Fundamental Limitation of van der Waals Homoepitaxy by Stacking Fault Formation in WSe₂

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ABSTRACT:

As interest in layered van der Waals (vdW) materials keeps increasing, fundamental knowledge about their synthesis is gaining more and more value. The defect-free heteroepitaxial integration of vdW materials on large-area substrates is currently thoroughly being researched since it might encompass a successful transition of these materials to industrial applications. To date, Transition Metal Dichalcogenides (TMDs) are considered as one of the most promising vdW materials within the field of nanoelectronics. Nevertheless, the electrical characterization of heteroepitaxially grown TMDs still shows inferior performance as compared to exfoliated TMD flakes. This is mainly attributed to the high density of defects resulting from their challenging vdW heteroepitaxial synthesis. In this work, we have investigated in depth the vdW homoepitaxial synthesis of the WSe₂ TMD compound. We have demonstrated that even for homoepitaxy, the simplest type of crystal growth, challenges such as the formation of 60° twins need to be addressed. We evidenced the presence of 60° twins during vdW homoepitaxy which is assigned to stacking faults. The formation of these stacking faults is associated with their very similar binding energy as revealed by Density Functional Theory (DFT) calculations. Therefore, stacking faults are identified in this work to be the fundamental limitation of lowly-defective TMD vdW epitaxy. Furthermore, a generalized model is developed that determines the lower limit of the defect density based on the degree of control on the bilayer stacking phase and the nucleation density of the TMD compound. This model therefore assesses and quantifies for the first time the ultimate defect density level that can be achieved with vdW epitaxially grown 2D materials.

KEYWORDS: Molecular Beam Epitaxy, van der Waals epitaxy, Transition Metal Dichalcogenides, WSe₂, homoepitaxy, stacking faults, DFT.

1. INTRODUCTION

Thanks to the finding and the subsequent widespread research on graphene¹, interest in van der Waals (vdW) materials has increased expressively for the purpose of future semiconductor technologies^{2,3}. Like graphene, vdW materials are characterized by strong covalent intralayer bonding in coexistence with weak vdW interlayer bonding. A very promising class of vdW materials are the Transition Metal Dichalcogenides (TMDs)⁴. One monolayer (ML) of such a vdW material is composed of a layer of metal atoms (M) covalently sandwiched between two layers of chalcogen atoms (X₂). Accordingly, they are classified as MX₂ where they can exist in various compounds such as WSe₂, MoS₂, HfTe₂,...⁵ Unlike graphene, TMDs are characterized by the presence of a bandgap within a desirable energy range (0.5–2.0 eV)^{6,7} which makes them promising material candidates for (opto-)electronic applications^{8–11}. In addition, the recent observation of Weyl fermions¹², massless Dirac fermions¹³ and charge-density waves¹³ in various phases of TMD compounds expand the potential application even further.

Regarding the epitaxy of these materials, the specific feature of the weak vdW interlayer interactions has important implications. Pioneering work on vdW heteroepitaxy has learned that due to the absence of dangling bonds, the interactions at the heterointerface are governed by weaker vdW interactions as compared to the strong covalent interactions for conventional heteroepitaxy¹⁴. This aspect of vdW epitaxy generally results in relaxed lattice matching requirements which makes these materials even more promising for nanoelectronic applications¹⁵. Indeed, unique properties can now be engineered by stacking various vdW layers on top of each other without critical lattice matching or defect formation caused by strain relaxation^{16,17}.

Weak vdW interlayer interactions however also induce negative aspects regarding the heteroepitaxy. This can be seen from the difficult enforcement of a unique in-plane epitaxial relation between the vdW layer and the growth substrate^{18–20}. Recently, the engineering of the interfacial interactions during vdW heteroepitaxy has demonstrated to advance the integration of vdW materials onto commercial substrates^{21,22}. Nonetheless, additional challenges such as the relatively large in-plane mosaicities^{23–25} and the continuous presence of 60° twins^{26–28} are also to be resolved. As for the former, yet no clear solution but increasing the growth temperature is proposed²⁹, the latter might be improved by enforcing step-edge guided nucleation^{30,31} or clever surface engineering^{32,33}. On the other hand, even if the heteroepitaxy of TMDs is revealed to be very challenging, no studies were done until now on the homoepitaxy of TMD compounds due to the nonexistence of TMD substrates. In this work, we propose to

fabricate virtual TMD substrates to better understand the vdW nucleation and growth behavior in the simple case of TMD vdW homoepitaxy. This, to better address the twinning/stacking control that the research community is currently facing during vdW heteroepitaxy processes.

2. RESULTS AND DISCUSSION

In this work, the crystal growth of the WSe₂ TMD compound is in-depth investigated on a single crystalline WSe₂ surface. The virtual WSe₂ substrate is obtained by first performing an exfoliation of 2D WSe₂ flakes onto silicon substrates. This allows to study the nucleation and growth of WSe₂ directly on single crystalline WSe₂(0001) surfaces (see Supporting Information). Subsequently, the virtual 2D substrates are inserted into the ultra-high vacuum molecular beam epitaxy chamber. The WSe₂ homoepitaxy is then performed using the Plasma-Assisted Molecular Beam Epitaxy (PA-MBE) technique^{21,34}. After the PA-MBE growth, the samples are immediately *ex-situ* characterized by Atomic Force Microscopy (AFM) and Plane-View Transmission Electron Microscopy (PV-TEM).

2.1. AFM and crystal analysis

The homoepitaxy of WSe₂ is characterized using AFM and algorithmically analyzed in Figure 1. Figure 1a represents the AFM image of ~0.3 ML of WSe₂ homoepitaxy with optimal growth conditions at 450 °C and 0.15 ML h⁻¹ as attested by the well-defined equilateral triangular shape of the grown WSe₂ crystals. The nominal growth is limited to ~0.3 ML in order to prevent the coalescence process as to better highlight the shape, size and orientation of the initial WSe₂ crystals. The height histogram of the corresponding AFM image is presented in Figure 1b. The peak centered around the lowest heights corresponds to the pixels originating from the WSe₂ flake surface while the peak at higher heights corresponds to the pixels from the MBE WSe₂ crystals. The histogram emphasizes a clear separation between the WSe₂ epilayer and the WSe₂ virtual substrate. This, despite the very small thickness of the grown ML-thick WSe₂ crystals (~0.6 nm). The nucleation density is calculated to be as large as ~5E+10 cm⁻².

An algorithm that senses the characteristic equilateral triangular shape of the grown WSe₂ crystals is developed and applied for the supporting quantitative analysis of the AFM image of Figure 1a. When a certain WSe₂ crystal is detected having an equilateral triangular shape, the algorithm can accurately extract crystal properties such as the crystal's grain size 'a' and its azimuthal in-plane alignment 'α', as defined and illustrated in Figure 1c. The algorithmic analysis is therefore able to construct the triangular grain size distribution (Figure

Figure 1: Homoeopitaxy of WSe₂ characterized by AFM and quantitatively analyzed. a) AFM image of WSe₂ nucleated and grown on the single crystalline WSe₂ surface. Scale bar is 200 nm. Height scale is 2 nm. b) Height histogram of the AFM image presented in (a), fitted with two Gaussians corresponding to the WSe₂ flake and the MBE-grown WSe₂. c) Illustration of the characteristic equilateral triangular shape of the WSe₂ crystals, defining the triangular grain size and relative azimuthal orientation respectively noted by 'a' and 'α'. 'O' corresponds to the center of mass of the crystal. d) Triangular grain size distribution of the WSe₂ homoeopitaxy obtained from the algorithmic crystal analysis of the presented AFM image in (a). e) Distribution of the relative in-plane azimuthal orientation of the WSe₂ crystals for the WSe₂ homoeopitaxy, obtained from the algorithmic crystal analysis of the presented AFM image in (a).

1d) and the relative azimuthal orientation distribution (Figure 1e) of the WSe₂ homoeopitaxy which capture important insights.

The grain size distribution of the equilateral triangles is presented in Figure 1d and is quantified to be skewed Gaussian. This originates from the coexistence of a high density of small triangles (~20 nm) together with a lower density of larger triangles. It indicates that for the time frame studied (1) a saturated nucleation density is not yet reached and that (2) spontaneous Ostwald ripening is not observed for this epitaxial system. Both these observations could be explained by the small adatom diffusion length of the involved atomic species in the epitaxial process³⁵. The minimal grain size for proper triangular crystal detection was set at 15 nm. The largest grain size of uncoalesced triangles (for a nominal growth of only ~0.3 ML) is probed at ~80 nm. This is similar to literature results of MBE-based TMD heteroepitaxies performed on 2D crystal surfaces^{35–39}.

The degree of in-plane epitaxial alignment is quantified relying on the distribution of the relative azimuthal orientation of the triangular crystals. This distribution is presented in Figure 1e. A clear preferential in-plane alignment is observed from the histogram which indicates the good homoepitaxial registry of the MBE-grown WSe₂ crystals with the WSe₂

substrate. Two distinct peaks are clearly noticed in the presented histogram, originating from the large probability to find equilateral triangular crystals with a relative azimuthal orientation at respective angles of 15° and 75° . Surprisingly, the peaks are separated from each other by 60° which indicates that the homoepitaxy is characterized by a 6-fold in-plane rotational symmetry. The lack of in-plane inversion symmetry that makes TMDs however only 3-fold symmetric in-plane²¹, will as a consequence have a significant impact on the defect density of the grown homoepitaxial WSe₂ layer.

2.2. TEM and stacking analysis

The homoepitaxial stack is picked-up and transferred to the TEM grid for subsequent structural analysis. This study is presented in Figures 2a and 2b and is once more supported by a quantitative analysis relying on the developed algorithm (Figures 2f and 2g). Figure 2a represents the Selected Area Electron Diffraction Pattern (SAEDP) of the WSe₂ nucleated and grown on a single crystalline WSe₂ bilayer. The single-dot-like hexagonal diffraction pattern confirms the perfect epitaxial registry of the WSe₂ crystals with the surface of the WSe₂ flake. This is in good agreement with the observed in-plane distribution of the WSe₂ crystals as quantified by the algorithmic analysis on the AFM image (Figure 1e). It also confirms the absence of any strain in the grown WSe₂ likely originating from the absence of lattice mismatch between the WSe₂ epilayer and WSe₂ virtual substrate.

A color-coded Dark-Field (DF-)TEM image that is sensitive to the WSe₂ bilayer stacking configuration is presented in Figure 2b. The construction of this image is thoroughly explained in the Supporting Information based on the homoepitaxy of WSe₂ on a WSe₂ single-layer. Three different bilayer stacking configuration are differentiated from the color-coded DF-TEM image: 2H:AA', 3R:AB and 3R:AC. They are respectively presented in Figures 2c-d-e using cross-sectional ball-and-stick schematics in agreement with their occurrence as highlighted by the black line in Figure 2b. The 2H:AA' bilayer stacking configuration has simultaneously the chalcogen and metal atoms of the ML layer stacked on respectively the metal and chalcogens atoms of the bottom ML. This is only enabled by a 60° in-plane rotation of one ML with respect to the other. A bilayer that is stacked in the 3R phase lacks this relative 60° in-plane rotation and is therefore only able to stack the metal atoms of one ML on top of the chalcogen atoms of the other, or vice versa. Accordingly, the 3R:AB bilayer stacking configuration has the chalcogen atoms of the top ML stacked on the metal atoms of the bottom ML, whereas the 3R:AC configuration has the metal ones stacked on the chalcogens. The

Figure 2: Homoepitaxy of WSe₂ characterized by TEM and quantitatively analyzed. a) SAEDP of the WSe₂ nucleated and grown on the single crystalline WSe₂ bilayer. The green and red triangles assemble the diffractions spots that correspond to the different {1100} families. The encircled green and red diffraction spots are used for the reconstruction of the image presented in (b). b) Color-coded DF-TEM image of the WSe₂ homoepitaxy. The different colors represent the various bilayer stacking configurations. The yellow color corresponds to the 2H:AA' configuration. The green and red colors correspond to respectively the 3R:AB and 3R:AC bilayer stacking configuration. Scale bar is 100 nm. c, d, e) Cross-sectional schematic representations of respectively the 2H:AA', 3R:AB and 3R:AC bilayer stacking configurations. f) Correlation between the average triangular grain size (left axis) and the bilayer stacking configuration. The relative occurrence of the stacking configuration is presented on the right axis in blue. g) Correlation between the average relative in-plane azimuthal orientation of the MBE-grown WSe₂ crystals and the bilayer stacking configuration. Top-view schematic representations of the various bilayer stacking configurations are shown in the center of the graph.

presented color-coded DF-TEM image enables to study the WSe₂ crystal grain size and its in-plane alignment in function of the type of bilayer stacking configuration. The quantitative values that are obtained from this analysis are discussed in the next paragraphs and summarized in Table S1 in the Supporting Information. As will follow, this study will enable an appropriate quantification of the defect density which remained to date highly challenging for 2D vdW epitaxial systems.

The impact of the bilayer stacking configuration on the average triangular grain size is presented in Figure 2f. As seen from this figure, it is found that the average triangular grain size is similar for all the three observed stacking configurations. The calculated average grain sizes are 12.4±4.6, 15.5±3.2 and 13.9±5.0 nm for respectively the 2H:AA', 3R:AB and 3R:AC bilayer stacking configurations. They demonstrate that the growth rate of the WSe₂ crystals during vdW homoepitaxy is independent from the bilayer stacking configuration. The average crystal growth rate (defined as the average growth rate of every nucleated crystal) is estimated to be as low as 13±2.4 adatoms min⁻¹ for W and 26±4.8 adatoms min⁻¹ for Se.

Unlike the average WSe₂ triangular crystal growth rate, the average WSe₂ nucleation rate shows a clear dependency on the bilayer stacking configuration. This is seen from the differences in relative occurrence of the various stacking configurations and is presented in blue on the right Y-axis of Figure 2f. A relative occurrence of 41 %, 49 % and 10 % is respectively measured for the 2H:AA', 3R:AB and 3R:AC bilayer stacking configuration. These correspond to respective average nucleation rates of 5.4E+08, 6.5E+08 and 1.3E+08 nuclei cm⁻² min⁻¹. The average nucleation rates of the 2H:AA' and the 3R:AB configurations are calculated to be close to each other, while the nucleation rate of the 3R:AC configuration is significantly lower (> x4). Hence, not all bilayer stacking configurations are believed to be energetically equivalent. A more in-depth discussion on this will be presented later in the manuscript relying on Density Functional Theory (DFT) calculations.

The correlation between the in-plane alignment of the WSe₂ crystals and the bilayer stacking configuration is highlighted in Figure 2g. Here, the average relative azimuthal orientation of the MBE WSe₂ crystals is presented in function of the bilayer stacking configuration. For the 2H:AA' configuration, an average in-plane angle of 88±5° is calculated. The in-plane angles that are calculated for the 3R:AB and 3R:AC configurations are respectively 30±7° and 25±9°. A relative in-plane azimuthal difference of 61±7° is therefore calculated between the 2H and 3R bilayer stacked phases. This highlights that the MBE crystals that are stacked in the 2H-phase are in-plane rotated by 60° relative to the MBE crystals that are stacked in the 3R-phases (see top-view ball-and-stick schematics in Figure 2g).

The clear correlation between the in-plane azimuthal angle and the bilayer stacking configuration proves that the orientation of the 2D crystals and the stacking phase are clearly related one-to-one⁴⁰. This is particularly helpful when one wants to distinguish both phases of the bilayer stacking (2H versus 3R) without performing demanding and complex plane-view TEM analyses. A clear differentiation can now also be made from AFM analyses. In specific, the distribution of the in-plane alignment obtained from the AFM analysis that is presented in Figure 1e, can now link each individual peak to one specific phase of the bilayer stacking (2H/3R). Once more, this highlights that both the 2H and 3R bilayer phases are simultaneously formed during the WSe₂ homoepitaxy.

2.3. DFT calculations

As discussed in Section 2.2, our TEM analysis suggested that not all bilayer stacking configurations have a similar average nucleation rate (see also Table S1 in the Supporting Information). The 3R:AB bilayer stacking configuration was found to have the highest

nucleation rate closely followed by the 2H:AA' configuration. The 3R:AC configuration was found to have a significantly lower nucleation rate which as will follow might be explained by the presence of defects in the WSe₂ starting surface such as Se vacancies⁴¹. To elaborate further on this, various bilayer stacking binding energies are calculated relying on *ab-initio* calculations⁴² (Figure 3a). These binding energies are calculated for the case of a completely defect-free WSe₂ bilayer stack (black circles Figure 3a) and for a stack having Se vacancies in the upper chalcogen plane of the bottom ML (blue stars Figure 3a). The impact of other type of defects (such as Se or W vacancies in the top ML) on the binding energy can be found in the Supporting Information.

Figure 3: DFT calculations with corresponding relaxed structures. a) Calculated binding energies per unit cell of the WSe₂ bilayer in function of the bilayer stacking configuration. The energies are calculated for the case of a defect-free bilayer (black circles) and for the case of a bilayer having Se vacancies in the upper plane of the bottom ML (blue stars). b) Tilted cross-sectional ball-and-stick schematic of the relaxed WSe₂ bilayer stacked in the 2H:AA' configuration having a Se vacancy in the top chalcogen plane of the bottom ML. c) Tilted cross-sectional ball-and-stick schematic of the relaxed WSe₂ bilayer stacked in the 3R:AB configuration having a similar Se vacancy. The Se vacancies are highlighted with an asterisk.

The calculated binding energies of the defect-free bilayer stack reveal that the 2H:AA' configuration has a slightly larger binding energy as compared to the 3R:AB and 3R:AC configurations that both have a very similar binding energy. This implies that the 2H:AA' bilayer stacking configuration is energetically preferred compared to the other configurations and would therefore have the highest nucleation rate. However, since all calculated binding energies differ only by few meV per unit cell, the nucleation rates of both the 3R:AB and 3R:AC configurations are only expected to be slightly lower as compared to the nucleation rate of the 2H:AA' configuration. Nonetheless, the nucleation rates that are obtained in our experiments do not completely follow the proposed trends as revealed by our calculations on a defect-free WSe₂ bilayer stack. This explanation is therefore only believed to cover part of the phenomena that are observed.

The plausible presence of Se vacancies at the WSe₂ growth surface during the WSe₂ homoepitaxy however, is found responsible for the shift in stacking energy that explains our experimental observations. The presence of these vacancies are predicted to severely decrease the binding energy of the 2H:AA' bilayer stacking configuration, and additionally to lift the degeneracy of the 3R:AB and 3R:AC configurations towards a higher binding energy for the 3R:AB bilayer stacking configuration. The presence of Se vacancies at the growth surface are therefore found to favor a higher nucleation rate of the 3R:AB configuration as compared to the 2H:AA' configuration, and additionally as compared to the 3R:AC configuration. The relaxed simulated (4x4x1 supercells) structures having one Se vacancy at the growth surface for the 2H:AA' and the 3R:AB bilayer stacking configuration are presented in Figures 3b and 3c respectively using tilted cross-sectional ball-and-stick schematics. The combination of nucleation at both defect free areas (2H:AA' slightly preferred) and at areas with Se vacancies (3R:AB slightly preferred) can explain the experimentally observed trends in stacking-dependent nucleation rate.

2.4. Defect density model and calculation

The simultaneous presence of various bilayer stacking configurations and consequently the lack of control on the bilayer stacking phase, even for the simplest type of crystal growth (i.e. homoepitaxy), is highlighted in this manuscript to be highly problematic. Indeed, the coalescence of crystals originating from both these dissimilar bilayer stacking phases will create defective 60° Grain Boundaries (GBs) as a result of the corresponding 3-fold in-plane symmetry of the TMD compounds^{43,44}. Therefore, the lack of control on the bilayer stacking phase will set a fundamental limitation on the minimal defect density of the grown TMD. Even more, the inability to control the stacking configuration might be typical for vdW materials in general, since weak vdW interlayer interactions are indeed expected to only weakly couple with the underneath substrate⁴².

The effect of the inability to control the bilayer stacking phase during the WSe₂ homoepitaxy on the defect density is presented in Figure 4. When two WSe₂ crystals coalesce during the homoepitaxial growth, a defective 60° GB is formed when both crystals are stacked in a various bilayer stacking phase (3R versus 2H). This phenomenon is illustrated using High-Resolution (HR)-STEM in Figure 4a. The green triangle represents the crystal that is stacked in the 3R:AB bilayer stacking configuration, whereas the yellow triangle represents the crystal stacked in the 2H:AA' configuration. Since they are stacked in a various phase, their

Figure 4: Defect density as a result of 60° grain boundaries. a) HR-STEM image of the WSe₂ homoepitaxy. The green triangle highlights the WSe₂ crystal that is stacked in the 3R:AB bilayer stacking configuration. The yellow triangle highlights the WSe₂ crystal that is stacked in the 2H:AA' configuration. The coalescence of such two crystals results in the formation of a 60° grain boundary as surrounded in the image with the white rectangle. In the inset of (a), the enlarged image of the 60° grain boundary is presented. The grain boundary is highlighted using a blue dashed line. Scale bar is 2 nm. b) The calculated lower limit for the defect density of TMD epitaxy in function of the nucleation density and the control on the bilayer stacking phase. On the left Y-axis, the linear defect densities are presented per cm. On the right Y-axis they are expressed in equivalent areal defect densities per cm². c) Top-view representation of a fully closed WSe₂ ML with a nucleation density of 5E+10 cm⁻² and a control on the bilayer stacking phase of 60 %/40 %. The combination of this specific nucleation density and bilayer stacking control is highlighted in (b) using the letter 'c'. The white triangles represent the initial nucleation sites and their in-plane azimuthal orientation correspond to a particular bilayer stacking phase. The triangles that are pointing upwards (0°) are stacked in the 3R phase while the triangles that are pointing downwards are stacked in the 2H phase (60°). The black lines correspond to the presence of 60° grain boundaries. d) Similar representation as in (c) but with an improved control on the bilayer stacking phase (90₁₀ instead of 60₄₀), highlighted in (b) using the letter 'd'. e) Similar representation as in (c) but with an improved nucleation density (5E+08 cm⁻² instead of 5E+10 cm⁻²), highlighted in (b) using the letter 'e'.

coalescence will result in the formation of a 60° GB. This coalescence process is highlighted with a white rectangle in Figure 4a, where in the inset the 60° GB is marked with a blue dashed line. Accordingly, the WSe₂ homoepitaxy that is characterized by a high nucleation density (~5E+10 cm⁻²) in combination with a lack of control on the bilayer stacking phase (60 %/40 % 3R_{2H}) will result in a highly defective material synthesis with degraded electrical performances^{45,46}.

In order to quantify the defect density, the homoepitaxial nucleation and growth is modelled and the outcomes are presented in Figure 4b. This figure represents a lower limit for the total defect density of TMD epitaxy in function of the nucleation density and the control on the bilayer stacking phase. The defect densities are quantified for nucleation densities ranging from ~5E+08 to ~5E+11 cm⁻² and for a control on bilayer stacking ranging from 50₅₀ to 90₁₀ (3R_{2H}). The linear defect densities (i.e. per cm) are calculated along three symmetrical

$\langle 1\bar{1}00 \rangle$ in-plane directions and averaged. Additionally, the averaged linear defect densities are squared to equivalent areal defect densities expressed per cm^2 . A summary table of the specific examples that are discussed in the next paragraphs together with their corresponding defect densities is presented in the Supporting Information (Table S2). Note, that the quantified defect densities are an underestimation of the total defect density since the model only accounts for 60° GBs that are formed between the coalescence of crystals that are consecutively stacked in the 2H and 3R bilayer phases. The model therefore excludes point defects such as vacancies and defects that are formed between crystals that are stacked in the same phase but from a different configuration (e.g. 3R:AB versus 3R:AC). Nonetheless, the model represents and reveals novel understandings in the quantification of the defect density of TMD epitaxy, which remained to date highly unidentified.

The visual representations of the calculated defect densities are presented in Figures 4c-d-e. These figures correspond to top-view images of fully closed WSe_2 MLs. The initial nucleation sites and the bilayer stacking phases are indicated using a white triangle having a certain in-plane orientation ($0^\circ = 3\text{R}$ and $60^\circ = 2\text{H}$). The presence of the 60° GBs resulting from the coalescence of crystals that are stacked in the various bilayer phases (3R/2H) are highlighted using black lines. From these images, an appropriate quantification of the defect density for TMD epitaxy is obtained. Figure 4c represents our current optimal homoepitaxial nucleation and growth of WSe_2 by PA-MBE. This growth was characterized by a nucleation density of $\sim 5\text{E}+10 \text{ cm}^{-2}$ and a stacking control of 60 %₄₀ % (3R/2H). The lower limit of the equivalent areal defect density is correspondingly calculated as large as $2.6\text{E}+10 \text{ cm}^{-2}$.

Two possible routes to improve the homoepitaxy and hence lower the defect density are extracted from the graph presented in Figure 4b. The first route relies on improving the control on the bilayer stacking phase (3R versus 2H). The increased control on the bilayer stacking phase (from 60%₄₀ to 90%₁₀) reduces the areal defect density to $3.2\text{E}+09 \text{ cm}^{-2}$. This improvement is visually represented in Figure 4d. The second route relies on decreasing the nucleation density of the TMD epitaxy. This is visually represented in Figure 4e. Here, the nucleation density is reduced by 2 orders of magnitude to a value of $\sim 5\text{E}+08 \text{ cm}^{-2}$ as compared to the nucleation density represented in Figure 4c. This results in a reduction of the areal defect density down to $2.9\text{E}+08 \text{ cm}^{-2}$.

Although both the improvement on the stacking control and the reduction of the nucleation density reduces the defect density for TMD epitaxy, according to our model, both routes are not equally promising. From Figure 4b, it is seen that the route relying on the improvement of the stacking control is only able to reduce the areal defect density by a factor

~ 10 , which is only obtained when the bilayer stacking control is increased towards its upper boundary limits ($90_{/10}$). Taking into account that obtaining a stacking control of $90_{/10}$ will be extremely challenging as a consequence of the very similar binding energies for the various bilayer stacked phases due to the weak vdW interlayer interactions as revealed from our *ab-initio* calculations, a factor-10-gain in areal defect density can be considered as only marginal. Only an almost complete control on the bilayer stacking phase ($\sim 100_{/-0}$) is predicted to significantly reduce the equivalent areal defect density. Accordingly, this work reveals that the lack of complete control on the bilayer stacking phase is a fundamental limitation of lowly-defective TMD vdW epitaxy.

To overcome this limitation, we emphasize the second route that relies on the reduction of the nucleation density of the vdW epitaxy. Here, the model reveals that when the nucleation density is reduced by a factor 10, the areal defect density also reduces by a factor ~ 10 . Since we believe the window for improvement on the nucleation density of TMD epitaxy is still relatively large, this route is highlighted to be more promising and is believed to be key towards a lower-defective TMD vdW epitaxy. Counterintuitively, the defect density of homoepitaxially grown TMDs, is thus highly dependent on its nucleation density.

Lastly, one can argue if the in-plane epitaxial seeding of TMDs for their integration on large-area substrates is still essential or not? Indeed, our work highlights that complete control on bilayer stacking is anyhow extremely challenging and therefore has only a marginal gain on the defect density. Consequently, the epitaxy of TMDs will always be characterized by a high density of stacking faults as a result of weak vdW interlayer coupling, which will eliminate the beneficial effect of the in-plane epitaxial seeding by the formation of 60° GBs. Depending on the requirements of the targeted application, the gain of the in-plane epitaxial seeding can become marginal and other approaches such as selective nucleation by surface engineering⁴⁷ or textured deposition directly on Silicon substrates⁴⁸ might become preferred.

3. CONCLUSION

The vdW homoepitaxy was investigated in-depth by performing PA-MBE nucleation and growth of WSe₂ on single-crystalline WSe₂ exfoliated flakes. We found that the vdW homoepitaxy of the TMD compound was characterized by a high density of stacking faults, similarly as the observation of 60° twins as for the case of vdW heteroepitaxy. The presence of the stacking faults was assigned to the too subtle differences in binding energy between the different bilayer stacking configurations as a result of the weak vdW interlayer interactions as explained by our *ab-initio* calculations. Two different bilayer stacking phases (3R and 2H)

were found to coexist simultaneously. Remarkably, the 3R:AB and 3R:AC bilayer stacking configurations were found not to be equally distributed which was explained by the presence of Se vacancies at the homoepitaxial growth surface. The coexistence of both the 3R and 2H bilayer stacking phases resulted in a high density of defective 60° GBs upon closure of the ML, which was extracted from our generalized epitaxial nucleation and growth model. This model was developed to quantify a lower limit of the defect density for TMD epitaxy in function of the nucleation density and the degree of control on the bilayer stacking phase (3R/2H). The careful analysis of the outcomes of this model has highlighted that the inevitable presence of stacking faults is the main and fundamental limitation of lowly-defective TMD vdW epitaxy. This might open a potential for other synthesis approaches of vdW materials that reach beyond classical epitaxy.

4. EXPERIMENTAL SECTION

4.1. The virtual 2D crystal substrate

See Supporting Information.

4.2. PA-MBE growth of WSe₂

The WSe₂ is nucleated and grown using the technique of Plasma-Assisted Molecular Beam Epitaxy (PA-MBE)^{21,34}. A W atomic flux generated from an electron-beam evaporator and a metallic Se atomic flux generated from a H₂Se radio frequency plasma cell are simultaneously introduced in the growth chamber to form the stoichiometric WSe₂ crystals. The growth rate is set at 0.15 ML h⁻¹ which corresponds to a W flux of 0.16E+15 atoms cm⁻² h⁻¹. The partial pressure of the selenium plasma is set at 2.0E-05 Torr, corresponding to a flow rate of 24 sccm. The growth temperature is optimum at 450 °C.

4.3. WSe₂ flake exfoliation, pick-up and transfer

The WSe₂ bulk crystals are supplied by HQ Graphene and have a purity of > 99.995 %. The flakes are exfoliated onto the thermally oxidized 90-nm-thick SiO₂ dielectric of the 2-inch Si substrates. For the TEM analysis, directly after the WSe₂ homoepitaxy, the flakes are *ex-situ* picked-up and transferred to the TEM-grid according to the procedure described in the reference⁴⁹.

4.4. Plan-view HR-TEM characterization

A Titan3 G2 60-300 (FEI) with high brightness XFEG electron source is used for the HR-TEM analysis. The electron source is operated at 120 kV. SAEDPs are obtained using a beam diameter on the image plane of ~ 780 nm. Quantifoil TEM-grids having 2 μm diameter holes at a pitch of 4 μm are used.

4.5. AFM characterization

AFM images are taken with a Bruker Dimension at a scan rate of 0.6 Hz and with a resolution of 512 x 512 pixels per image.

4.6. DFT calculations

The *ab-initio* calculations are performed using DFT, as implemented in the SIESTA code⁵⁰. The generalized gradient approximation (GGA) is used for the exchange-correlation functional, as parametrized by Perdew-Burke-Ernzerhof⁵¹. Core electrons are described by norm-conserving pseudopotentials⁵² and valence electrons are described using double-zeta polarized basis sets. The energy cut-off is fixed to 350 Ry, and a (4x4x1) and (20x20x1) k-point mesh is used for the structural relaxation and binding energy calculations, respectively, with a convergence threshold for the residual atomic forces fixed to 0.01 eV $\text{\AA}^{-1}$. Long-range van der Waals interactions are included by using the DFT-D2 Grimme dispersion corrections⁵³. The computations are performed on (4x4x1) WSe₂ supercells with a vacuum layer of approximately 15 $\text{\AA}$ to avoid spurious interactions between the neighboring cells.

4.7. Defect density calculation

The 60° GB defect densities are calculated from 3.0 μm x 3.0 μm simulations. The presented linear defect densities (expressed per cm) are calculated from the average of three linear defect densities measured along the three symmetrical $\langle 1\bar{1}00 \rangle$ directions. These linear defect densities are individually quantified as the average of 20 linear defect densities that are calculated using 20 contours separated by 0.12 μm with a length of 2.4 μm . Additionally, the averaged linear defect densities are squared towards equivalent areal defect densities expressed per cm^2 . For improved statistics, every simulation is repeated 10 times. These repeated simulations have various but uniform nucleation sites in agreement with their corresponding nucleation density and control on bilayer stacking phase.

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