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Growth, structure and phase transitions of epitaxial nanowires of III-V semiconductors

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Abstract. We review and illustrate the impact of TEM on the study of nanowires of non-nitride III-V semiconductors, with particular emphasis on the understanding of the thermodynamics and kinetics of their formation assisted by nano-sized catalyst particles. Besides providing basic information about the morphology of the nanowires and their growth rate as a function of diameter, TEM offers insights into the peculiar crystalline structure that they adopt. We discuss the formation of the unusual wurtzite hexagonal crystalline phase and that of planar stacking defects in these nanowires and show that they are kinetically controlled. We also demonstrate the transformation of wurtzite into cubic sphalerite upon epitaxial burying of the nanowires. Nanowires are particularly interesting in that they allow the fabrication of precisely positioned quantum dots with well-defined geometries. In this respect, we discuss the formation of strained quantum-size inclusions in nanowires, their critical dimensions and the kinetic and thermodynamic factors governing the changes of the crystalline structure that sometimes occur around a hetero-interface.

1. Introduction
Free-standing wires with diameters ranging from hundreds down to a few nanometers are nowadays commonly fabricated from a large range of semiconductor materials [1-6]. These 1D nanostructures have remarkable physical properties and many potential applications, yet the control of their growth and final characteristics is still far from optimal.

In this paper, we illustrate the impact of transmission electron microscopy (TEM) on the study of nanowires (NWs) of III-V semiconductors with particular emphasis on the understanding of the thermodynamics and kinetics of their formation. To be specific, we restrict the scope of our study in terms of materials and growth methods, by considering III-V compounds containing no nitrogen and grown by Molecular Beam Epitaxy (MBE) assisted by nano-sized gold "catalyst" particles. However, some of our conclusions remain valid for other material systems, growth methods and catalysts. We consider NWs growing on the \( \{111\} \) surface (often called \( (111)B \)) of a III-V compound, which is by far the most common case. In all our images, \( (111)B \) points upwards. Growth on the \( (001) \) surface, which would be highly desirable for applications, has not been achieved reproducibly so far.

Let us first summarize the basics of our current understanding of metal-catalyst-aided NW growth by MBE. The catalyst nanoparticles deposited on the substrate before growth define the wire diameter. According to the vapour-liquid-solid (VLS) growth mechanism, the atoms are fed from the vapour phase to the solid wire through this particle (or droplet), which remains liquid during growth [7]. The
growth of the NWs competes with that of the catalyst-free portion of the sample located between the NWs (the "non-activated" surface), which always occurs, albeit at a slower rate. This (111)B surface is typically fairly rough and grows by a combination of 2D nucleation and step flow whereas the NWs grow via the nucleation of new solid atomic layers at the top interface with the catalyst droplet. The droplet is a mixture of metal (here Au) with the wire elements. In most experiments, it is liquid during growth, as required for proper VLS. We checked this in situ for InAs NWs [8]. In some cases, the catalyst might however remain solid [3]. In MBE, the droplet is not a chemical catalyst which would facilitate the decomposition of precursor molecules, as in chemical vapour deposition methods, since the type-III elements are delivered as atomic beams and the type-V molecular beams are thermally decomposed. Instead, the droplet increases the growth rate at the top of the NW, probably by decreasing the nucleation barrier and by providing a dense feeding medium.

2. Basic investigations

2.1. Nanowire
The basic geometrical features of the NWs are not only important for the properties of the devices into which they may subsequently be incorporated. They also provide invaluable insights into the growth processes. To our knowledge, in situ TEM has only been performed for NWs of type-IV elements [9-10], whereas III-V NWs have only been examined ex situ. We shall see in section 3.2 that the way in which the growth is terminated before the NW is removed from the epitaxy chamber may marginally alter its geometry and structure, but in general the NWs remain largely unaffected by the transfer.

The first two dimensions to be determined are obviously the length and diameter of the NW. In the simplest case, each NW grows with a uniform diameter determined by the size of the interface between the top facet of the NW and the droplet, which itself depends on the droplet volume and on its contact angle with the top facet. Hence, when the Au nanodrops are formed by annealing, because of their size distribution, a range of NW diameters is obtained (ordered arrays of droplets of uniform sizes may however be deposited ex situ, for instance through a mask patterned by electron lithography). The length/diameter relationship is best determined by examining a large number of such NWs by scanning electron microscopy. It provides key information about the processes that limit the growth velocity of the NWs. For instance, the inverse relationship between length and diameter that is often observed indicates that growth is limited by the diffusion of the atoms to the NWs from the non-activated areas situated between the NWs [11].

Our NW volume measurements prove that the amount of material incorporated in the NW is larger than the amount impinging on the droplet. This confirms that part of the material reaches the top of the NW via diffusion from the substrate. In modern MBE machines the beams are inclined to the substrate normal (by about 30°), so that the NW material is also partly collected from the NW sidewalls. Initially overlooked in NW growth modelling, this fact is increasingly recognized as important [12].

In addition, individual NWs may have non-uniform diameters. The regular overall NW tapering observed at low growth temperature [6] indicates that the diffusing species tend to nucleate on the sidewalls of the NW before reaching the droplet. The localized tapering observed at higher growth temperature at the top of long NWs attests in turn that these species desorb if the NW length exceeds their diffusion length [4,12]. We sometimes observe double tapering at top and bottom; we attribute the former to a shadowing of the foot of the NW from the molecular beams by the neighbouring NWs.

2.2. Catalyst
In VLS growth, the catalyst droplet plays a critical part. Most often, the gold catalyst is first deposited as a film of roughly uniform thickness and then annealed to induce the formation of nanodroplets. Gold is usually deposited in a chamber separate from the epitaxy machine. On the contrary, we use an Au source located in the MBE chamber; this avoids any contamination of the coated substrate and significantly speeds up the fabrication cycle [4].

We have observed the catalyst particles not only after growth but also immediately after annealing,
before exposing the sample to the growth fluxes. All chemical analyses performed in the TEM reveal a mixture of gold and type-III element. Type-V atoms are not detected, for two main reasons. First, their solubility in gold is very low (a few atomic percents at most). Second, since their equilibrium pressures are rather high, they probably escape from the droplet when the latter is cooled after annealing or after NW growth. Most often, the solid droplets are truncated spheres (spherical caps), another strong indication that they have been cooled from the liquid state.

Even after mere annealing, before being exposed to the molecular beams, the particles are not pure gold. The TEM lattice images show that around each particle a few atomic layers have been removed from the top of the substrate and the corresponding type-III atoms have been incorporated in the droplet (Fig. 1). In the case of a GaAs substrate, we have identified by transmission electron diffraction (TED) that the particles are Au$_7$Ga$_2$ crystals. This gives a lower limit to the Ga-content of the annealed droplets, since some of the dissolved Ga might have been lost during cooling. This content is consistent with the common view that VLS occurs at rather low temperature (430-620°C for GaAs in our MBE system) thanks to the formation of a eutectic between the catalyst and the substrate element(s). In the present case, gold liquefies by forming a eutectic with gallium, which may happen below 400°C for Ga concentrations of about 30%.

We also analyzed the catalyst particles after growth of GaAs NWs [4]. Their composition depends much on the growth history and in particular on how growth was terminated. When the Ga and As fluxes are stopped simultaneously, we observe the Au$_7$Ga$_2$ or AuGa crystalline phases. This is consistent with composition measurements made by other authors [13]. Together with our calculation of a typical temperature drop of only a few kelvins between substrate and NW apex during growth [14], this strengthens the picture of a liquid catalyst. It is only when growth is terminated by stopping the Ga flux while maintaining the As flux during cooling that we observe almost pure gold. In this case, most of the Ga atoms of the droplet have been used to continue forming NW layers with the As atoms of the beam (see section 3.2).

**Figure 1.** TEM lattice image of the catalyst droplets deposited on a GaAs substrate, after annealing and before nanowire growth. The substrate and the solidified Au$_7$Ga$_2$ catalyst are distinguished thanks to their differently spaced lattice planes, (111) and (111) respectively. Dashes mark the top of the substrate before its local dissolution in the droplets.

### 3. Crystal structure of the nanowires

#### 3.1. Prevalence of the wurtzite phase in nanowires of cubic III-V compounds

Under bulk form, all N-free III-V semiconductors crystallize in the cubic sphalerite structure, also known as zinc blende (ZB). A surprising feature of the NWs of these materials is that they very often adopt the hexagonal wurtzite (WZ) structure. This has been observed for most ZB III-V materials and growth techniques [1,3,4,15,16].

ZB and WZ are closely related structures. Both are stacks along a given direction (*e.g.* [111]B in ZB) of identical biatomic planes, or monolayers (MLs), which differ by their transverse positions. Three such positions (A, B and C) are allowed. ZB corresponds to a periodically repeated ABC sequence, whereas WZ consists of a periodic AB stack. ZB and WZ can be identified either by TED or by high resolution TEM (HREM), as shown in the inserts of Fig. 2. In HREM images, the 3-ML periodicity of ZB is clearly distinguished from the 2-ML periodicity of WZ (Fig. 2(b)).

More complicated periodic stacks are also encountered in NWs, for instance polytypes [16]. Indeed, any aperiodic sequence is allowed, provided it does not include twice the same letter (A, B or C) consecutively. A stacking defect is a local disruption of the ZB or WZ periodicity (stacking fault).
or a boundary between differently oriented grains of the same phase. Although often dominantly of WZ structure, the NWs usually contain stacking faults and sequences of ZB structure (Fig. 3(a)). Since the coexistence of two phases impedes basic studies as well as applications, phase purity control has become one of the main challenges of III-V NW fabrication.

The prevalence of WZ (a high pressure phase observed in no other nanostructure) in NWs of III-V cubic materials is surprising. Until recently, its formation had not been explained satisfactorily. The difference in cohesive energy between ZB and WZ bulk III-V materials is typically of a few tens of meV per III-V pair (24 meV for GaAs). Several \textit{ab initio} calculations have shown that the total energy of NWs can indeed be lower in the WZ structure than in the ZB structure because of a lower specific energy of some specific sidewall facets \cite{17-19} or of their vertical edges \cite{20}. However, for the contributions of these 2D or 1D features to compensate the difference in bulk cohesive energies, the NWs must be very thin: the calculated critical radii under which WZ might be favoured over ZB are only of a few nm, whereas WZ is observed in NWs up to radii of several 100 nm.

Moreover, the standard theories of NW formation are based on nucleation \cite{21-23} and the occurrence of planar faults normal to the NW axis (see e.g. Figs. 2(c) and 3(a)) suggests that, once a nucleus of critical size forms at the solid/liquid interface, it rapidly spreads out laterally over the whole interface \cite{5,16} unless the wire is very wide \cite{23}. Hence, the reason for the formation of WZ must be searched for in the formation of WZ nuclei rather than in the total energies of fully constituted NWs. This is done in sections 3.2 and 3.3, where we consider the specific case of GaAs.

### 3.2. TEM observation of the systematic formation of zinc blende sections in wurtzite nanowires

Although WZ is largely prevalent in GaAs NWs, TEM demonstrates that ZB forms systematically during two particular stages of the growth. The first one corresponds to the very beginning of growth. By growing GaAs NWs for only a few seconds, we could observe the foot of each wire before its burying by the growth of the non-activated surface. The samples were thinned to obtain cross-sectional views, with the NWs still epitaxially attached to their substrate. The images identify unambiguously ZB as the sole phase formed in this initial stage (Fig. 2(a)). When the NW height reaches about 30 nm, growth switches abruptly to WZ stacking (Fig. 2(b)).

The second case where ZB forms systematically is when we terminate MBE growth by switching off the Ga flux while maintaining an As flux during cooling. Over a few tens of nm, the final section of the NW is of cubic structure (Fig. 2(c)). Persson \textit{et al.} had already reported the formation of a short terminal ZB section in the case of chemical beam epitaxy, when growth was terminated under As only \cite{3}. In both cases, growth continues in the absence of a fresh supply of Gallium by consuming the Ga atoms present in the drop, whereas As can only be provided by the beam (see section 2.2). Since the volume and the base area of the drop then decrease, the final section of the NW is tapered (Fig. 2(c)).

Our TEM experiments reveal that ZB forms systematically in two transient growth regimes during which the supersaturation in the liquid droplet (with respect to the solid) is less than during steady NW growth. Before growth, the deposited undersaturated Au droplets dissolve the substrate locally to achieve equilibrium with it (Fig. 1), and hence zero supersaturation. When vapour fluxes are turned on, the supersaturation increases until a permanent regime settles. The opposite happens during growth termination: then, the Ga concentration in the droplet, and hence supersaturation, decrease, since the atoms used to build the final NW MLs are not replaced. This shows that ZB systematically forms when the supersaturation is less than some critical value and suggests that, conversely, WZ formation requires a high supersaturation.

### 3.3. Nucleation at the triple phase line and wurtzite formation: a TEM-supported explanation

Following arguments developed by Ostwald at the end of the 19th century \cite{24}, the basic idea is that the phase that forms is not necessarily the stable bulk phase (ZB) but the one having the lowest nucleation barrier $\Delta G^\phi$, because the main dependence of the nucleation probability at temperature $T$ is in $\exp(-\Delta G^\phi/k_BT)$. The formation of WZ may thus be searched for in its lower nucleation barrier as compared with ZB. Standard nucleation theory \cite{25} gives the energy barrier for the formation of a 2D
solid nucleus of radius \( r \) and height \( h = 1 \) ML of a given phase \( \phi \) on the NW top facet:

\[
\Delta G^\phi = -ar^2h\Delta \mu^\phi + bhr^\phi + ar^2\gamma_{SN}^\phi
\]  

(1)

where \( a \) and \( b \) are shape-dependent coefficients (\( a=\pi \) and \( b=2\pi \) for a disk), \( \Delta \mu^\phi > 0 \) is the difference of chemical potential between liquid and solid per unit volume of solid, \( \gamma_{SN}^\phi \) is the interface energy between the top facet of the NW and the nucleus, and \( \gamma_i^\phi \) is the specific energy of the lateral interface between the nucleus and its environment.

Figure 2. (a) TEM image of a very short GaAs NW with HREM close-up showing the pure ZB structure (s: substrate, c: catalyst). (b) A short GaAs NW soon after the ZB \( \rightarrow \) WZ transition, with HREM image of the transition zone. (c) When growth is terminated under As only, the final tapered section of the GaAs NW (above dashed line) is pure ZB (with a stacking fault, pointed by arrow): the TED pattern from the main body of the NW (left) shows only WZ whereas the pattern from an area including also the terminal section (right) shows a superposition of WZ and ZB (arrowed spots).

We argued elsewhere that, whatever the crystalline phase, nucleation at the triple phase line (TPL), the border of the top facet of the NW (where solid, liquid and vapour coexist), is strongly favoured with respect to nucleation anywhere else on the top facet [26]. The reason is simply that, in the former case, part of the pre-existing liquid-vapour interface is destroyed and replaced by a nucleus-vapour interface. Then, \( \gamma_i^\phi = (1-\alpha)\gamma_{LV}^\phi + \alpha(\gamma_{LV}^\phi - \tau\gamma_{LV}) \), where \( \alpha \) is the fraction of the nucleus perimeter in contact with the vapour, \( \gamma_{LV}^\phi \) and \( \gamma_{LV} \) are the specific energies of the lateral nucleus-liquid and nucleus-vapour interfaces, \( \gamma_{LV} \) the liquid-vapour interface energy and \( \tau \approx 1 \) a factor accounting for the droplet geometry at the TPL [26]. Hence, nucleation at the TPL (\( \alpha \neq 0 \)) may considerably reduce the nucleation barrier \( \Delta G^\phi \). This is somewhat supported by recent in situ TEM experiments which
show that Si crystals tend to nucleate at the edge of Au-Si droplets deposited on a membrane [27-28].

To compare the free energies of formation of ZB and WZ nuclei at the TPL, one may consider that, because of the difference in cohesive energies, $\Delta \mu^\theta$ is lower for WZ than for ZB. However, a 2D nucleus is not intrinsically of ZB or WZ structure. In accordance with the description of ZB and WZ as different stacking modes of otherwise identical MLs, it is only the lateral positioning of the nucleus that decides if the sequence formed with the underlying MLs is locally of WZ or of ZB type [26]. Thus, it is preferable to use the same $\Delta \mu^\theta$ in Eq. (1) for ZB and WZ and two different NW/nucleus interface energies $\gamma_{SN}^{ZB} = 0$ and $\gamma_{SN}^{WZ} > 0$ (the two approaches are equivalent since both contributions vary as $r^2$). Maximizing $\Delta G^\theta$ with respect to $r$ yields the radii of the critical nuclei of the two phases (or, rather, for nucleation in ZB and WZ positions) and the corresponding nucleation barriers $\Delta G_c^\theta$:

$$\Delta G_c^{ZB} = b \frac{h (\gamma_{SN}^{ZB})^2}{4\Delta \mu}, \quad \Delta G_c^{WZ} = b \frac{h (\gamma_{SN}^{WZ})^2}{\Delta \mu - \gamma_{SN}^{WZ}}$$  \hspace{1cm} (2)

Eq. (2) shows that there are two conditions for the critical nucleus in WZ position to have a lower free energy of formation than the nucleus in ZB position. The first one is material-related: one must have $\gamma_{SN}^{WZ} < \gamma_{SN}^{ZB}$. Careful consideration of the atomic arrangements for the ZB and WZ nuclei positions indicates that this difference is not likely to arise from differences at the nucleus-liquid interface [26], although this may also play a part [29]. On the other hand, the nucleus-vapour interfaces that form during nucleation at the TPL are clearly different and the corresponding energy may be lower for the WZ nucleus position [26], as also suggested by calculations showing that the specific energies of some extended facets are lower for WZ than for ZB [17-19]. From Eq. (2), there is however a second condition for WZ nucleation to be favoured, namely that the supersaturation be high enough to overcome the larger NW-nucleus interface energy:

$$\Delta \mu \geq \Delta \mu_c = \frac{(\gamma_{SN}^{ZB})^2}{(\gamma_{SN}^{ZB})^2 - (\gamma_{SN}^{WZ})^2} \frac{\gamma_{SN}^{WZ}}{h}$$  \hspace{1cm} (3)

To summarize, the frequently observed formation of the WZ phase in NW of cubic III-V materials is due to the preferential formation of nuclei in WZ lateral position at the triple phase line. This preferential formation in turns results from a lower energy of the edge of the nucleus when it is in WZ position as compared with ZB position. This condition recalls the arguments based on total energy calculations for fully formed NWs [18,20]. However, at variance with the latter purely thermodynamic explanation, ours is intrinsically kinetic, in that it is based on barrier-height-dependent nucleation probabilities. This kinetic character is also manifested by our second condition for WZ formation, namely the existence of a lower critical value of the chemical potential difference between liquid and solid. Even with differences $\gamma_{SN}^{ZB} - \gamma_{SN}^{WZ}$ as low as a few tens of mJ m$^{-2}$, we find that differences $\Delta \mu$ of the order of a few hundreds of meV per III-V pair are sufficient to promote WZ nucleation. This is indeed the order of the differences of chemical potential between vapour and solid that we estimate for our MBE growth conditions, although the actual $\Delta \mu$ between liquid and solid remains unknown.

The nucleation of each new ML has a probabilistic character. The formation of a stacking defect in WZ (Fig. 3(a)) may thus be interpreted as arising from the chance nucleation of a single ML in ZB position, occurring because $\Delta \mu$ is not sufficient to insure a near certain nucleation in WZ position. On the other hand, WZ formation requires nucleation of each ML in WZ position. This opens prospects of single-phase growth, by setting high supersaturation conditions for pure WZ or, alternatively, low
supersaturation for pure ZB. However, our efforts in this direction have not been successful yet. In particular, supersaturation cannot be lowered under a limit below which the NWs cease to grow.

Nevertheless, several TEM-based results from other groups strengthen our arguments. Following the latter, Shtrikman et al. managed to obtain pure ZB GaAs NWs in MBE by deliberately attempting to achieve a low supersaturation [30]. Caroff et al. noticed that, in InAs NWs grown by MOVPE, the proportion of the WZ phase increases at low growth temperature [31]. We propose that this can be due to the increase of both the chemical potential difference $\Delta \mu$ and the relative difference of nucleation probabilities at low $T$. Conversely, if the material and supersaturation conditions are such that ZB formation prevails, lowering the temperature may again increase the difference of nucleation probabilities, this time in favour of ZB, and hence reduce the density of stacking defects, as observed by Johansson et al. [5] and Joyce et al. [32].

4. Phase transformation upon epitaxial burying

Despite some successes, it remains very difficult to fabricate reproducibly single-phase III-V NWs in a single growth operation. We have however devised a method to transform highly faulted hexagonal WZ GaAs NWs into perfect cubic ZB ones [33].

4.1. Experiments

The method is based on deliberately altering the relative growth rates of the NWs and of the non-activated substrate by changing the growth temperature $T_G$. Whereas in our standard growth conditions, for $T_G \leq 620^\circ C$, the NWs grow faster than the non-activated substrate (section 1), the reverse holds at $T_G \geq 620^\circ C$, so that any previously grown NW will get buried by the substrate.

![Figure 3](image.png)

**Figure 3.** (a) TEM image of an unburied NW, with horizontal striations due to stacking defects. (b) HREM image of a partially buried NW (with low resolution inset). In the buried part, the dashed line marks the vertical interface between burying layer (BL) and NW (right). (c) Image of a fully buried NW. Note the absence of striation. (d) HREM image of the interface between NW, shell and burying layer after complete burying.

The standardly-grown NWs have the WZ structure with a high density of stacking defects (Fig.
3(a)). We first wrap them in a nm-thick protective Al$_{x}$Ga$_{1-x}$As shell to prevent their disappearance at elevated temperature. Because it results from epitaxial nucleation on the sidewalls of the NWs, the shell adopts the latter’s WZ structure. By increasing the growth temperature to 640 °C, we then shift to a regime where the supporting non-activated cubic GaAs substrate grows faster than the wires, effectively burying them. The whole sequence is carried out in the same MBE chamber.

The samples were examined by TEM at various stages of the burying process. We first notice that the burying layer naturally adopts the cubic ZB structure of the GaAs substrate from which it grows. Examination of partially buried NWs (Fig. 3(b)) shows that the part emerging from the burying layer has not changed: it is still WZ with stacking defects. However, below the top level of the burying layer, the material is entirely of cubic structure. This means that the buried portion of any NW has changed to ZB. Hence, the growing non-activated substrate transforms the buried portion of the NW from WZ to ZB. This phase transformation is very fast, since the phase boundary is right at the level of the top ML of the burying layer (Fig. 3(b)).

Further growth leads to complete burying. Each NW can still be localized via the faint contrast of its AlGaAs shell (Fig. 3(c)). TED and HREM images (Fig. 3(d)) confirm that the whole sample is pure ZB. The burying is very efficient, in that it eliminates all the stacking faults (Fig. 3(c,d)). We thus end up with perfect cubic NWs embedded in a cubic matrix. Thanks to the AlGaAs shell, each NW retains its one-dimensional character.

4.2. The mechanism of the phase WZ → ZB phase transformation as revealed by HREM

Our TEM experiments on partially buried NWs show that, when the burying material reaches the periphery of a NW, it transforms the hexagonal structure of the latter into its own cubic one (Fig. 3(b)). To understand how TEM may also reveal the microscopic mechanism of the phase transformation, we must consider the burying process in more detail. First recall that, along the [111]$_B$ ZB or [0001] WZ direction, any type-III atom sits directly above the underlying type-V atom. The A, B, or C character of each III-V ML is therefore determined by the lateral positioning of its type-V atoms [26]. Let us assume that the burying layer has already transformed the lower part of the NW to its ZB stacking (Fig. 4(a), stage $\alpha$) and consider how the next sequence of six yet unburied WZ MLs may transform into ZB.

When the advancing top ML of the burying GaAs reaches the NW sidewall (Fig. 4(a), $\alpha$), the As atoms in the burying ML and in the corresponding ML of the NW are not in lateral registry. This fault in the NW (with respect to ZB) can be eliminated by a rigid shift of the emerging part of the NW (As plane included), which brings two more MLs in ZB position (Fig. 4(a), $\beta$). When the burying layer reaches the level of the next fault, two MLs above the previous one (Fig. 4(a), $\gamma$), the process repeats (Fig. 4(a), $\delta$), and so on every other ML. Three shifts suffice to transform 6 MLs (Fig. 4(a), $\epsilon, \phi$).

The lateral contact between the top burying ML and the out-of-registry NW ML produces a Shockley partial dislocation (albeit only partly surrounded by material). Since our NWs have vertical sidewalls parallel to the six \{10\overline{1}0\} WZ (\{\overline{2}11\} ZB) planes, the edges of the NW ML are \{1\overline{1}0\}-oriented. The Burgers vector of the partial dislocation is one of three translations allowed at each step, namely $\frac{1}{2}$[211] or $\frac{1}{2}$[121] or $\frac{1}{2}$[112] (or the complementary set, depending on the ZB variant). As the dislocation glides along the (111)B plane into the NW, the As atoms shift into ZB position. This translation of the whole As layer fully eliminates dislocation and stacking fault [33].

A type II transformation may also be imagined, whereby only one or two MLs of the NW are translated at each step, all other MLs retaining their lateral positions (Fig. 4(b)). The same partial dislocation is initially generated (Fig. 4(b), $\alpha$) but the first step of the process is now the translation of the sole NW ML that it borders (Fig. 4(b), $\beta$). This eliminates the fault in this ML but produces a characteristic twin-like ABCBA sequence [34]. The next two NW MLs cannot be translated before the third one, which occurs when the burying material reaches its level (Fig. 4(b), $\gamma$), again by translation of a single ML, producing a “double-twin” BCBAC sequence (Fig. 4(b), $\delta$). Finally, the two already
buried intermediate MLs can transform (Fig. 4(a), \(\varepsilon,\varphi\)), albeit only if they are not yet entirely surrounded by the burying layer or if they can exchange atoms. The latter reservations make the type II process less likely than the type I.

\[\text{Figure 4.} \text{(a,b) Schematics of the transformation of a WZ nanowire into ZB. Type I (a) and II (b) processes for the transformation of the 6 MLs located between the dashed lines. Greek letters index the successive stages of each process. Each coloured rectangle represents a monolayer of the substrate (S) or NW. Its lateral position is colour-coded (see insert). Arrows give the step flow direction. (c) Fourier-filtered HREM image of the interface between the transformed and untransformed parts of a nanowire. The arrow marks the topmost ML in the ZB sequence. (d) Schematics of the transformation of a NW ML from WZ to ZB stacking positions (top view). The area not yet translated is shaded. Solid lines track the glide of the partial dislocation initially formed (dashed line) at the boundary between burying and NW MLs.}\]

These two types of transformation of WZ into ZB can be distinguished by HRTEM via differences in stacking sequences at the interface between the untransformed and transformed parts of the NW. We first identify the topmost NW MLs that have already adopted the ZB stacking (Fig. 4(c)). At any stage of a type I process (Fig. 4(a)), the next NW MLs repeat the last two MLs of the ZB sequence (e.g. ABCABC/BCBC... at stage \(\delta\)) whereas during a type II process (Fig. 4(b)), the same sequence is found only at stage \(\alpha\) or \(\varphi\) (ABCAB/ABAB...), other well-defined twin-like sequences occurring at stages \(\beta\) to \(\varepsilon\). In the many HRTEM images examined, we found only the stacking sequence characteristic of the type I process (Figure 4(c)) and no evidence of the other sequences occurring in a type II process. This indicates that, at least for GaAs and in our burying conditions, type I is the dominant transformation mechanism, if not the only one.

4.3. Interpretation
The driving force for the type I phase transformation is the joint elimination of the partial dislocation that forms at the NW/burying material boundary and change of structure of the NW from WZ to ZB. The length of the partial dislocation segments formed between burying layer and NW and the area of the faulted interface between the transformed and untransformed parts of the NW determine the system energy. Fig. 4(d) describes schematically how these change during the transformation of each ML. As overgrowth proceeds, the NW sidewalls get surrounded by the top burying ML extending by step flow and the partial dislocation is generated at the periphery of the corresponding hexagonal-shape NW ML. As soon as the dislocation forms along at least two sides of the hexagon, any of its
parts can glide inward without any length increase and therefore, without any energy increase. The area of the NW ML swept by the dislocation transforms to ZB stacking with respect to the underlying ZB portion of the NW. We calculate that eliminating the fault corresponds to a decrease of energy of about 28 mJ m\(^{-2}\) \[34\]. Hence, the total energy of the defects decreases continuously during each elementary step of the transformation (Fig. 4). Of course, when a NW ML is already in the correct ZB position, no dislocation is created and hence no driving force for translating the upper part of the NW. This happens in particular when there is a stacking defect or a ZB segment in the yet unburied WZ NW and explains why all such pre-existing defects (Fig. 3(a)) get eliminated (Fig. 3(c)).

According to this simple analysis, there is no energy barrier to the transformation, in agreement with the fact that the translation of the whole ML occurs very soon after the burying layer reaches it, which leads to abrupt horizontal interfaces between the transformed and untransformed parts of the NW (Figs. 3(b) and 4(c)). In addition, there is no critical NW radius for the transformation, which explains why the structure of any NW shifts to ZB. The NW geometry makes the WZ \(\rightarrow\) ZB transformation much easier than in bulk samples where, even for the type I transform, there is a barrier corresponding to the nucleation of a transformed domain of finite critical size \[35\]. Here, the dislocation is formed when the burying layer reaches the NW, and nothing hinders the translation of the top part of the NW. Since three translation (Burgers) vectors adding to zero are allowed, the net tilt of each NW remains nearly null (Fig. 3(c)). The former analysis however neglects the Peierls barrier impeding the glide of the partial dislocation, which might kinetically limit the transformation. This might be responsible for the incomplete transformation that we tend to observe in InP NWs.

5. Thermodynamics and kinetics of heterostructure formation in NWs

Nanowires are particularly interesting in that they allow the fabrication of precisely positioned quantum dots with well-defined geometries. In this section, we consider the formation of heterostructures in NWs as regards strain relaxation and crystalline structure.

5.1. Critical dimensions for mismatched axial heterostructures in nanowires

A major advantage of NWs appears when one compares the growth of a given misfitting material on a bulk substrate and on an already grown NW base. In the latter case, the heterostructure is termed axial to distinguish it from radial (core-shell) heterostructures. For a given substrate/layer misfit, the critical thickness for plastic relaxation is always larger in the NW case because the sidewalls allow the strains efficiently to relax \[36\], all the more if the NW diameter is small. Moreover, for each material couple, there exists a critical NW radius below which the critical thickness becomes infinite, which allows the growth of arbitrarily thick layers. We derived simple formulas for the radius-dependent critical thickness and for the critical radius \[36\]. The former are consistent with our own TEM experiments (e.g. the absence of dislocation in the long insertions of Fig. 5) and with the limited amount of experimental data available in the literature.

5.2. Fault suppression and structural phase changes at an axial hetero-interface

In VLS growth, sharp axial heterostructures are invariably fabricated by switching the type-V element (or modifying the fluxes of several type-V elements) because the type-III element, present in high concentration in the droplet (see section 2.2), tends to be incorporated even after its supply from the vapour phase is interrupted (see section 3.2). Changing the fluxes changes the thermodynamic growth conditions and may have profound effects not only on the composition of the grown material but also on its structure. We indeed frequently observe structural changes at hetero-interfaces.

A first example is given by a double InP/InP\(_{1-x}\)As\(_x\)/InP axial heterostructure (Fig. 5(a)). A thick InP shell was later grown around the thin NW core. In the core, InP and InP\(_{1-x}\)As\(_x\) (\(x \sim 0.35\)) both adopt the WZ structure. However, whereas InP is highly faulted, the InPAs insertion is free from any extended defect. Note that the stacking defects created during growth of the InP core propagate laterally in the WZ shell whereas the InP shell around the InPAs insertion is defect-free. The reason is that the shell material nucleates on the NW sidewalls, at variance with the burying material considered in section 4.
In light of the discussion of section 3.3, the high density of faults in the WZ InP core indicates that the difference of chemical potential $\Delta \mu$ is high enough to favour WZ but not sufficient to insure that each ML will nucleate in WZ position. On the contrary, the absence of any fault even in long InPAs insertions (Fig. 5(b)) indicates that, in this case, the probability for nucleation in ZB position is negligible. Since the insertion is grown by adding an As flux to an unchanged P flux, it is tempting to attribute this effect to an increased $\Delta \mu$. However, the deposited solid changes, and even though the liquid is still mainly Au-In, its composition might also change (as happens in chemical beam epitaxy [37]), so that the relation between the fluxes and $\Delta \mu$ is far from straightforward. Moreover, the contribution of the type-V elements to the chemical potential in the liquid is unknown. In addition, over and above the chemical potential condition, the balance between WZ and ZB nucleation also depends on the edge energy $\gamma_l^\phi$ of the nucleus, as discussed in section 3.3. When nucleation occurs at the TPL, the edge is partly in contact with the vapour and the surface energies (and reconstructions) of III-V materials are known to depend on the vapour fluxes [38]. The changes of chemical potential and edge energy might thus both play a part in the absence of fault in the alloy segment.

The formation of the heterostructure may have an even more striking effect: when a GaAs$_{1-x}$Sb$_x$ alloy is grown axially above a GaAs WZ NW base, it adopts the ZB structure [39]. In this case, we observed by TEM that, in the GaAs cap above the insertion, the transition to (faulted) WZ is not abrupt but involves a section of the 4H polytype. Since in the latter, half the MLs nucleate in ZB position and the other half in WZ position, this phase can be considered as intermediate between ZB and WZ [34]. It seems more likely that such a delayed ZB $\rightarrow$ WZ transition is due to a gradual return of the chemical potential in the droplet to its pre-insertion value after the Sb flux is stopped, rather than to a surface effect which probably follows the changes of fluxes more closely in time.

Figure 5. (a) TEM bright field image of an InP$_{1-x}$As$_x$ axial insertion about 100 nm high in an InP NW. The NW core diameter during axial growth (about 12 nm) is indicated by dashed lines and the hetero-interfaces by horizontal black arrows. The whole core was subsequently wrapped in a thick InP shell (double-ended white arrows). The contrast along the vertical edges of the insertion is due to strain relaxation. (b) A long fault-free InP$_{1-x}$As$_x$ insertion in a sample of similar structure.

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