel A, Chang-Hasnain C J 2013 ACS Nano 7 100
[6] Zhang X, Dubrovskii V G, Sibirev N V, Ren X 2011 Cryst. Growth Des. 11 5441
[7] Ameruddin A S, Caroff P, Tan H H, Jagadish C, Dubrovskii V G 2015 Nanoscale 7 16266
[8] Messing M E, Wong-Leung J, Joyce H J, Zanolli Z, Gao Q, Tan H H, Wallenberg L R, Johansson J, Jagadish C 2011 Growth of straight InAs on GaAs nanowire heterostructures Nano Lett. 11 3899
[9] Dick K A, Bolinsson J, Borg B M, Johansson J 2012 Nano Lett. 12, 3200
[10] Zannier V, Ercolani D, Gomes U P, David J, Gemmi M, Dubrovskii V G, Sorba L 2016 Nano Lett. 16 7183
[11] Qian F, Li Y, Gradecek S, Lieber C M 2004 Nano Lett. 4 20
[12] Sekiguchi H, Kishino K, Kikuchi A 2010 Appl. Phys. Lett. 96 231104
[13] Kuykendall T, Ulrich P, Aloni S, Yang P 2007 Nat. Mater. 6 951
[14] Priante G, Glas F, Patriarche G, Pantzas K, Oehler F, Harmand J C 2016 Nano Lett. 16, 1917.
[15] Glas F 2017 Cryst. Growth Des. 17 4785
[16] Ghasemi M, Johansson J 2017 Cryst. Growth Des. 17 1630
[17] Dubrovskii V G, Koryakin A A, Sibirev N V 2017 Mater. Des. 132 400
[18] Dubrovskii V G 2015 Cryst. Growth Des. 15 5738
[19] Johansson J, Ghasemi M 2017 Phys. Rev. Materials 1 040401(R)
[20] Roche E, André Y, Avit G, Bougerol C, Castelluci D, Réveret F, Gil E, Médard F, Leymarie J, Jean T, Dubrovskii V G, Trassoudaine A 2018 Nano Lett. (submitted)
[21] Dubrovskii V G, Grecenkov J 2015 Cryst. Growth Des. 15 340
[22] Dubrovskii V G 2009 J. Chem. Phys. 131 164514
[23] Glas F 1987 J. Appl. Phys. 62 3201
[24] Karpov S Yu 1998 MRS Internet J. Nitride Semicond. Res. 3 16
[25] Gil E, Dubrovskii V G, Avit G, André Y, Leroux C, Lekhal K, Grecenkov J, Trassoudaine A, Castelluci D, Monier G, Ramdani M R, Robert-Goumet C, Bideux L, Harmand J C, Glas F 2014 Nano Lett. 14 3938
[26] Adhikari J, Kofke D 2004 J. Appl. Phys. 95 6129
[27] Jung C S, Kim H S, Jung G B, Gong K J, Cho Y J, Jang S Y, Kim C H, Lee C, Park J 2011 J. Phys. Chem. 115 7843