Growth-Related Formation Mechanism of I3-Type Basal Stacking Fault in Epitaxially Grown Hexagonal Ge-2H

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The hexagonal-2H crystal phase of Ge has recently emerged as a promising direct bandgap semiconductor in the mid-infrared range providing new prospects of additional opto-electronic functionalities of group-IV semiconductors (Ge and SiGe). The controlled synthesis of such hexagonal-2H Ge phase is a challenge that can be overcome by using wurtzite GaAs nanowires as a template. However, depending on growth conditions, unusual basal stacking faults (BSFs) of I3-type are formed in the metastable 2H structure. The growth of such core/shell heterostructures is observed in situ and in real time by means of environmental transmission electron microscopy using chemical vapor deposition. The observations provide the first direct evidence of a step-flow growth of Ge-2H epilayers and reveal the growth-related formation of I3-BSFs during unstable growth. Their formation conditions are dynamically investigated. Through these in situ observations, a scenario can be proposed for the nucleation of I3-type BSFs that is likely valid for any metastable hexagonal 2H or wurtzite structures grown on m-plane substrates. Conditions are identified to avoid their formation for perfect crystalline synthesis of SiGe-2H.

1. Introduction

Polytypism of semiconductors is explored to achieve new heterostructure configurations and modify electronic and photonic properties for additional functionalities, such as crystal phase quantum dots,[1,2] and tuning the magnitude and the nature of the semiconductor band gap.[3] The stable crystal phase of Si and Ge is the well-known cubic diamond structure (herein noted 3C) corresponding to the lowest total energy.[4,5] The diamond hexagonal structure 2H has the second lowest energy;[6] the difference in total energy is around 0.015 eV per atom for both Si and Ge.[4] By epitaxy on a hexagonal structure with a suitable lattice parameter, one can overrule this energy configuration in defiance of the 3C bulk stability to obtain the 2H phase. This was first demonstrated with Si/GaP core/shell heterostructures grown by metal organic chemical vapor deposition (MOCVD) as a Si-2H structure was epitaxially grown on the sidewalls of a <0001>-oriented wurtzite (WZ) GaP nanowire.[7,8]

For Ge-2H, the ideal template is wurtzite GaAs (GaAs-WZ) because their lattice constants are almost identical (Δa = 0.03% and Δc = 0.11%).[9] While GaAs bulk has a zinc-blende (ZB) structure, nanowires grown by the vapor–liquid–solid process may exhibit a WZ structure depending on growth parameters.[10–12] Thus, control over the GaAs-WZ phase in nanowires gave a decisive opportunity to transfer the structure to a Ge shell.[9] This crystal structure transfer method enabled the synthesis of Si1–xGe2H shells from x = 1 down to x = 0.6, which exhibit direct band gap emission.[9] Clearly, a controlled synthesis of Si1–xGe2H would revolutionize the optoelectronic industry by providing an efficient light emitter compatible with the Si-platform, this so long considered as the “holy grail”.

For both core/shell systems, Si-2H/GaP-WZ and Ge-2H/GaAs-WZ, unusual I3-type basal stacking faults (I3-BSF) are frequently observed.[13,14] Their atomic configuration was described in ref [14] using HR-STEM (high resolution scanning transmission electron microscopy). Although I3-BSF in Si1–xGe2H may have no deleterious influence on optical properties as reported by Fadaly et al., their presence may affect the electrical and mechanical behavior of the material.[14] Such defects are intrinsic faults with a characteristic sequence ABAABCABABA where only one C-plane replaces a B-plane (or an A-plane in the sequence BABAABCABABA). On both sides of the C-plane the crystal remains perfect, i.e., unshifted (no associated Burgers vector). The configuration of the I3-BSF is almost never found in the hexagonal system, although it was theoretically predicted in nitrides as a growth-related defect with the second-lowest formation energy configuration.

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energy just above that of I\textsubscript{1}-BSF.\cite{15} We think that similar defects are observed in InAs/GaAs core/shell structures but their nature needs to be confirmed.\cite{16} Indications of this unusual defect have been found in GaN grown on (11-20) 4H-SiC and in the defected tip of GaAsP nanowires.\cite{17–19} High-resolution scanning transmission electron microscopy (STEM) imaging showed a change in the orientation of the dumbbells in the \{0001\} planes with a null total Burgers vector.\cite{18} So far, an explanation for the formation mechanism of this poorly known defect has not been proposed and it is the purpose of the present study.

Although I\textsubscript{3}-BSF in Si\textsubscript{1-x}Ge\textsubscript{x}-2H may have no deleterious influence on optical properties as reported by Fadaly et al. their presence may affect the electrical and mechanical behaviour of the material.\cite{14} Here, we study in detail the conditions for I\textsubscript{3}-BSF formation in Ge-2H, using correlated in situ and ex situ experiments, in order to optimize the synthesis of high quality and defect-free 2H polytype of SiGe compounds. Firstly, the ex situ growth experiments presented in ref.\cite{14} are extended here by further exploring the defect shape in the basal plane and the location of the nucleation. We quantitatively investigate the effects of both temperature and shell volume on the defect density. We also assess the influence of the chemical surface treatment for removing gold from the GaAs NW prior to the Ge shell growth. In these experiments, structural characterization is performed by means of post-growth transmission electron microscopy (TEM) studies. Second, with in situ environmental transmission electron microscopy, we dynamically monitor the growth of Ge-2H and we examine the parameters influencing the defect nucleation. This in situ TEM study is carried out using the NANOMAX microscope (http://www.tempos.fr/?q=node/3) implemented with gas precursors for chemical vapor deposition (CVD) growth. This microscope provides unique real-time and atomic-level information about the growth dynamics, useful to understand involved mechanisms in growth and defect formation. Real-time observations give direct insight into the different growth modes depending on temperature and precursor flows. We report on the growth kinetics and we show that under certain growth conditions a step-flow mode supports a perfect replica of the hexagonal structure Ge-2H on the specific (1-100) sidewalls, perpendicular to the \langle0001\rangle axis. This step-flow mode is observed for the first time in this Ge-2H structure. The real-time observations provide also evidence that the original I\textsubscript{3}-type defects in SiGe-2H are growth related. The observations reveal a correlation in the growth conditions under which the destabilization of the step-flow growth and the nucleation of an I\textsubscript{3}-BSF occur. The results provide us with convincing arguments to propose the very first plausible scenario for the formation of I\textsubscript{3}-BSF during the growth of metastable hexagonal structures.

2. Theory

Before we start discussing the experimental results, we give the structural characteristics of the I\textsubscript{3}-BSF in Ge-2H. Figure 1a shows a schematic view of a representative core/shell
GaAs-WZ/Ge-2H structure featuring the crystallographic directions. The GaAs-WZ nanowire is grown along the <0001> axial direction and displays prismatic {1-100} sidewalls. High-resolution STEM micrographs acquired along the <11-20> zone axis enable to identify the nature of the defects present in these wires. Lamellar twins with an I₁ or I₂ stacking fault configuration may be formed during the axial growth of the GaAs-WZ core nanowires corresponding to a local ZB structure. Those defects are consequently replicated by epitaxy in the Ge shell. Their density can be minimized by tuning the GaAs growth parameters to obtain long GaAs-WZ cores. Here, for ex situ analyses, we use GaAs-WZ core nanowires with I₁ and I₂-type SFs as low as 5 SFs/μm. Upon shell growth, additional intrinsic I₃-BSFs are formed, which can be observed as dark lines starting and extending across the Ge-2H shell on the basal (0001) planes (Figure 1b). These I₃-BSFs do not appear in the GaAs-WZ cores as confirmed in the supporting information in ref. [14].

A detailed description of the atomic stacking within these particular defects is also given in ref. [14]. In figure 1, we summarize the foremost structural characteristics of the I₃-BSFs in the Ge-2H shell based on TEM analyses (Figure 1), providing insights in the stacking structure, the boundary of the faulted layer and the shape of the I₁-BSF and we complete here with tilted off axis analyses showing the location and the planar shape of the defect:

i) Along the [0001] direction, the defective sequence ABACABA is equivalent to a local twinned cubic structure with only one faulted bi-atomic layer. There is no glide of the upper and lower part of the 2H crystal (Figure 1d). The defects are mostly constituted of one faulted plane, we rarely observe two or more faulted planes.

ii) Viewing along a <11-20> direction, one can define a topological defect with a translation of two successive monoatomic layers (forming two partial 30° dislocations on the glide plane) resulting in a change in the orientation of the dumbbells on either side of the faulted (0001) plane with respect to the dumbbells in the perfect hexagonal stacking. The core of the defective boundary shows two vacancy rows bounding the two translated monoatomic layers (see Figure 1c).

iii) With a tilted view away from the <11-20> viewing direction, the defects are visible with moiré fringes due to the overlay of one faulted plane with the undefected lattice (Figure 1c). The moiré pattern is localized in a restricted area. The majority of defects exhibit a triangular shape with one side lying on the growth surface and the opposite apex corresponding to the nucleation point of the defect inside the bulk of the Ge-shell. In the basal plane, the resulting equilateral triangle is bounded by two defective lines along <11-20> directions, indicating a point source of the defect nucleation at the triangle apex. This equilateral triangular shape implies that the maximum projected length of the defect (i.e., the triangle height) observed along a <11-20> direction is equal to the shell thickness and can thus be identified using a <11-20> zone axis view. It is important to note that these triangular defects are not necessarily formed at the GaAs-WZ/Ge-2H interface. They may start at random positions in the shell and most of them have thus length smaller than the shell thickness.

iv) Additionally, we have occasionally observed few elongated defects with a projected length larger than the shell thickness and a shape different from a triangle (results of elongated defects are not shown here). They are still bounded by <11-20> defected lines, but they do not have a point origin. They are always anchored on the GaAs interface along a <11-20> row and they are never found to be created within the shell, conversely to triangles.

It appears that both defects, i.e., with triangular and elongated shapes, have a different starting configuration: at a point and a line, respectively. After nucleation both defects grow bounded by <11-20> dislocation lines. Elongated defects are always formed at the interface and thus their density does not evolve with the growth while triangle defects are randomly formed in the Ge shell during growth. The study in this manuscript focuses on the triangular defect formation. A follow-up paper will discuss separately in detail the elongated defects which may have a different origin.

3. Results

We start by studying ex situ the kinetics of I₁-BSF nucleation by quantitative consideration of their density evolution with the growth time, i.e., with the shell volume and the growth temperature (information for the calculation of their density was provided in supporting information of ref. [14]). As shown in Figure 2a, at all growth temperatures, the linear dependence of density with volume indicates that the nucleation probability scales with the expanded growing surface. Together with the random position of the nucleation points, at least for the concerned triangular defects, this linear density is consistent with a growth-related defect formation dismissing the hypothesis of a strain relief due to thermal expansion. The plot of Figure 2a also evidences a higher nucleation rate at lower temperatures. The intersection of each linear curve with the y-axis gives the initial I₁-BSF density at the start of the growth, i.e., at the GaAs/Ge interface. At low growth temperatures, a finite I₁-BSF density is present from the beginning of the shell growth while at higher temperatures the curve may intersect the x-axis implying a defect free start of the shell growth. The use of a high growth temperature seems to hinder or delay the nucleation of I₁-BSFs.

In Figure 2b, the effect of growth temperature on the defect density is plotted in the range 405 °C (low temperature)–565 °C (high temperature) for two different GaAs core surface conditions: one is an as-grown nanowire with the presence of the Au catalyst particle on top and the second is an analogous nanowire treated to etch away the Au catalyst particle. For both, the I₁-defect linear density is inversely proportional to the temperature. The shells grown on chemically treated nanowires are more defective than those grown on the untreated, as-grown GaAs wires yet showing no Au contamination. Remarkably, the TEM micrographs (Figure 2c) show that in the chemically treated NW the defects are mostly anchored at the core/shell interface. Thus, a chemical etching of the GaAs template may induce deleterious surface effects such as roughness or contamination that enhances the nucleation of I₁ defects at the interface. However, the convergence of the density curves at high growth temperature suggests an improvement of the GaAs surface quality, either by desorption of chemical contaminants or by evaporation of GaAs, thereby flattening the
sidewall surfaces. Actually, we find that the deleterious effect of the chemical etching of the GaAs nanowire can be restored by thermal annealing at 613 °C under AsH₃ pressure before Ge shell growth; the Ge growth is carried out using a dedicated Ge reactor lining, such that the As background pressure is low during Ge growth.

As a first statement, roughness and/or impurities may have an influence on the defect nucleation at the interface and growth conditions such as temperature appear to influence the possibility of formation of defects. To minimize the formation of defects in the Ge-2H shell, the highest possible growth temperature should be used. In practice, this implies a temperature around 650 °C, as at higher temperatures As evaporation under vacuum conditions affects the GaAs core quality and morphology.[20]

3.1. In Situ Growth-Related I₃-BSF

To understand the process of the I₃-BSF formation, we need to study the conditions under which they are formed during growth and gain insights into the parameters affecting their density. On top of this, we aim to identify the origin of their nucleation. For this goal, in situ electron microscopy provides unique opportunities. Starting on the GaAs-WZ NW template, after an incubation time that likely depends on temperature, Ge grows on {1-100} sidewalls by perfectly replicating the hexagonal structure of the GaAs-WZ core (Figure 3 and Video S2, Supporting Information), which is thermodynamically most favorable. However, depending on growth conditions, especially when the Ge flux is increased, I₃-BSFs appear with increasing number. This may lead to a very defective structure as shown in Video S3 (Supporting Information) and Figure 3b. This real-time observation confirms unambiguously that such defects are growth-related and are definitely not due to a thermal expansion coefficient mismatch.

With the sequential micrographs in Figure 4 we can follow the formation and the evolution of an isolated I₃-BSF, although it does not allow us to see the exact origin of the defect due to the projection view. However, this particular defect exhibits a “C” basal plane in place of an “A” basal plane in the sequence ABABACABAB along <0001> resulting in a local distortion of the

Figure 2. a) I₃-BSFs density evolution as a function of the substrate surface temperature for various conditions of preshell growth surface treatments. b) I₃-BSFs density evolution as a function of the shell volume for different growth temperatures on as grown and chemically treated NWs. High temperature annealing was also performed on chemical treated samples at 613 °C. c) Bright field-TEM images of three different samples: i) grown at relatively low substrate temperature with as-grown GaAs-WZ cores without any pre-growth surface treatments, ii) grown at relatively low temperature with the GaAs-WZ cores chemically treated prior to the Ge-2H shell growth, and iii) grown at high temperature, as indicated in panel (a).
position of the (1-100) planes. This distortion can be visualized by constructing the inverse filtered Fourier transforms (IFFT) of the atomic resolution TEM images. In Figure 4, the IFFT corresponding to the HRTEM micrograph acquired at 100 s displays the appearance a dark contrast indicated by a red arrow. This dark area becomes more and more clear with time and with additionally grown Ge layers indicating a small perturbation in the column of atoms. At 120 s the (1-100) fringes in the IFFT are locally cut implying there is a discontinuity of the (1-100) planes. After 150 s, a large bending of the fringes is clearly discernable with a further increased contrast signifying the presence of a I$_3$-BSF. No strain field is observed in the surrounding planes before and after the appearance of the I$_3$-BSF and there is no dissociated dislocation. At 225 s, a second I$_3$-BSF is observed indicated with a yellow arrow. The additionally grown Ge (1-100) planes will continuously display this bending with respect to the other perfectly aligned fringes. Thus, we can see a slight distortion of the (1-100) fringes in the IFFT before it is possible to see the faulted stacking sequence in the image. These successive snapshots reveal that a local perturbation in the (1-100) planes may provoke the formation of the I$_3$-BSF at random positions during growth. As soon as the I$_3$-BSF nucleates, the distortion of the (1-100) planes is replicated on the next planes.

These defects appear randomly with increasing number and size as the growth proceeds. During real-time experiments, we could observe I$_1$-BSF starting at the very beginning of shell growth, especially in the case of low temperature and high Ge$_2$H$_6$ flow (see S4, Supporting Information). Their formation can be

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**Figure 3.** TEM micrographs recorded along the <11-20> zone axis during in situ growth. a–d) Starting from a GaAs-WZ core nanowire template, defect free Ge-2H is grown on m-plane sidewalls at a temperature around 450 °C with 1 sccm of Ge$_2$H$_6$/H$_2$ (1/10) and a pressure of around 2 × 10$^{-3}$ mbar. The growth rate is about 1.5 Å min$^{-1}$. e–h) Defected Ge-2H after growth at 450 °C with 2.5 sccm diluted Ge$_2$H$_6$ (P = 5.3 × 10$^{-3}$ mbar). I$_3$-BSFs are formed during growth. The growth is observed in real-time as shown in Videos S2 and S3 (Supporting Information). The density of I$_3$-BSFs increases during the growth (as the shell volume increases). Scale bar is 5 nm.

**Figure 4.** HR-TEM images recorded at different times during the growth of Ge-2H, as shown in video S3 (Supporting Information) and their corresponding filtered IFFT constructed using the (1-100) spatial frequencies in the FFT. IFFT images show the evolution of the I$_3$-BSFs attested by the fringe shifting, as indicated by the red and yellow arrows. Every defect is pointed at with the same color. The scale bar is 5 nm.
delayed to a later stage in thick shells if we grow the Ge shell at low flow, and I\textsubscript{3} appear after an increase of Ge\textsubscript{2}H\textsubscript{6} flow. This is consistent with the plot in Figure 2a, showing an increased defect density at the interface for lower growth temperature. This means that I\textsubscript{3}-BSFs are not related to strain accumulation and their appearance is not forced by a thickness threshold of the Ge shell. This is expected given the very small mismatch between GaAs-WZ and Ge-2H (\(\Delta a = 0.03\%\) and \(\Delta c = 0.1\%\) at room temperature, where \(a\) and \(c\) are the dimensions of the hexagonal unit cell).

During all the real time experiments, we have clearly observed that the density of I\textsubscript{3}-BSFs increases with decreasing temperature and/or increasing precursor flow. Conditions of low temperature and high flow lead to very defective Ge-2H as illustrated in Figure 3b. The density of I\textsubscript{3}-BSF can be reduced using a low precursor flow. At high temperature, their formation is prevented if the flow is not too high and in that case the growth rate does not have any influence (see S5, Supporting Information). Thus, these observations are in agreement with the ex situ quantitative analyses of the growth temperature influence on the I\textsubscript{3} density.

In addition, the effect of certain chemical impurities on the defect formation has been studied in situ by adding precursors such as TMGa or TBAs or SiH\textsubscript{4} during growth. Throughout our observations, none of those added precursors have shown any effect on the formation of I\textsubscript{3}-BSFs in the Ge-shell. Moreover, by comparing qualitatively the shell growth on Au catalyzed and self-catalyzed NWs, SFs appear to be equally formed on both type of NWs. Thus, there is no evidence for Au, As, Ga, and Si impurity atoms to have any effect on the growth surface that could directly provoke the nucleation of an I\textsubscript{3} defect. This point will be discussed further below.

Comparing Figure 3a,b, in addition to the presence of I\textsubscript{3}-BSFs we observe a striking difference in the roughness and growth modes. This observation suggests it is essential to control the surface roughness on the nanoscale as a prerequisite to gain understanding in the crystal growth kinetics and the I\textsubscript{3}-BSF defect formation mechanism.

### 3.2. Growth Modes of Ge-2H

The step-flow regime for the growth of planar films has been studied for several decades and has been directly observed by various means such as optical microscopy, reflection electron microscopy, scanning probe microscopy and also TEM, for different film/substrate systems.\cite{21, 22, 23, 24, 25, 26} However, our system Ge-2H/GaAs-WZ is singular in the sense that we grow a metastable crystal phase, which opens up new questions about phase
stability and possible defect formation during step growth. Here, we describe the first qualitative observations to draw a global picture of the growth process of Ge-2H on m-plane surfaces.

Videos S4 and S5 (Supporting Information) and extracted snapshots in Figure 5a,b reveal a step-flow growth mode favorable for the epitaxy of Ge-2H on the GaAs-WZ with standard conditions of high temperature (500–550 °C) and low partial pressure in the range 1–3 × 10⁻³ mbar with a flow around 1 sccm. In Figure 5a, the overview of the growth surface, observed along the <11-20> zone axis, i.e., when the electron beam is parallel to one of the {1-100} growth surfaces, shows several successive steps indicated by arrows with a nearly regular advancement. The bi-atomic layer step (consisting of a dumbbell of Ge atoms) advancement can be more easily followed with a tilted view on the [1-100] m-plane (snapshots of S5, Supporting Information in Figure 5c), revealing additional information on the advancement of the step. When the growth proceeds, straight steps move one after another over the NW sidewalls. In the <0001> direction, the step front progresses “row-by-row.” Adatoms are incorporated at the kink of the row to finish a step before starting a new one, the step proceeding from one edge to the other on the [1-100] sidewall. Thus, the hexagonal m-plane surface is replicated layer-by-layer, step by step and we can say row after row.

Cubic segments initially existing in the GaAs core are also reproduced in the otherwise perfect Ge-2H shell. The nucleation of the step seems to be preferentially initiated at the surface position of the local cubic structure. The enhanced probability of nucleation at these positions might be either due to a lower nucleation barrier for the cubic phase, or to the altered atomic arrangement at the hexagonal-to-cubic stacking sequence. There is no preferential direction of the flow along an NW, i.e., the step-flow can move upward or downward the NW and is not related to a miscut of the surface. Remarkably, in case of initial sidewall roughness of the GaAs NW (see S6, Supporting Information), this step-flow growth mode favors a surface flattening that may be explained by surface diffusion of adatoms and higher sticking probability as the step edges of lower layers (i.e., chemisorbed Ge atoms complete the lower layers).

The growth rate can be tuned by the precursor flow and in a lesser extent by the temperature which may also modify the precursor cracking. Remarkably, decreasing the growth temperature and/or increasing precursor flow induces instabilities of the step-flow of Ge-2H such as step meandering (Figure 5d and Video S6, Supporting Information). Starting from a slightly destabilized step-flow (with 1 sccm of Ge₂H₆ at 450 °C) the snapshots in Figure 5d show how the growth evolves toward more pronounced step meandering upon lowering the growth temperature to 420 °C. Consequently, the steps become highly irregular in shape as well as in advancement speed. A large destabilization leads to a change in growth mode as illustrated in Figure 6. Keeping precursor flow and pressure constant and decreasing the growth temperature by more than 100 °C, the growth mode evolves promptly from step-flow to the formation of hillocks and 2D-nucleation along with the nucleation of I₃-BSFs.

Similarly, a sudden change in precursor flow during growth while keeping the temperature constant results in an evolution from step-flow to 2D nucleation (compare Figure 5a,b). At 0 s in Figure 5b, the precursor flow is doubled from 1 to 2 sccm. The growth evolves continuously from step flow to a random 2D nucleation growth mode: small hillocks visible as bumps appear on the surface and subsequently disappear rapidly, characteristic of the birth and spread of numerous nuclei in the 2D nucleation model. The growth mode is further substantiated by dark and bright contrasts indicating a difference in thickness along the <11-20> zone axis. With increasing deposition rate, the 2D-nucleation rate increases and the size of 2D nuclei decreases. So, this regime results in a large increase of the overall [1-100] sidewall roughness.

It is of major importance to mention that the formation of hillocks on [1-100] Ge-2H facets is different from the strain-induced Stranski–Krastanov mode for which the growth is initially layer-by-layer until a critical thickness is reached at which the formation of 3D islands becomes energetically favored. The GaAs-WZ and Ge-2H lattices are close as mentioned previously. Thus, no strain-induced morphology change can be expected. In our experiments, there is no thickness threshold nor any presence of misfit dislocation. Moreover, the formation of hillocks can be initiated at any stage in the growth, also at the very beginning of the growth if the precursor flow is high at low temperature (S4, Supporting Information). Thus, this growth mode has a kinetic origin, as will be discussed below.

Figure 6. Bright field-TEM images viewed along the <11-20> zone axis showing the growth of Ge-2H grown at different temperatures: a) T > 600 °C, and b) T < 500 °C. Growth is performed using 1.5 sccm of diluted Ge₂H₆ with a pressure range of 3 × 10⁻³ mbar. A sudden decrease of temperature results in the rapid change in growth mode from a rapid step flow process at panel (a) to a hillock mode as in panel (b).
For a comprehensive review of the step-flow process see refs. [27–31] The step-flow is generally stable if the surface diffusion of the growth species is sufficiently high compared to the deposition rate. When surface diffusion is fast enough, adatoms can rapidly move to the most energetically favorable site on a step edge which progresses forward as described by the classical thermodynamic terrace-ledge-kink model developed by Kossel and Stranski. [32–33] If the precursor flow is increased, the deposition rate also increases and the system moves away from equilibrium. The adatoms do not reach the energetically favorable incorporation sites because of a too short diffusion length. This diffusion length becomes smaller than the distance between steps and 2D nucleation takes place on terraces leading to the hillock growth mode. Alternatively, decreasing the temperature while maintaining the deposition rate constant will reduce the mobility of adatoms. A step meandering may establish and finally a reduced surface diffusion length may also lead to random 2D-nucleation and thus surface roughening. In our experiments the growth mode of Ge-2H on m-plane GaAs-WZ can range from step-flow at high temperature, via unstable step-flow (step meandering) to 2D-nucleation stated by random hillock formation at low temperature and high deposition rate.

3.3. Formation Mechanism of I\textsubscript{3}-BSF during Growth

Both I\textsubscript{3}-BSF nucleation and the growth mode are tuned by the growth temperature and precursor flow. At first sight, one could suppose that I\textsubscript{3}-BSFs formation is correlated with the induced roughness consecutive to destabilized step-flow. However, an initial surface roughness created by inhomogeneous thermal desorption of the GaAs NW does not cause the formation of defects, provided that the step flow mode is maintained and indeed flattens the surface (see S5, Supporting Information). Likewise, the high density of terraces on vicinal sidewalls (i.e., tapered sidewalls, making an angle with the m-plane) always formed on the surface of self-catalyzed NWs does not play a noticeable role on the formation of I\textsubscript{3} defects (see S3, Supporting Information). In case of vicinal surfaces, step-flow flattens again the surface and I\textsubscript{3}-BSFs are only formed in case of destabilized step-flow at high flow and low temperature. So, the surface roughness (craters or steps) is not a direct cause of I\textsubscript{3} formation and the relationship between roughness and I\textsubscript{3}-BSF formation is thus not straightforward and must be considered as an indirect relationship.

Although the enhanced roughening during destabilized growth is not directly the cause of I\textsubscript{3} defect formation, it is
obvious that I$_3$-BSFs and hillocks appear in the same growth condition regime and both phenomena are due to kinetics effects. In our in situ studies, no I$_3$ defect has been observed in case of step-flow. The more the step-flow is destabilized the higher the density of I$_3$ defects. Vice versa, the presence of numerous I$_3$-BSFs may successively worsen the surface roughness. We argue that the mechanisms involved in the chemisorption of adatoms on the surface not only guide the evolution of the surface morphology but also impact the formation of I$_3$ defects. In this paper, we assume and demonstrate that a lacking dangling bond may be at the origin of the I$_3$ defect and this is enhanced at high flow and low temperature. The cause of a missing dangling bond (vacancy, impurity, distortion...) is not yet established but discussed later.

In Figure 7a–f, we propose a possible scenario to explain the formation of I$_3$-BSFs trying to account for all the observations. The specific triangular shape is of major importance indicating that the I$_3$ defect locally nucleates due to either a lacking dangling bond or the presence of an H atom, an unknown foreign atom or a vacancy in the Ge lattice that likewise prevents the chemisorption of the adatom at the right place. In Figure 7a, the initial growth surface is seen in perspective view with an upward m-plane and a step-flow propagation in the <0001> direction from left to right. Based on the step-flow growth mode, the adsorbing surface is only the {1-100} surface and the Ge adatoms are forced to follow the stacking ruled by the {1-100} surface. We assume that the growth proceeds via step-rows along the <11-20> direction, and row-by-row in the <0001> direction. As discussed above, this growth mode enables to replicate a perfect 2H structure with the stacking of successive layers. The grown layer is in fact assumed to be constituted of 2 mono-atomic planes: each lower Ge atom is stacked and bonded with two upper Ge atoms.

In Figure 7b, at some point on the surface we place a “wrong atom” that hinders other atom to bond to it. This can also be a “regular” Ge atom that is passivated by a hydrogen atom, as will be discussed below. Consequently, on the (1-100) surface an upward dangling bond is missing, preventing the chemisorption of the next upper Ge adatoms on the (1-100) surface. For the sake of simplification, we consider here the successive sticking of 3 Ge atoms that complete the tetrahedra on the surface. Consequently, a single atom vacancy in a lower plane of a layer will induce a double atom vacancy in the upper plane of the bi-atomic layer. The first Ge layer above this missing dangling bond will then display three vacancies as shown in Figure 7c. This configuration opens an empty space that forces two Ge atoms to stack in the <0001> direction rather than on the (1-100) surface. The opened {0002}$_{2H}$ basal plane corresponds to the {111}$_{3C}$ plane and thus will favor a cubic ABC stacking in the <0001> direction. So, a third Ge atom will sit in a faulted C position as shown in Figure 7d. In Figure 7e, the next row of adatoms will continue to sit on the (1-100) surface except beside the faulted atom. To satisfy the <0001>-oriented dangling bond with the faulted Ge atom the neighboring atom is forced to take a faulted C position. Elsewhere, the growth continues by step-flow on the (0001) surface. Therefore, on the first grown bi-atomic layer, the missing dangling bond has provoked the formation of a dumbbell of faulted atoms (Figure 7f). This is the seed of the I$_3$-BSF. For the next layer, Ge ad-atoms again satisfy the bonds on the {1-100}
surface via a step-flow mode. Successively grown layers reproduce the stacking fault (Figure 7g,h). The number of faulted atoms increases by one on each grown layer and the faulted (0002) plane is bounded by a vacancy on each side (Figure 7i). Following the proposed scenario, a triangular $I_3$-BSF is formed in an overall perfect Ge-2H structure. The projections of the defect in various directions are shown in Figure 8. They perfectly represent the observed TEM images of the defect (Figure 1). A slice of the faulted planes forming the $I_3$ defect viewed in the $<0001>$ zone axis shows the arrangement of the triangular defect and the bounding vacancies. It is also important to mention the configuration of the $I_3$ defects when observed along the $<11\overline{2}0>$ lines.

This model is thought to be applicable for the 2D-growth of Ge-2H, Si-2H, as well as for the metastable WZ structures, as long as growth occurs on a nonpolar m-plane facet. The formation of $I_3$-BSF is very likely in the polytype structures where the ZB structure is of lower formation energy than for the WZ one such as GaAs-WZ, GaP, GaN, InN, AlN.[56]

### 3.4. Discussion on the Origin of $I_3$-BSFs

The proposed model is consistent with the ex situ and in situ observations. The following conclusions are of particular importance:

i) We observe a random nucleation at a discrete point and a triangular shape of the $I_3$-BSF. This may be explained by a single lacking dangling bond acting as a source for $I_3$-BSF formation. The triangle with $<11\overline{2}0>$ sides is the consequence of the layer-by-layer (1-100) stacking on top of the point source. There is an incremental increase of the number of faulted atoms with each layer.

ii) We do not see any influence of Au, Ga, As and Si contamination. It is important to note that Ga, As and Si have the same sp$^3$ configuration as Ge and thus do not change the dangling bond configuration on the surface. The fact that those impurities seem not to have any influence on the defect nucleation is consistent with the increased $I_3$-density with higher Ge$_2$H$_6$ flow while the contamination influence should be lower for higher Ge$_2$H$_6$ precursor flow. On the other hand, Au may act as liquid catalyst and it is highly mobile on the surface. Again, its possible influence would not be expected to increase with Ge$_2$H$_6$ flow.

iii) Indeed, the nucleation probability of $I_3$-BSFs relies on growth kinetics. It is unambiguously related to the growth conditions and probably to the growth kinetics as we will discuss below, i.e., influenced by temperature and deposition rate. $I_3$-BSFs are associated with a destabilized step-flow. The more the step-flow is destabilized, the more the density of $I_3$-BSFs increases. No defects are observed with a continuous step-flow growth mode when surface diffusion is high enough.

The last point requires further examination of the cause of step-flow destabilization and the identification of the missing dangling bond at the origin of the nucleation of $I_3$-BSFs. This new configuration of the m-plane growth surface for Ge and Si requires a global study of dangling bonds and surface reconstruction. We believe that surface chemistry and particularly hydrogen coverage—being highly dependent on the growth temperature—may be the major cause. It is important to note that H atoms can passivate the dangling bonds while Ga, As and Si do not.

The presence of H on the growth surface is inherent to the chemical vapor deposition (CVD) growth process and cannot be suppressed when using hydride precursors. H coverage during growth process affects diffusion processes and thus dramatically changes the growth kinetics and the surface morphology.[34–36] It is well documented that H coverage is influenced by both the temperature and the deposition flow [37,38] and it plays a critical role on the quality of cubic Si and Ge films during CVD growth.[34,39–44] The kinetics are governed by hydrides physisorption and H desorption which are thermally activated processes. The hydride sites are inactive for chemisorption unless H is released and leaves a dangling bond useful for an adatom or a hydride molecule. Thus, the sticking probability of new growth species depends on available active sites (dangling bonds) and surface mobility. Studies on CVD of cubic Si and Ge have shown that, at low temperature and high flux, the H desorption is the rate-limiting process while at high temperature and low flux the rate is limited by adsorption.[97] The hydrogen during CVD of Ge and Si epitaxy has two cumulative effects: first, H coverage reduces the adatom surface mobility by increasing the diffusion barrier and in turn provokes enhanced surface roughening, second, it saturates the step-edges, favoring island growth over step-flow growth.[45,46]

Thus, we assume that H passivation of dangling bond is the main cause of the observed morphological instabilities (step meandering) as well as roughening at low temperature or high flow rate. Thus far, no information is available regarding the H coverage of the Ge [1-100] surface. For cubic Si and Ge, the chemisorption mechanism is dependent on the crystallographic orientation.[40] For the [1-100] surface of hexagonal Si and Ge, it was reported that there are two dangling bonds per unit cell and the number of dangling bonds is not reduced upon reconstruction.[48] We can speculate that also for the m-plane, H coverage of dangling bonds may in some way reduce adatom mobility. The observed step-flow is consistent with the dangling bond diffusion proposed by Kuwahara et al. rather than a diffusion of adatoms.[49] Further study will be necessary to precisely determine the role of H in changing the growth modes of Ge-2H on the m-plane. Various experiments are planned to study the influence of H by comparing molecular beam epitaxy using atomic beam and CVD using hydrides gases but also introducing atomic hydrogen on the surface during growth.

### 4. Conclusion

In situ TEM observations provide the very first direct evidence that the formation of unusual $I_3$-BSFs is associated with the instabilities of the step flow growth mode depending on deposition rate and thermal conditions. Therefore, the formation of $I_3$-BSFs may be avoided at high temperature providing the deposition flow is low enough to keep a continuous step-flow regime. In the specific case of Ge-2H/GaAs-WZ, the temperature should be as high as possible while considering the limit
of 650 °C imposed by the sublimation temperature of GaAs and the desorption rate of Ge atoms. We have emphasized the importance to understand the growth mechanisms to achieve defect-free Ge-2H growth on m-planes. Finally, the results provide us credible arguments to propose a model for the formation of I₃-BSF in the metastable 2H structures based on a missing dangling bond on the (1-100) surface that forces a Ge atom to sit on a faulted cubic position. The model accounts for the nucleation on discrete points and the resulting triangular shape of the I₃ defect. Any cause of reduction of surface diffusion leading to destabilization of step-flow must be suppressed. For instance, hydrogen passivation must be further investigated.

5. Experimental Section

In this study, we utilize Au-catalyzed GaAs-WZ nanowires as a template for the growth of Ge-2H shells in both ex situ and in situ TEM characterization experiments.

**Ex Situ Growth:** For the ex situ, post-growth characterization experiments, the GaAs/Ge core/shell nanowires were grown in a low pressure (50 mbar) Aixtron close coupled shower head metal organic chemical vapor deposition (CCS-MOCVD) reactor. The growth of both the core and shell nanowires was performed at a total reactor flow of 8.2 standard liters per minute (slm) utilizing hydrogen (H₂) as the carrier gas. The GaAs nanowires were grown via catalyst-assisted growth following the vapor–liquid–solid (VLS) mechanism utilizing gold (Au) catalyst seeds. The Au catalyst seeds were deposited in nanodisks arrays arrangement on a GaAs (111)B substrate for the GaAs/Ge nanowires. For the GaAs nanowires, the growth template was annealed at a surface temperature of 565 °C (equivalent to thermocouple set temperature 635 °C) under an AsH₃ flow set to a molar fraction of $X_{\text{AsH}_3} = 6.1 \times 10^{-3}$. Then, the GaAs-WZ nanowires growth was performed at a temperature of 615 °C with TMGa and AsH₃ as material precursors set to molar fractions of $X_{\text{TMMG}} = 1.9 \times 10^{-3}$, $X_{\text{AsH}_3} = 4.55 \times 10^{-5}$, respectively, achieving a total flux $V/III$ ratio of 2.4. After the growth of the GaAs core nanowires, they are chemically treated with a diluted (1:10) potassium cyanide (KCN) aqueous solution, followed by a diluted ammonia solution ($\text{NH}_4\text{OH}$) step to remove residual GaAs oxide prior to subsequent Ge shell growth by MOCVD. Eventually, the GaAs nanowires were reintroduced in the MOCVD reactor and were used as a hexagonal material template and are overgrown with Ge. We used germane (GeH₄) (11%) diluted as a gas precursor for the Ge shell growth. The Ge shells were grown at substrate surface real-time monitored temperatures in the range of 405–565 °C (equivalent to 550–650 °C set temperature by a thermocouple) and at GeH₄ molar fraction of $X_{\text{GeH}_4} = 8.5 \times 10^{-2}$ for a certain growth period according to the desired shell volume. It is worth mentioning that the growth of each material family (GaAs and Ge) was performed utilizing a separate inner quartz kit and a substrate holder, i.e., susceptor in the MOCVD growth chamber to avoid materials cross-contamination. The details of the GaAs/Ge core/shell nanowires growth were summarized in S1 (Supporting Information).

In this study, multiple surface treatment conditions were investigated for the GaAs core nanowire templates prior to the Hex-Ge shell growth as explained in S1 (Supporting Information). The following three different GaAs nanowire templates have been utilized to mimic three different interface qualities to study their possible impact on the formation of the I₃ BSFs in the Hex-Ge shell:

1. **As-grown GaAs core nanowires:** after growth, the as-grown, Au-catalyzed GaAs nanowires were stored in a glove box under an ambient of nitrogen (N₂) to prevent surface oxidation and contamination. The utilization of the as-grown GaAs nanowires was meant to avoid any possible contamination or different surface termination that may occur during the chemical treatment of the nanowires’ surface to remove the Au particles. Hence, this type of GaAs cores template was referred to, hereafter, as “untreated as-grown” core surface, yet with Au particles. It is worth mentioning that after the chemical etching step of Au particles, APT experiments were performed on the etched GaAs core nanowires and the as-grown GaAs/Ge core/shell nanowires structures with Au present at the top, and no Au traces were detected as shown in refs. [9,11]. Hence, the concentration of Au impurities—if any present—was beyond the APT detection limit. So, the influence of Au on the crystal structure of Hex-Ge could be neglected.

2. **Chemically treated GaAs core nanowire:** in this template, the as-grown GaAs nanowires were chemically treated with a diluted cyanide (KCN in deionized water) solution to etch away the Au particles. They were then treated with diluted ammonia ($\text{NH}_4\text{OH}$ in deionized water) to remove residual GaAs oxides. This template will be referred to as a “chemically treated” core surface.

3. **Annealed GaAs core nanowires:** to obtain a clean core surface, free of potential wet chemical contaminants, after the Au etching step, the GaAs cores were annealed at a high surface temperature 613 °C under high AsH₃ pressure to desorb any existing contaminants after the annealing step. This template will be referred to as the “annealed” core template.

**In Situ Growth:** The growth of GaAs NWs and the epitaxy of Ge shells were observed in situ using a Cs-corrected Titan environmental TEM (ETEM) operated at 300 kV. Movies were recorded using a Gatan US10000 camera at a rate of 4 fps. The images in the article were snapshots extracted from the videos. A Protochips FUSION sample holder was used with heating chips featuring a SiC membrane with nine holes of 10 μm diameter and providing uniform heating in the observation area. Because of the polycrystalline nature of the SiC membrane, NWs were grown in arbitrary directions on the substrate. Some of them were anchored on the edge of a hole and might be freely suspended to be observable in a hole. Although the FUSION chips were calibrated by the manufacturer, huge fluctuations of temperature from one chip to another were observed. So, a range of temperature was empirically estimated using the melting point of Au on Si at 320 °C and looking at the tapering of Au catalyzed Ge nanowires (i.e., no tapering under 400 °C and increasing tapering with temperature).

The VLS growth of GaAs NWs was performed using trimethylgallium (TMGa) and tertiarybutylarsine (TBAs) and the Ge shell was grown using digermane (Ge₂H₆) diluted in H₂ (10% by volume). TMGa, TBAs, and Ge₂H₆ gases were installed in a gas cabinet. Diluted Ge₂H₆ was stored in a cylinder at a pressure of 5 bars and the flow was controlled by an MFC (mass flow controller). The TMGa and the TBAs liquids were stored in bubblers with a vapor pressure at 20 °C of 246 and 166 mbar, respectively; these low vapor pressures were sufficient to regulate their flow rates by conventional MFCs without the need for an additional carrier gas. The mixture was then delivered to the microscope column by an injector connected near the pole piece. During growth experiments, the pressure near the pole piece was measured by a Pirani pressure gauge. An additional compensated vibrational home-made pumping system was mounted on the column; this system was based on two identical bellows from either side of the additional turbo pump (80l/s). The column pressure was thus tuned (by setting the rotation rate or closing the valve) for a given precursor flow rate.

For the growth of GaAs nanowires, Au nanoparticles were deposited by evaporation on the heating chip. The in situ growth of the GaAs template was described in S2 (Supporting Information) both for Au and self-catalyzed GaAs NWs. The Au catalyst was useful to control the ZB to WZ crystal phase transition, the diameter of the W part (around 10–30 nm), and the morphology with very flat sidewall surfaces. In the case of self-catalyzed GaAs NWs, the lateral overgrowth was enhanced and very large NWs were obtained with inevitably high cutoff vicinal sidewall surfaces. Moreover, it was quite difficult to maintain the Ga droplet smaller than 50 nm in the WZ mode growth which was
detrimental for high-resolution analyses. These NWs may however be used to understand the influence of the initial surface roughness or steps as well as potential effects of Au contamination on the Ge shell (in S3, Supporting Information).

After the growth of GaAs NWs, organometallics were simultaneously stopped and diluted Ge$_2$H$_6$ was injected.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
TJu/e part : E.F. performed the growth of the nanowires, M.A.V. done the TEM experiments. E.F., M.V, W.H.P., M.A.V., and E.P.A.M.B. analyzed the data. M.A.V. and E.P.A.M.B. have co-supervised the ex situ part of the project.C2N part : L.V., C.R., and D.B. designed and conducted the in situ experiments with assistance of F.P. and I. F. L.V. analyzed the data from in situ experiments, developed the model, and wrote the manuscript. All authors discussed the results and commented on the manuscript. All authors gave approval to the final version of the manuscript. E.P.A.M.B. and L.V. acquired the research funding that supported this study.

Data Availability Statement
The data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.5602171, reference number 5602171.

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[38] S. H. Wolff, S. Wagner, J. C. Bean, R. Hull, J. M. Gibson, *Appl. Phys. Lett.* **1989**, *55*, 2017.
[39] S. M. Gates, S. K. Kulkarni, *Appl. Phys. Lett.* **1992**, *60*, 53.
[40] J. E. Vasek, Z. Zhang, C. T. Salling, M. G. Lagally, *Phys. Rev. B* **1995**, *51*, 17207.
[41] K. Oura, V. G. Lifshits, A. A. Saranin, A. V. Zotov, M. Katayama, *Surf. Sci. Rep.* **1999**, *35*, 1.
[42] J. E. Ayers, S. K. Ghandhi, *J. Cryst. Growth* **1988**, *89*, 371.
[43] V. Günther, F. Mauß, C. Klauer, C. Schlawitschek, *Phys. Status Solidi C* **2012**, *9*, 1955.
[44] P. Acoka-Kumar, S. Szpala, B. Nielsen, C. Szeles, K. G. Lynn, W. A. Lanford, C. A. Shepard, H. J. Gossmann, *Phys. Rev. B* **1995**, *51*, 4630.
[45] J. Owen, K. Miki, D. Bowler, C. Goringe, I. Goldfarb, G. Briggs, *Surf. Sci.* **1997**, *394*, 91.
[46] I. Goldfarb, J. H. G. Owen, P. T. Hayden, D. R. Bowler, K. Miki, G. A. D. Briggs, *Surf. Sci.* **1997**, *394*, 105.
[47] F. Hirose, M. Suemitsu, N. Miyamoto, *Jpn. J. Appl. Phys.* **1990**, *29*, L1881.
[48] E. Scalise, A. Sarikov, L. Barbisan, A. Marzegalli, D. B. Migas, F. Montalenti, L. Miglio, 2020, arXiv:2009.13630.
[49] T. Kuwahara, H. Ito, K. Kawaguchi, Y. Higuchi, N. Ozawa, M. Kubo, *Sci. Rep.* **2015**, *5*, 9052.