Wurtzite phase control for self-assisted GaAs nanowires grown by molecular beam epitaxy

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Received 29 October 2020, revised 27 December 2020
Accepted for publication 11 January 2021
Published 25 January 2021

Abstract
The accurate control of the crystal phase in III–V semiconductor nanowires (NWs) is an important milestone for device applications. Although cubic zinc-blende (ZB) GaAs is a well-established material in microelectronics, the controlled growth of hexagonal wurtzite (WZ) GaAs has thus far not been achieved successfully. Specifically, the prospect of growing defect-free and gold-catalyst-free wurtzite GaAs would pave the way towards integration on silicon substrate and new device applications. In this article, we present a method to select and maintain the WZ crystal phase in self-assisted NWs by molecular beam epitaxy. By choosing a specific regime where the NW growth process is a self-regulated system, the main experimental parameter to select the ZB or WZ phase is the V/III flux ratio. Using an analytical growth model, we show that the V/III flux ratio can be finely tuned by changing the As flux, thus driving the system toward a stationary regime where the wetting angle of the Ga droplet can be maintained in the range of values allowing the formation of pure WZ phase. The analysis of the in situ reflection high energy electron diffraction evolution, combined with high-resolution scanning transmission electron microscopy (TEM), dark field TEM, and photoluminescence all confirm the control of an extended pure WZ segment, more than a micrometer long, obtained by molecular beam epitaxy growth of self-assisted GaAs NWs with a V/III flux ratio of 4.0. This successful controlled growth of WZ GaAs suggests potential benefits for electronics and opto-electronics applications.

Supplementary material for this article is available online

Keywords: nanowires, molecular beam epitaxy, wurtzite, VLS, GaAs, wetting angle, RHEED

(Some figures may appear in colour only in the online journal)
observed in bulk GaAs. Controlling the crystal phase in such materials would be an important achievement for device applications. WZ and ZB phases exhibit distinct optical [3–5], electronic [6] and piezoelectric [7, 8] properties, and a slightly different electronic band structure [9]. The development of a wide range of heterostructures such as quantum dots or monolayer (ML) thin quantum disks and superlattices [10] is also promising.

The ZB phase is mostly obtained in self-assisted GaAs NWs, while the WZ phase mainly occurs in their gold-catalyzed counterparts. Recent studies explained the growth mechanism of the ZB and the WZ phases as depending on the position of the nucleation point of a new ML, either inside the catalyst droplet for the ZB phase or at the triple phase line for the WZ phase [2, 11–15]. Moreover, it has been shown that the position of the nucleation point highly depends on the contact angle of the catalyst droplet, and thus on the size of the catalyst droplet [16–19]. Recent experimental studies highlighted a critical contact angle \( \beta_1 \) in the 121°–124° range for the gold-catalyzed GaAs NWs [16, 17], and in the 125°–127° range for the self-assisted ones [18, 19], above which the transition from the WZ to ZB phase occurs. Very recently, Panciera et al experimentally observed a second critical angle \( \beta_2 \) in the 85°–100° range, below which a transition from WZ to ZB phase occurs in self-assisted GaAs NWs [19]. In situ transmission electron microscopy (TEM) studies performed by Jacobsson et al highlighted the presence of truncated facets at the top facet of the NWs for wetting angles greater than \( \beta_1 \), forcing a nucleation inside the catalyst droplet and thus the growth of the ZB phase [16]. The contact angle of the droplet depends directly on its volume, which is mainly function of the growth parameters, and more particularly the Ga and As fluxes in the case of self-assisted GaAs NWs. Thus tuning the Ga and/or the As fluxes to obtain the desired crystal phase, WZ or ZB, has been reported in several studies [12, 14, 18, 20–24].

In order to achieve a precise control on the droplet volume and hence on the contact angle, an in situ monitoring technique is highly desirable. Recent studies report on the use of in situ TEM to characterize and control the growth of gold-catalyzed GaAs NWs [16, 17], and of self-assisted GaAs NWs [19]. However, despite tremendous progress in the development of in situ TEM over the last decade, monitoring materials in their real growth environment and growth conditions is still to be achieved for, e.g. the growth of NWs in standard molecular beam epitaxy (MBE) reactors. Reflection high energy electron diffraction (RHEED) on the other hand, is directly coupled to MBE reactors and used to characterize the structural properties during growth. To date only a few studies report on the use of RHEED for the growth of self-assisted GaAs NWs. For instance, RHEED has only been used to investigate the consumption of the catalyst droplet at the end of the growth [25], while Bastiman et al reported on the incubation time for the growth of the GaAs NWs [26]. The use of RHEED as an in situ characterization tool of the growth of NWs coupled with numerical simulations has been reported recently by Jakob et al [27]. Jo et al and Dursap et al have coupled RHEED data with post mortem TEM measurements to characterize the crystal phase of catalyst-free InAs NWs [28] and of self-assisted GaAs NWs [29], respectively.

During the preparation of this manuscript, Jansen et al [30] reported on the growth of extended WZ structure of self-assisted GaAs nanowires, and confirm our experimental results reported in [31]. While Jansen et al carried out the growth of self-assisted GaAs NWs by controlling the Ga flux on prepatterned substrates, we managed to obtain an extended WZ segment on non-patterned substrates by tuning the As flux.

In this work, we achieve the growth of self-assisted GaAs NWs with an extended pure WZ segment, controlled by in situ RHEED and supported by simulations. We demonstrate the existence of WZ growth conditions to maintain a constant contact angle of the Ga droplet in a desired range using a fine tune of the As flux. The growth of the WZ crystal phase was confirmed with TEM and PL measurements.

### Conditions for the self-assisted NW growth in the WZ phase

It is well-known that for the self-assisted GaAs growth, the ZB or WZ phase of the NWs is determined by the wetting angle [2], \( \beta \), defined schematically in the inset of figure 1. For instance, when the Ga flux is suppressed and the As atoms feed the droplet by direct impingement, the wetting angle of the droplet decreases and the crystal structure evolves from

![Figure 1. Values of the wetting angle \( \beta \) obtained for NWs with \( r = 50 \) nm for various V/III flux ratio. The area highlighted with the yellow circle represents the conditions for the NW growth (V/III flux ratio = 2.4 at \( q_{Ga} = 3.53 \) atm nm\(^{-2}\) s\(^{-1}\)) in the first 25 min. The experimental values of the wetting angle obtained on tens of NWs after an extended WZ growth of 5 min, 10 min and 20 min are represented with the blue star, triangle and diamond, respectively. Additional figures for \( r = 40 \) nm and \( r = 60 \) nm are presented in the SI figure S1.](image-url)
the ZB to WZ phase, and then back to the ZB phase. Experimental results in Panciera et al [19] show that the WZ phase is obtained for a wetting angle in the (approximate) 90°–125° range. The main question we address here is the following: is it possible to provide values for the V/III flux ratio that ensure a fixed wetting angle in the 90°–125° range, thus ensuring the growth of the WZ phase?

The positive answer to this question is a consequence of the general remark that the self-assisted NW growth is a self-regulated system [32]. Under fixed values of As and Ga fluxes the NW radius, the droplet size, and the wetting angle evolve toward stationary values, a situation in which the amounts of Ga and As atoms feeding the droplet are equal. However, this ‘constant growth regime’ may be attained only once the NW length overcomes a first-stage ‘transient’ regime.

Previous results [20, 32–35] on the self-assisted GaAs NW growth show that the Ga atoms are supplied to the droplet through three different sources: diffusion on the SiO2 terminated substrate, diffusion along the NW facets, and direct impingement of the Ga flux on the droplet surface. Meanwhile, the single source of As atoms is the direct impingement on the droplet surface. Recent experimental results obtained by using two Ga sources with different orientations with respect to the substrate [32] show that the contribution from the on-substrate diffusion disappears when the NW length overcomes the diffusion length on the NW facets, which is typically in the 1–2 μm range. For this reason, our experimental procedure starts by a so-called ‘standard’ self-assisted NW growth using a V/III flux ratio equal to 2.4, with a Ga growth rate of 0.5 ML s⁻¹, quoted in units of equivalent growth rates of GaAs 2D layers measured by RHEED oscillations on a GaAs substrate [36], for 25 min, and provides NWs longer than 2 μm. Beyond this length, the Ga supply from the on-substrate diffusion can be neglected, and thus the equal amount of Ga and As atoms supplied to the droplet can be expressed as:

\[ S(\alpha_{Ga}, \beta, r) q_{Ga} + 2r \lambda_{ facets} \sin(\alpha_{Ga}) q_{Ga} = S(\alpha_{As}, \beta, r) q_{As}, \]

(1)

where \( q_{Ga} \) and \( q_{As} \) are the nominal fluxes of Ga (and As), \( \alpha_{Ga} \) and \( \alpha_{As} \) are the angles of the Ga source (As source) with respect to the normal to the substrate, \( r \) is the NW radius, \( \lambda_{ facets} \) is the diffusion length of Ga atoms along the NW facets, and \( S(\alpha, \beta, r) \) is the projected area of a droplet with wetting angle \( \beta \) sitting on top of a NW with radius \( r \) on the plane normal to the flux direction, as given by Gläs et al [37].

The first terms on both sides of (1) represent the droplet supply by direct impingement, while the second term in the left-hand side (LHS) represents the amount of Ga atoms feeding the droplet by diffusion on the NW facets.

Formula (1) also explains why the system is self-regulated: in the As-rich regime, the right-hand side (RHS) in (1) is larger than the LHS so that the droplet volume decreases. Therefore, the wetting angle decreases also down to a value for which the difference between the direct impingement terms is balanced by the surface diffusion term. In the Ga-rich regime, the volume of the droplet increases, and so does the wetting angle. As both direct impingement terms increase and the V/III flux ratio is >1, the RHS increases faster than the LHS. In both situations, the evolution of the system tends to a stationary growth regime.

If the source orientations \( \alpha_{Ga} \) and \( \alpha_{As} \) are known, for a given radius \( r \) and diffusion length \( \lambda_{ facets} \), a wetting angle \( \beta \) (90°–125°) can be achieved by using the V/III flux ratio given by:

\[
\frac{q_{As}}{q_{Ga}} = \frac{S(\alpha_{Ga}, \beta, r) + 2r \lambda_{ facets} \sin(\alpha_{Ga})}{S(\alpha_{As}, \beta, r)} = \frac{S(\alpha_{Ga}, \beta, 1) + 2 \gamma \sin(\alpha_{Ga})}{S(\alpha_{As}, \beta, 1)},
\]

(2)

where the last equality holds since \( S(\alpha, \beta, r) \) is quadratic with respect to \( r \), and \( \gamma \) denotes the number \( \lambda_{ facets} \). This equation also shows that a fixed V/III flux ratio leads to different wetting angles for different NW radii, so that the ideal situation is the monodisperse case. Using the model that accounts for the droplet evolution and a variable NW radius presented in Vettori et al [32], the numerical value of \( \lambda_{ facets} = 1.8 \mu m \), and our reactor settings \( (\alpha_{Ga} = 28^\circ, \alpha_{As} = 41^\circ) \), we compute the values for \( \beta \) \( (\beta_{Ga}, \beta_{As}) \), further called asymptotic as they equilibrate the amount of Ga and As atoms for various radii and V/III flux ratios.

Figure 1 illustrates the asymptotic values of the \( \beta \) angle for a large range of \( (q_{As}, q_{Ga}) \) couples. The yellow circle on the left side of figure 1 (V/III flux ratio = 2.4 and \( q_{Ga} = 3.53 \) atm nm⁻² s⁻¹) represents the standard conditions used to initiate the growth process and to overcome the 2 \( \mu m \) NW length during the first 25 min of the experiment. As indicated in figure 1, for a V/III flux ratio greater than 4, the asymptotic value of the wetting angle is lower than 125°. However, larger values of the V/III flux ratio stop the VLS growth process due to the extinction of the droplet.

Scanning electron microscope (SEM) images of a typical sample after a standard 25 min growth is shown in figures 2(a) and (b). The NWs grown were about 2.7 ± 0.2 \( \mu m \) long with a diameter in the 90–100 nm range and a density close to 2 \( \mu m \)⁻². The wetting angle was measured to be close to 140°, in accordance with Panciera et al [19] and the expected value circled in yellow in figure 1. The typical RHEED pattern obtained along the [1-10] azimuth at the end of the self-assisted GaAs NW growth, i.e. after closing the Ga and As shutters, is illustrated in figure 2(c). The visible diffraction spots are uniquely that of the twin planes of the ZB structure. An indexed RHEED diagram is provided in figure S2 of the supporting information (available online at stacks.iop.org/NANO/32/155602/mmedia).

Thus, the numerical implementation of the model suggests the following recipe: a first VLS growth stage using the standard conditions (ZB phase) in order to overcome the transient regime due to the on-substrate diffusion, followed by an increase of the V/III flux ratio from 2.4 to a value between 4 and 7. We notice that for large diameter NWs the VLS growth process stops, while for NWs with diameters smaller than a critical threshold the VLS growth continues with a wetting angle \( \beta > 125^\circ \). However, considering a typical diameter distribution, we estimate that about 90% of the
sample will switch from ZB phase to a stationary growth in the WZ phase.

**Experimental evidences of the extended WZ phase**

The stationary growth of the WZ phase was followed in real time using *in situ* RHEED, and the evolution of the RHEED pattern was continuously recorded during the growth of the extended WZ segment. The intensities of the ZB and WZ spots were then extracted in order to obtain the evolution of the RHEED intensity ratios (IR) $\frac{I_{ZB}}{I_{ZB} + I_{WZ}}$ and $\frac{I_{WZ}}{I_{ZB} + I_{WZ}}$ during the growth, referred thereafter as ZB IR and WZ IR respectively. Figure 3(a) illustrates the ZB IR and WZ IR obtained during a 20 min growth with a V/III flux ratio = 4.0, following the 25 min growth with the standard conditions. The horizontal axis represents the growth time under high-As flux. The moment when the As flux increases is designated by $t = 0$ s. The WZ IR starts to rise around 20 s after the increase of the As flux, as observed in previous studies [29]. A progressive disappearance of the ZB signal.
during the growth is clearly visible in figure 3(a), as well as in figures 3(b)–(d), and proves the growth of a WZ phase. The growth was ended by stopping the As and Ga fluxes simultaneously, in order to maintain the droplet at the top of the NWs. The wetting angle of the droplet was then measured on 9, 12, and 16 NWs after 5 min, 10 min and 20 min (figures 3(e)–(g), respectively) of growth using SEM, respectively. After 5 and 10 min, the wetting angle was measured close to 120°, as predicted in figure 1 (circled in green). However, at the end of the 20 min growth, a slight decrease of the diameter is observed, and the wetting angle is around 100°. Thinner NWs were observed and exhibit a bigger droplet at their top, as predicted by the simulations (see SI figure S1). This NW morphology represents about 10% of the NW population and might be responsible of the weak ZB signal observed in figure 3(d). These measurements, coupled to the RHEED IR analysis, are indirect evidences of the growth of an extended WZ segment. The presence of the droplet after a 20 min growth using a V/III flux ratio = 4.0 suggests that the growth of the WZ segment could be extended even further. Additional IR curves and RHEED patterns obtained using different V/III flux ratios are illustrated in figure S3 of the supporting information.

The crystalline structure of these NWs was investigated using high-resolution high angle annular dark field (HAADF) imaging in the scanning transmission electron microscope (STEM), as well as dark-field (DF) TEM imaging. Figure 4(a) shows a STEM-HAADF overview of a single NW after the 45 min growth (25 min growth with a V/III flux ratio = 2.4 followed by a 20 min growth with a V/III flux ratio = 4.0). The NW initially crystallizes in the ZB structure, as evidenced by the atomic structure revealed by the STEM-HAADF image in figure 4(c). The transition region between the ZB and WZ phase consists of alternate WZ and ZB domains, as highlighted in the DF-TEM image in figure 4(b). An example of such succession of ZB and ZB domains is shown in the STEM-HAADF image in figure 4(d). After the transition, a WZ segment of about 1.3 μm long is evidenced in the DF-TEM image, obtained using a [1100] g vector specific to the WZ phase, as shown in figure 4(b). Only 2 stacking faults (SFs) are visible in the whole segment (pointed by the red arrows in figure 4(b)), separating the 1.3 μm long WZ segment into 3 sub-segments of 620 nm, 180 nm and 480 nm of pure WZ. The WZ structure is confirmed by high-resolution STEM-HAADF, as shown in figure 4(e), up to the head of the NW (figure 4(f)). It is worth noting that the last few crystallized atomic planes, just below the Ga droplet, correspond to the ZB structure. This portion of ZB crystal is expected due to a wetting angle close to the critical angle β2, in the 85°–100° range [19], when the NW growth was purposely stopped. Further investigation of the NW atomic structure by STEM-HAADF reveals that the ZB and WZ segments of the NW are As-polarized, with a [111] growth direction, as shown in figures 4(g) and (h) respectively. In the present growth conditions, this result is in agreement with the expected polarity of the ZB and WZ crystalline phase [38].

To investigate the photoluminescence (PL) of the sample, we use a specific property of high refractive index NWs: due to the waveguiding properties of the NWs, the absorption efficiency is strongly related to the incident light wavelength λ [40]. In the case of a 95 nm diameter GaAs NW, the absorption is strongly localized in the upper part of the NW (WZ section) when λ = 532 nm, whereas the absorption is mainly observed in the bottom part (ZB section) when λ = 671 nm (see figure S6 in supporting information). Figure 5 shows the 12 K PL spectra of the sample for a 532 and a 671 nm continuous wave optical excitation at low excitation power (21 W cm−2). Both spectra reveal a broad emission in the 1.46–1.49 eV range. This energy range is known to be related to a type II ZB/WZ emission [41, 42], which is consistent with the TEM images. When the sample is excited by a λ = 671 nm laser, a peak is observed at 1.516 eV (peak A), i.e. 3 meV below the low temperature band gap of ZB GaAs (Egap = 1.519 eV). If peak A is related to the recombination of free excitons, their recombination energy should be equal to:

\[ E = E_{gap} + E_{\text{strain}} + E_{\text{QC}} - E_{\text{binding}} \]

where \( E_{\text{strain}}, E_{\text{QC}} \) and \( E_{\text{binding}} \) are the energy shifts induced by the strain, the quantum confinement and the exciton binding energy, respectively. Firstly, we can neglect the strain in our NWs: no shell has been grown to passivate the GaAs and the NWs are not lying on a host substrate avoiding any substrate-induced strain during sample cooling [43, 44]. The quantum confinement, if any, is weak. Using the formula of [45], a 1–2 meV confinement energy is expected for a cylindrical shaped ZB GaAs NW with a 90–100 nm diameter. Secondly, an exciton binding energy in the order of 4.2 meV has been reported for bulk ZB GaAs [46, 47]. Therefore, the peak A emission energy agrees with the recombination of free excitons in ZB GaAs and with a laser absorption in the lower part of the NWs.

In the case of the 532 nm excitation wavelength, the PL emission is quite different: the PL emission is dominated by a peak at 1.5235 eV (peak B), whereas peak A appears as a low-energy shoulder. Peak B, located above the ZB GaAs band gap, is only observed when a WZ segment is grown on the upper part of the NWs (see supplementary information). As a consequence, we assume that peak B is related to free exciton recombinations in the WZ section of the NWs in agreement with the strong absorption of the 532 nm laser in the upper part of the NWs. This result is also close to low temperature PL studies performed by other groups on ZB GaAs NWs grown by metalorganic vapor-phase epitaxy (catalyst-free) or by MBE (Au or Mn catalysts) [48–50], where ZB emission are observed at 1.522 eV, 1.519 eV, and 1.518 eV, respectively. To determine the low temperature band gap of WZ GaAs, we must consider the quantum confinement and the exciton binding energy for this crystallographic phase. The calculations are performed using the dielectric constant \( \varepsilon_0 \) = \( \sqrt{\frac{\varepsilon_{\text{GaAs}}}{\varepsilon_{\text{Ga}}}} \) = 12.77 from [51] and an exciton reduced mass \( \mu = 0.05–0.06 \) from [52]. We find that the quantum confinement (1–2 meV) and the binding energy (4–5 meV) of WZ GaAs are very similar to those of ZB GaAs. Therefore, we estimate that the band gap of WZ GaAs is located 6–9 meV above that of the ZB phase.
We notice that both peaks are quite narrow: about 7 meV for peak A and 8.5 meV for peak B. These linewidths are comparable or better than the 7 meV \[48\] and 18 meV \[49\] values reported for non-passivated WZ GaAs NWs, and not far from the 4 meV linewidth obtained on single passivated NWs \[50, 53\].

In conclusion, numerical simulations were used to provide a set of parameters meant to stabilize the wetting angle of the Ga droplet in self-assisted GaAs nanowires grown by MBE for an extended time, thereby obtaining an extended pure WZ segment longer than a micrometer: the applicability of this theoretical model was demonstrated experimentally.

The growth of the ZB or WZ crystalline phase was monitored in situ RHEED. Evidence of a 1.3 \(\mu\)m long extended WZ segment, grown with a V/III flux ratio equal to 4.0, was provided by high-resolution STEM-HAADF and DF-TEM analysis, and the luminescence properties were shown by PL measurements. This work demonstrates that the precise tuning of the As flux opens the way to control the length of pure WZ crystalline segments in self-assisted GaAs nanowires. The possibility to grow a pure WZ the self-assisted GaAs NWs

Figure 4. (a) STEM-HAADF overview of a single NW. Broken pieces of other NWs are positioned at the top and bottom. Scale bar: 1 \(\mu\)m. (b) DF-TEM image of the extended WZ segment. The red arrows indicate the stacking faults visible in the WZ segment. Scale bar: 500 nm. High-resolution STEM-HAADF images showing (c) the foot of the NW with a ZB crystalline structure, (d) the beginning of the extended WZ segment with a 3 MLs long ZB segment, (e) a portion of the extended WZ segment and (f) the end of the extended WZ segment with the Ga droplet/NW interface. (c)–(f) Correspond to the regions highlighted with colored squares, magenta, red, green, and cyan, respectively, in (a) and (b). The ZB and WZ spots of the FFT are highlighted with the yellow and orange circles, respectively. Scale bars on (c)–(f) are 5 nm. The ZB structure in (c), (d), (g) is observed in the [110] zone axis, and the WZ structure in (e), (f), (h) is seen in the [1120] zone axis. (g) High-resolution STEM-HAADF image and intensity profile of the ZB segment near the NW foot. (h) High-resolution STEM-HAADF image and intensity profile of the WZ segment near the NW head. Scale bars on (g) and (h) are 1 nm. The overlayed atomic models of WZ and ZB highlight Ga (green) and As (purple) atomic column positions, and were made using the VESTA software \[39\].

Figure 5. Photoluminescence spectra of the sample at 12 K for a 671 nm excitation wavelength (red curve) and a 532 nm excitation wavelength (green curve). The spectra have been normalized to the strongest emission peak and offset for clarity.
could be investigated by the constant tuning of the As flux over time, in order to compensate the variation of the amount of Ga supplied to the droplet. This combined experimental and numerical demonstration is of major interest to tune the properties of III–V nanostructures on demand, and for the fabrication of semiconducting heterostructures with novel functionalities.

Methods

The GaAs NWs were grown on epi-ready Si(111) substrates using a solid-source MBE reactor. Each substrate was cleaned during 5 min in both acetone and ethanol, and degassed at 200°C in ultra-high vacuum before introduction inside the MBE reactor. On each substrate, the native SiO2 oxide was preserved to enable the self-assisted growth [54]. To form the Ga droplets, the substrate was heated to 450°C and 1 monolayer (ML) of Ga was pre-deposited [55, 56] at a deposition rate of 0.5 ML s⁻¹, quoted in units of equivalent growth rates of GaAs 2D layers measured by RHEED oscillations on a GaAs substrate [36]. Then, the substrate temperature was increased to 600°C, the growth temperature. Finally, the opening of the Ga and As fluxes initiated the growth of the NWs. The MBE system was handled by a homemade software that finely controls the Ga and As4 fluxes, the valves and shutters. The NWs were grown with Ga and As4 fluxes of 0.5 ML s⁻¹ and 1.2 ML s⁻¹, respectively, corresponding to a V/III flux ratio = 2.4. In order to investigate the influence of the V/III flux ratio on the wetting angle, different As fluxes (1.5 ML s⁻¹, 1.75 ML s⁻¹, 2.0 ML s⁻¹ and 2.15 ML s⁻¹) were used for the growth of the extended WZ segment and for each As flux three different growth times were used (5 min, 10 min and 20 min). The growth was systematically stopped by interrupting the As flux in order to preserve the droplet shape and it wetting angle. All the samples were characterized by RHEED at 30 keV to obtain real time information on the crystal structure evolution of the NWs. The samples were rotating during the growth under the standard conditions. The rotation was then stopped during the growth of the extended WZ segment in order to precisely record the intensity evolution of the ZB and WZ spots. The RHEED IRs and RHEED diffraction patterns of each experiment are represented in SI figure S3. Each sample was then observed and characterized with a JEOL SEM using a liquid-nitrogen cooled silicon based array detector coupled to a monochromator.

Acknowledgments

The authors thank the NanoLyon platform for access to the equipments and J B Gioure for technical assistance. The authors acknowledge the French Agence Nationale de la Recherche (ANR) for funding (project BEEP ANR-18-CE05-0017-01). NC acknowledges funding from the ANR (project HEXSIGE ANR-17-CE30-0014-04). The (S)TEM work was performed at the consortium Lyon-St-Etienne de microscope. The authors are grateful to Y Lefkir and S Reynaud for technical assistance using the Jeol NeoARM instrument.

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