Role of Stronger Interlayer van der Waals Coupling in Twin-Free Molecular Beam Epitaxy of 2D Chalcogenides

Wouter Mortelmans,* Karel De Smet, Ruishen Meng, Michel Houssa, Stefan De Gendt, Marc Heyns, and Clement Merckling*

1. Introduction

The discovery of graphene and its unique transport properties has boosted recent interests in a broad variety of 2D materials. In this framework, layered chalcogenides are a promising class of 2D van der Waals (vdW) materials. The transition metal dichalcogenides (TMDs) having the chemical form of MX₂ and the topological insulators (TIs) having the chemical form of group-V₂VI₃ are important examples. TMD materials such as WSe₂, MoS₂, etc. are highly interesting for opto- and nanoelectronics, thanks to their semiconducting properties and a direct bandgap at monolayer (ML) thickness. TI materials such as Bi₂Se₃, Sb₂Te₃, etc. (and their alloys) are most promising for their strong spin–orbit coupling and band inversion, enabling new states of quantum matter useful for topological electronics.

The large-area integration of 2D chalcogenides is of crucial importance for these materials to enable industry-compatible devices. The growth of vdW materials through the process of epitaxy is one of the most promising approaches to meet the demanding requirements of single-crystalline quality, large-area uniformity, and large-scale throughput. Therefore, the quasi-vdW and vdW epitaxy of 2D materials is one of the most promising approaches to meet these requirements. The formation of 60° twin defects in (quasi-)vdW epitaxy is one of the major concerns in (quasi-)vdW epitaxy of these materials.

Large-area epitaxy of layered materials is one of the cornerstones for a successful exploitation of van der Waals (vdW) materials in the semiconductor industry. The formation of 60° twin stacking faults and 60° grain boundaries is of major concern for the defect-free epitaxial growth. Although strategies to overcome the occurrence of these defects are being considered, more fundamental understanding on the origin of these defects is highly essential. This work focuses on understanding the formation of 60° twins in (quasi-)vdW epitaxy of 2D chalcogenides. Molecular beam epitaxy (MBE) experiments reveal the striking difference in 60° twin occurrence between WSe₂ and Bi₂Se₃ in both quasi-vdW heteroepitaxy and vdW homoepitaxy. Density functional theory (DFT) calculations link this difference to the interlayer vdW coupling strength at the unit cell level. The stronger interlayer vdW coupling in Bi₂Se₃ unit cells compared to WSe₂ unit cells is explained to result in a reduced twin occurrence. Hence, such compounds show significantly more promise for defect-free epitaxial integration. This interesting aspect of (quasi-)vdW epitaxy reveals that the strength of interlayer vdW coupling is key for workable 2D materials and opens perspectives for other strongly coupled vdW materials.
WSe₂ and Bi₂Se₃ vdW homoepitaxy on respectively WSe₂(0001) and Bi₂Se₃(0001) exfoliated flakes. The similarities and differences of the various epitaxy processes are discussed and density functional theory (DFT) calculations are performed to shine more light on the fundamental aspect of 60° twin formation.

2. Experimental Section

The experimental methodology that is applied for the 2D chalcogenide MBE processes is illustrated using simplified schematics in Figure 1. The (1 × 1) reconstructed sapphire surfaces were obtained by thermal annealing at ≈900 °C under H₂ as reported and characterized previously.[23] The virtual WSe₂(0001) and Bi₂Se₃(0001) substrates were fabricated relying on mechanical exfoliation on silicon substrates.[33,34] The epitaxies were performed using plasma-assisted (PA-)MBE with H₂X radio frequency (RF) plasma sources[61] and electron-beam evaporation of elemental W transition metals (Figure 1a) and thermal evaporation of elemental Bi metals (Figure 1b). For the WSe₂ compound, the growths occurred at a temperature of 450 °C with low growth rates of ≈0.1–1.3 ML h⁻¹, driven by the W evaporation flux. The growths of the Bi₂Se₃ compound occurred at a lower temperature of 160 °C with higher growth rates of ≈5–12 ML h⁻¹, and similarly, driven by the Bi evaporation flux. In both cases, the higher growth rates corresponded to the quasi-vdW heteroepitaxies and the lower growth rates to the vdW homoepitaxies. The H₂Se fluxes were set to a total and maximal pressure of ≈2.0 × 10⁻⁵ Torr in the RF plasma source.

More details on these conditions and their justification are found in the Supporting Information.

3. Results and Discussion

3.1. Quasi-vdW Heteroepitaxy

The quasi-vdW heteroepitaxies of WSe₂ and Bi₂Se₃ on the sapphire surfaces are presented in Figure 2. They represent 1 ML of WSe₂ (Figure 2a,b) and 1 ML of Bi₂Se₃ (Figure 2c,d) on (1 × 1) c-plane sapphire substrates. The single-layer thickness is chosen to maximize the amount of quasi-vdW heteroepitaxy while avoiding the vdW homoepitaxy of the 2nd ML on the 1st ML. The atomic force microscopy (AFM) data of the sapphire substrate and the quasi-vdW heteroepitaxies are discussed in the Supporting Information.

The polar reflection high-energy electron diffraction (RHEED) characterization of the WSe₂ quasi-vdW heteroepitaxy clearly reveals the in-plane epitaxial registry of the WSe₂ crystals with the underlying Al₂O₃ surface (Figure 2a). The epitaxial relation is highlighted using yellow and blue diamonds for respectively WSe₂ and Al₂O₃ and is characterized as [1120]
The WSe₂(0001)//[11̂20]Al₂O₃(0001). This is a similar epitaxial relationship as previously reported for the growths of WSe₂/MoS₂ on various reconstructed sapphire surfaces.[21,33,37] The identical (01̂T) and (01) diffraction streaks observed from the diffraction patterns uncover an important limitation of the quasi-vdW epitaxy experiment. In Figure 2b, the RHEED pattern in the WSe₂ (11̂20) direction is presented where several intensity line profiles are extracted from various “kₜ” positions that give information about the out-of-plane ordering of the grown 2D crystal planes.[62] The equivalent intensities of the (0̂T) and (01) diffraction streaks confirm the absence of the expected threefold symmetric stacking hence the abundant presence of 60° twins.[26] This results from the lack of a preferred stacking in the [11̂20] WSe₂(0001)//[11̂20] Al₂O₃(0001) registry and consequently results in a high defect density of 60° grain boundaries which is known from literature to impact device performances.[63,64]

A striking difference with respect to WSe₂ quasi-vdW heteroepitaxy is observed in Bi₂Se₃ quasi-vdW heteroepitaxy. This is obtained from the polar RHEED characterization presented in Figure 2c,d. The epitaxial relation of the Bi₂Se₃ with the (1 × 1) sapphire surface is similar as for the case of WSe₂: [11̂20] Bi₂Se₃(0001)//[11̂20] Al₂O₃(0001) (Figure 2c, purple and blue diamonds for respectively Bi₂Se₃ and Al₂O₃). However, the stacking preference and hence the occurrence of 60° twins (and 60° grain boundaries) is dissimilar. This is corroborated from the inequivalent (0̂T) and (01) diffraction streaks of the Bi₂Se₃ quasi-vdW heteroepitaxy as observed from the Bi₂Se₃(11̂20) RHEED pattern (Figure 2d). The observation of these inequivalent streaks is in agreement with the threefold in-plane rotational symmetry of the Bi₂Se₃ crystal structure, and confirms the preferred and unique stacking of Bi₂Se₃ on sapphire and hence the reduced formation of 60° twins.[65] In summary, Bi₂Se₃ quasi-vdW heteroepitaxy on sapphire is less prone to stacking fault formation compared to WSe₂ (and in general TMDs)[21,34], despite the equivalent in-plane crystal structure symmetry and presence of vdW gap in both compounds. Consequently, Bi₂Se₃ shows significantly more promise for defect-free epitaxial integration.

### 3.2. VdW Homoeopitaxy

To further explore these interesting differences, a study is presented based on vdW homoeopitaxy of the highlighted 2D chalcogenides. The vdW homoeopitaxy experiments represent ~1/3 ML of WSe₂ and Bi₂Se₃ grown on respectively exfoliated WSe₂(0001) and Bi₂Se₃(0001) flakes, obtained by a reduction of the growth rate compared to the experiments performed on sapphire. Such partial ML thickness is preferred here, to enable the identification of the individual grown 2D chalcogenide crystals before coalescence and to avoid the onset of multilayer growth. The limited lateral sizes of the exfoliated flakes make RHEED characterization impractical. The focus is therefore set to AFM analysis.

The WSe₂ vdW homoeopitaxy is identified by a high density of characteristic triangular grains with crystal sizes up to ~50 nm. This is observed from the AFM image presented in Figure 3a. The algorithmic analysis[19] of the WSe₂ crystals nucleated and grown on the WSe₂(0001) surface enables to qualify the epitaxial relation and to reveal the presence of a preferred stacking. The distribution of the relative azimuthal in-plane orientation of the analyzed WSe₂ triangular grains is presented in Figure 3b. This distribution with a 60° difference between both consecutive peaks clearly reveals the sixfold in-plane periodicity, which is reported to result from the inability to control the bilayer stacking phase.[13] Consequently, both the 2H and 3R stacking phases are simultaneously present in the vdW homoeopitaxy resulting in the presence of a high density of 60° twins and 60° grain boundaries upon closure of the ML. Hence, our AFM and RHEED studies have shown that in both vdW homoeopitaxy and quasi-vdW heteroepitaxy, the WSe₂ compound systematically yields severe formation of stacking faults which is emphasized to be very challenging to control.

This observation is once more significantly different in the Bi₂Se₃ growth. The AFM characterization and crystal analysis of the Bi₂Se₃ vdW homoeopitaxy is presented in Figure 3c,d. The Bi₂Se₃ vdW homoeopitaxy yields characteristic equilateral triangles having a crystal grain size up to ~100 nm, and a threefold periodic in-plane alignment of the nucleated and grown crystals as in agreement with the symmetry of the Bi₂Se₃ crystal structure. The larger grain size is linked with the larger vapor pressure of the elemental bismuth, since adatom diffusion is previously reported to correlate with vapor pressure in vdW epitaxy of TMDs by MBE.[14,16] The Bi₂Se₃ vdW compound does not suffer from the fundamental limitation of stacking fault formation in vdW homoeopitaxy as generally observed in TMD vdW compounds.[21,33,34] This opens a window for defect-free integration.
of Bi$_2$Se$_3$ through the growth process of vdW homoepitaxy, and possibly also for other related vdW compounds.

3.3. Density Functional Theory

Theoretical DFT calculations are presented for the highlighted 2D chalcogenide materials, WSe$_2$ and Bi$_2$Se$_3$, to understand the striking differences in twin defect formation that are observed from the experimental data. The focus is placed on DFT calculations for the homoepitaxy cases. A generalization of these outcomes could be extended to the heteroepitaxy cases. The calculated binding energies using periodic structures are reasonable estimates of the binding energy of nuclei that consist of numerous unit cells.

In Figure 4, the binding energies of WSe$_2$ and Bi$_2$Se$_3$ are calculated for the set of most stable bilayer stacking configurations (details in the Supporting Information). The numerical values of the calculated binding energies are expressed in meV per unit cell (uc) and are presented in Figure 4a, with left and right axes corresponding to respectively WSe$_2$ and Bi$_2$Se$_3$. The various unit cell stacking configurations are defined by considering a bilayer representation of the atomic layers at the interface, as schematically illustrated in Figure 4b. The unit cell stacking configurations are then noted by assigning a letter for each bilayer at the interface in agreement with the void spaces A, B, and C, and a prime (′) is used when the bonding symmetry of the top bilayer is inversed with respect to the bonding symmetry of the bottom bilayer (see Figure 4b). This notation and bilayer representation enables an appropriate and physically relevant comparison between WSe$_2$ and Bi$_2$Se$_3$ units that respectively have a triple- and quintuple-layer structure.

Figure 4. Binding energy from DFT calculations for 2D chalcogenides. a) Calculated binding energy in meV per unit cell for both WSe$_2$ and Bi$_2$Se$_3$ bilayer homostuctures in function of the bilayer stacking configuration. The WSe$_2$ binding energies are plotted on the left Y-axis (yellow). The Bi$_2$Se$_3$ binding energies—that are significantly larger—are plotted on the right Y-axis (purple). b) Definition, schematic illustration, and notation of the various stacking configurations based on a bilayer representation of the atomic layers at the interface. Gray corresponds to the metal atom and yellow to the chalcogen atom. c) Numerical values of the bond angle, bond length, and lattice parameter for both WSe$_2$ and Bi$_2$Se$_3$ for the representation used in (b).

The usage of the prime (′) easily separates the 0° from the 60° twin, and results in six possible unit cell stacking configurations for each vdW compound (AA′, AB′, AC′, AA, AB, and AC). In Figure 4c, the bond angle ($\theta$), bond length (l), and lattice parameter (a) of both compounds are given to justify the representation used in Figure 4b.

The DFT calculations reveal two important aspects. The first aspect concerns the comparison of the most preferred stacking with the most preferred 60° twin for each vdW compound. As seen from Figure 4a, the preferred unit cell stacking in WSe$_2$ is noted as AA′ and has two stable 60° twins noted as AB and AC. The comparison of these configurations reveals that 60° twins in WSe$_2$ (AB and AC) are slightly less stable having a binding energy difference of $\approx$6 meV per uc ($\approx$2.4%) compared to the most preferred unit cell stacking (AA′). In the case of Bi$_2$Se$_3$, the most perfect unit cell stacking is noted as AB′ and similarly has two stable 60° twins (AB and AC). The preference of AB′ for Bi$_2$Se$_3$ compared to AA′ for WSe$_2$ could be linked to the differences in the unit cells like bond angle, bond length and lattice parameter (Figure 4c). The comparison reveals that for Bi$_2$Se$_3$, 60° twins are $\approx$11 meV per uc ($\approx$3.4%) less stable compared to the preferred unit cell stacking. Hence, both WSe$_2$ and Bi$_2$Se$_3$ only have very subtle differences in unit cell binding energy between 0° and 60° twins, and it is unlikely that the slightly larger imbalance in Bi$_2$Se$_3$ is fully responsible for the experimentally observed striking difference in 60° twin defect formation.

The second important aspect that is revealed from our DFT calculations is related to the absolute unit cell binding energies of the two vdW compounds. From Figure 4a, it is obvious that the binding energy in the Bi$_2$Se$_3$ unit cell, in general, is larger compared to the binding energy in the WSe$_2$ unit cell. This can be seen from the absolute values and energy-range difference of the WSe$_2$ and Bi$_2$Se$_3$ axes (left and right, respectively) in Figure 4a. In the preferred stacking, the Bi$_2$Se$_3$ unit cell results in an $\approx$94 meV per uc ($\approx$40%) lower (i.e., stronger binding) energy compared to the WSe$_2$ unit cell. It is this substantially stronger vdW interlayer coupling in Bi$_2$Se$_3$ unit cells that could explain the striking difference in twin defect formation.

The statement made above is supported by DFT calculations that consider the alteration of the unit cell stacking configuration by nucleus rotation. In Figure 5, the energy per unit cell (relative to the most preferred stacking) for the stacking alteration from the most preferred stacking configuration to the most preferred 60° twin is presented. In the case of WSe$_2$ unit cells (left panel), this is respectively from AA′ to AB. In the case of Bi$_2$Se$_3$ unit cells (right panel), this is respectively from AB′ to AB. As a result of the stronger interlayer vdW coupling in Bi$_2$Se$_3$ unit cells, the energy barrier for unit cell stacking alteration by nucleus rotation is significantly higher ($E_{\text{barrier}}$ = 122.2 meV per uc for Bi$_2$Se$_3$ compared to $E_{\text{barrier}}$ = 44.1 meV per uc for WSe$_2$). This is consequently related to the larger amount of energy that is required to rotate the Bi$_2$Se$_3$ nucleus from its stronger epitaxial registry with the underlying surface, and could be a potential mechanism obstructing the severe formation of 60° twins.

Moreover, the thermal energy per unit cell to enable this nucleus rotation from 0° to 60° is found insufficient to overcome this energy barrier ($E_{\text{barrier}}$) for the case of Bi$_2$Se$_3$ homoepitaxy ($E_{\text{thermal}} = 39.5$ meV per uc at $T = 160$ °C), while it is found
sufficient for the case of WSe$_2$ homoepitaxy ($E_{\text{thermal}} = 64.5$ meV per uc at $T_g = 450$ °C) (see Figure 5 gray zone). This would result in a more challenging and hampered Bi$_2$Se$_3$ nuclei rotation during nucleation/growth compared to WSe$_2$ nuclei, and could confirm the remarkable enhanced control on 60° twin defect formation in Bi$_2$Se$_3$ homoepitaxy and its related epitaxy processes.

4. Conclusion

It is shown how the formation of 60° twin defects in Bi$_2$Se$_3$ epitaxy is fundamentally better controlled compared to WSe$_2$ epitaxy. The quasi-vdW heteroepitaxy and vdW homoepitaxy of WSe$_2$ systematically yield a high density of stacking faults resulting from 1) the calculated subtle differences in unit cell binding energy for the 0° and 60° configurations and 2) the weak vdW interlayer coupling in the WSe$_2$ units. In Bi$_2$Se$_3$, the threefold character of the quasi-vdW heteroepitaxy and vdW homoepitaxy clearly reveal the striking difference having a preferred stacking sequence and reduced presence of 60° twin defects. Despite the similar subtle differences in unit cell binding energy for the 0° and 60° configurations, this is explained by the stronger interlayer vdW coupling in the Bi$_2$Se$_3$ unit cells.

Stronger interlayer vdW coupling challenges nucleus rotation from the most stable 0° configuration to the next stable 60° twin. The formation of 60° twins in (quasi-)vdW epitaxy is therefore not only related to the difference in unit cell binding energy between the 0° and 60° configurations, but also to the absolute strengths of the interlayer vdW interactions between the unit cells. The strength of the interlayer unit cell coupling becomes hence a crucial parameter to control the defect-density of epitaxially grown 2D chalcogenides. This opens perspectives for Bi$_2$Se$_3$ and other related vdW compounds with strong interlayer unit cell coupling to further accelerate the defect-free epitaxial growth of 2D materials. With the insights generated in this study on 60° twin formation in (quasi-)vdW epitaxy, a first step is taken for the development of mitigation strategies emphasizing on the control of the interlayer interaction strength.

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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D chalcogenides, density functional theory, molecular beam epitaxy, stacking faults, van der Waals epitaxy

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