1. Introduction

Single crystal manufacturing has promoted the rapid development of the semiconductor industry; the large-size high-quality silicon (Si) ingot makes the large-area integrated circuit with high density and reliability possible. However, the scaling of Si based transistors has approached its physical limit as the continuous upgrading. Thus, exploiting alternative materials is currently the key to realize the smaller, faster and cheaper chips in the future. Two-dimensional (2D) materials with thickness ranging from single- to few-atomic thick layer have become the most promising candidate to replace conventional materials to construct new-generation electronic and optoelectronic devices. A variety of device prototypes have been devised and demonstrated excellent performance and remarkable application potential. However, the prerequisite of industrial applications of 2D materials is the fabrication of large-area high-quality single crystals, which would possess superior intrinsic properties and high homogeneity to meet the demands of high-performance devices integration. Therefore, the preparation of single-crystal 2D materials is of great significance for their practical applications.

Two strategies have been developed to grow 2D single crystals. One is to make one nucleus grow up. In this growth regime, the precursors need to be well controlled to reduce the nucleation density or fed locally to allow only one nucleus to form and grow up, always leading to slower growth rate and more energy and time consumption. Although various techniques have been developed to enhance the growth rate effectively, this strategy is still not suitable for the large-scale production. The other is to make all the nuclei have the same orientation, then grow up and finally merge into a continuous film without grain boundaries. Mostly it is realized by the epitaxial growth on single-crystal substrate where millions of nuclei expand their size simultaneously and thus a large film could be obtained in a short time. Accordingly, epitaxial growth has been universally recognized as the most promising technique to realize the large-scale preparation of single-crystal 2D materials.

Up to now, different 2D materials have been epitaxially grown on various single-crystal substrates, including graphene and hexagonal boron nitride (h-BN) on copper (Cu), germanium (Ge), other transitional metals and metal alloys, and transition metal dichalcogenides (TMDCs) on sapphire and mica, and gold (Au). The heart issue in the epitaxy is to regulate the orientations of the 2D domains which is closely related to the interplay between 2D domains and the single-crystal substrates. In consideration of this, we have reviewed and summarized four epitaxial growth modes of 2D materials on different substrates based on their characteristic interactions,
namely, van der Waals (vdW) epitaxy, edge epitaxy, step-guided epitaxy and in-plane epitaxy (Figure 1). By focusing on the growth mechanism, we hope to gain a deeper insight into the epitaxial growth of 2D materials and explore the potential opportunities to realize large-scale production of high-quality 2D single-crystal materials.

2. Fundamentals of 2D Materials Epitaxy

Epitaxy on single-crystal substrates provides a feasible approach to accurately control the domain orientation of epitaxial materials to accomplish their large-area single-crystal growth. In the epitaxy of traditional three-dimensional (3D) materials, the epitaxial layer interacts covalently with the substrate due to the exist of dangling bonds on the surfaces, and strong chemical bonding forms at the interface, which determines the orientation of the epitaxial layer.[84] The epitaxy can be attained in systems where the substrate and the epitaxial layer are of the same materials or different from each other. The former is called homoepitaxy while the latter is heteroepitaxy. In the heteroepitaxy, the lattice mismatch between the substrate and epitaxial layer leads to the strain in epilayer or the misfit dislocations at the interface, which may degrade the quality of the epilayer (Figure 2a,b).[85] Besides, if the lattice mismatch is too large, the heteroepitaxy is unachievable. In general, lattice mismatch smaller than of 5–10% is required to achieve conventional epitaxy.[86] Hence, the rigid lattice matching demand in traditional 3D materials epitaxy extremely restricts the viable material combinations in the heteroepitaxy.

In 1984, Koma et al. first proved the epitaxial growth of Se on cleaved bulk Te crystals and NbSe$_2$ films on MoS$_2$, which was named as “van der Waals epitaxy”.[87] In comparison to conventional epitaxy, the vdW epitaxy features vdW interaction between the substrate and the epilayer, resulting from the vdW interface without surface dangling bonds. So the epitaxy can be realized in bulk materials of which surface dangling bonds have been passivated or in vdW materials which naturally have completely terminated surfaces (Figure 2c,d). The lack of strong covalent bonds at vdW interface significantly reduces the rigorous requirements for lattice matching in conventional epitaxy (the lattice mismatch could be as large as 50% in vdW epitaxy[88]), which extremely extends heteroepitaxial systems. Meantime, with the rise of 2D materials, the vdW epitaxy has attracted wider attention in the direction of 2D single crystal preparation. It is noteworthy the single-crystal 2D materials, serving as vdW substrates, also provide new opportunities for the fabrication of many functional materials, including the III-V compound semiconductors,[89,90] metals,[91,92] macromolecular polymers,[93,94] and so on.

The epitaxy of 2D materials has been achieved on various single-crystal substrate, but the nuances of epitaxy mechanism on different substrates have yet been discussed carefully. Therefore, the comprehensive understanding of the mechanisms for different 2D materials epitaxy on various types of substrates will be of great value to guide the experimental exploration of controllable synthesis of large-scale high-quality single-crystal 2D materials.

3. Epitaxial Growth of 2D Materials

Since the first unambiguously production and identification of graphene in 2004, a large amount of 2D materials have been successfully synthesized in the lab. In the aspect of epitaxial growth of single crystal, the most representative and widely studied 2D materials are semimetal graphene, semiconductor TMDC and isolator h-BN. These three kinds of 2D materials have also been recognized as the most potential candidates for the practical applications. Besides, they have different lattice structures and their epitaxial growth requires distinct substrates to realize the metal-catalyzed and noncatalytic epitaxy. By studying their epitaxial growth, we hope to gain a universal understanding of the epitaxy mechanism of different 2D single crystals. Thereby, in
In this review, we mainly focus on the epitaxial growth of graphene, h-BN and TMDC.

3.1. Van der Waals epitaxy

Van der Waals epitaxy, as the name suggests, is modulated by the vdW interaction between the 2D material and substrate, which requires that the substrate surface is free of dangling bonds. In view of this, 2D materials are perfect substrates for vdW epitaxy, and the stacking structure of 2D materials is called vdW heterostructure. With great efforts, various vdW heterostructures have been successfully grown.\[95–104\] Graphene/h-BN heterostructure was first directly grown by chemical vapor deposition (CVD) method in 2013 and many exotic properties have been observed in this heterostructure due to the formation of the Moiré pattern.\[95\] Figure 3a shows well aligned graphene domains epitaxially grown on the h-BN substrate, producing the Moiré pattern with a periodicity of $15 \pm 1 \text{ nm}$, by which we can know that the lattice directions of graphene and h-BN are parallel.\[95\] Similarly, in a WS$_2$/MoS$_2$ heterostructure prepared by vdW epitaxial growth, the edges of triangles are parallel with each other and an extra photoluminescence (PL) peak resulting from an interlayer excitonic transition can be observed (Figure 3b)\[96\] indicating a clean interface which can hardly achieved by mechanical transfer technique. VdW epitaxy can be achieved not only in vdW heterostructures consisting of 2D materials with similar lattice constants and structures, but also in the ones with large lattice mismatch or even different lattice structures.\[97–102\] The WSe$_2$/SnS$_2$ heterostructure with lattice mismatch of 14.3% was successfully grown by a two-step CVD method and their corresponding selected area electron diffraction (SAED) patterns show two parallel hexagonal diffraction patterns with the calculated lattice spacings consistent with the SnS$_2$ (0.32 nm) and WSe$_2$ (0.28 nm) (Figure 3c), respectively, also denoting the strain in the epitaxial layer is negligible by forming the commensurate structure of $7 \times 7$ SnS$_2$ on $8 \times 8$ WSe$_2$.\[97\] It has been proved that the vdW epitaxial growth of 2D materials is still valid even for a lattice mismatch as high as 50%.\[88\] TMDC monolayers, possessing three-atomic-layer structure with transition metal layer sandwiched between two chalcogen layers, are distinct from graphene and h-BN, while their heterostructures can also be prepared by vdW epitaxy, such as TMDC/graphene,\[98\] TMDC/h-BN.\[99–102\] Shi et al. achieved a direct growth of MoS$_2$ domains on CVD-grown graphene film by vdW epitaxy (Figure 3d), which have the same lattice orientation with underneath graphene film.\[98\] But, we should note here that the aligned hexagonal MoS$_2$ domains actually have two orientations with $60^\circ$ rotation, also named inversion orientations, which are energetically equivalent, but different in lattice structure. And when the neighboring two domains with inversion orientations merge together, twin boundary will form.\[105–106\]

VdW epitaxial growth can also be achieved on some inactive bulk substrates, such as mica, sapphire, gallium nitride (GaN) and so on. Fluorphlogopite mica (K$_3$Mg$_6$Al$_2$Si$_3$O$_{10}$F$_2$) with layered structure is acknowledged to be an excellent vdW epitaxy substrate for growing 2D materials, because it has atomic flatness, surface inertness and no dangling bonds. Centimeter-scale uniform monolayer MoS$_2$ on mica has been successfully synthesized with two preferential orientations of either 0° or 60° (Figure 3e).\[75\] It is noteworthy that the epitaxial relation was built by...
the rotation of MoS$_2$ lattice by 30° where the lattice mismatch was greatly reduced to only $\pm 2.7\%$, as the schematics shown in the insert in Figure 3e. Moreover, the vdW epitaxy also occurs when the surface of bulk substrate is passivated.\cite{107-109} Sapphire is a thermally stable substrate compatible with the harsh environments required for CVD growth of TMDC. Figure 3f displays WSe$_2$ domains epitaxially grown on the Se-passivated $c$-plane sapphire which also possess two preferential orientations.\cite{106,109} Similarly, h-BN could be successfully epitaxially grown on Ge(100) and Ge(110) surfaces passivated by nitrogen.\cite{109} Actually, even if the surface is not passivated, the interaction between the substrate and the 2D materials is also the vdW interaction. To distinguish from the epitaxy on dangling bond free substrate, we call the epitaxial growth of 2D materials on a surface with dangling bonds as quasi-vdW epitaxy. For example, MoS$_2$ can be grown on GaN(0001) with MoS$_2$ domain edges aligned with the (1100) plane of GaN (Figure 3g),\cite{101} confirming the epitaxial relation between GaN and MoS$_2$ lattices. Compared with the Raman spectrum of mechanically exfoliated monolayer MoS$_2$ on SiO$_2$/Si substrate, peak position for the strain-sensitive in-plane mode $E_{2g}^{1}$ is almost the same for MoS$_2$ directly grown on GaN, indicating negligible strain during the growth, while the 1 cm$^{-1}$ blue shift of the $A_{1g}$ peak together with no observable change in the position of $E_{2g}^{1}$ is suggestive of a strengthening vdW interaction between MoS$_2$ and GaN (Figure 3h).\cite{111} That means the interaction between the 2D material and the GaN substrate is enhanced by the dangling bonds, but no chemical bonds are formed. The different energy barriers for precursors absorbed onto dangling-bond and the dangling-bond free surfaces make the growth of uniform 2D materials monolayers more feasible in quasi-vdW epitaxy. The most common quasi-vdW epitaxial growth system is virtually the TMDC on $c$-plane sapphire, namely Al$_2$O$_3$(0001). The threefold symmetry of 2H-phase TMDC and its long-range commensurability with Al$_2$O$_3$(0001) result in an epitaxial orientation of TMDC domains that is either 0° or 60°.\cite{67-69} And both the theoretical calculation and optical characterization reveal the nature of vdW interaction between the TMDC and the sapphire substrates with dangling bonds.

In the traditional epitaxy the lattice orientation of epilayer is modulated by the strong chemical bonding between the epilayer and the lattice-matched substrate, and the lattice orientation of the epilayer is determined at the very beginning of the epitaxial growth. Markedly different from traditional epitaxy, the initially formed nuclei of 2D materials have random orientations in the...
vdW epitaxy due to the absence of strong chemical bonds. On the other hand, the weak vdW interaction between 2D materials and the substrate allows the small nuclei to rotate/translate a certain degree. Theoretical calculations have revealed that the binding energy between the 2D materials and substrate varied with the rotation angles and the small nuclei could rotate till to the most stable orientation at the growth condition. Hence, the epitaxial relation can be established by the nuclei rotation driven by the vdW interaction between 2D materials and the substrate. Although the nuclei rotation during the growth is only supposed theoretically, the rotations of small flakes of 2D materials on vdW surfaces have been widely observed.

Many studies have been carried out to explore the efficient way to modulate vdW epitaxy. By changing growth temperature, it was found that relatively high growth temperatures were conducive to obtain well aligned MoS$_2$ domains on Al$_2$O$_3$(0001) (Figure 4a–c). Combined with theoretical calculations, the MoS$_2$ domains with preferential orientations were demonstrated to have maximum binding energy with Al$_2$O$_3$(0001) (Figure 4d). It also means that the coupling between the 2D material and the substrate is stronger at the preferential orientations, in accordance with experimental observations that the photoluminescence signals from the aligned TMDC domains on sapphire were strongly suppressed compared with that of the randomly oriented ones owing to the strain induced by strong coupling. Experimentally, it was explained that as the temperature increases the thermodynamic energy ($k_B T$) could overcome the rotational barrier of the small nucleus to achieve the preferential orientation. Many works have demonstrated the synthesis of high-quality films with well-aligned domains at relatively high temperature.
whereas too high temperature can induce dispersed orientations of the initial nuclei where the binding energy differences for different orientations could possibly be smeared out by the thermodynamic energy.\textsuperscript{[68,108]}

In practice, the epitaxial growth of MoS\(_2\) can also be realized at relatively low temperature. Aljarb et al. reported that at the growth temperature of 750 °C smaller well-aligned MoS\(_2\) domains can be grown on c-plane sapphire substrate with high concentration of S feeding, while larger random oriented ones were obtained with low concentration of S feeding (Figure 4e–h).\textsuperscript{[116]} Similarly, high Se/W ratio contributed to the alignment growth of WSe\(_2\) on c-plane sapphire.\textsuperscript{[117]} In the CVD growth of TMDC, metal precursors are always in the solid state. If the metal-containing particles are not fully reduced during the growth, they would serve as the nucleation sites and the nuclei lose their rotational freedom, resulting in failure of vdW epitaxy.\textsuperscript{[118]} Hence, adequate reduction of metal precursors may facilitate the vdW epitaxy. Now it can be understood that high ratio of chalcogen and transition metals ensures sufficient reduction of metal precursors and thus the domains alignment. Besides, high chalcogen evaporation temperatures and early feeding of chalcogen vapors are also conducive to achieve the alignment of TMDC domains.\textsuperscript{[116,117]} It also should be noted that considering the smaller nucleus has lower barrier to rotate, the growth rate of nucleus should be as slow as possible that it has enough time to rotate to the preferred orientation.\textsuperscript{[116,117]} To sum up, from the perspective of precursor reaction, sufficient reduction of metal precursors and appropriate reaction rate are favorable for vdW epitaxy. Meantime theoretical calculation results revealed that TMDC domain alignment on sapphire with Al-terminated surface is more feasible due to higher absorption energy.\textsuperscript{[119]} In the experiments, early feeding of sulfur and hydrogen at high temperature can reduce sapphire surface by removing oxygen, resulting in an Al-terminated surface and further better domains alignment.\textsuperscript{[69,119,120]}

VdW epitaxial growth of 2D materials can achieve well-aligned domains and thus improve film quality after the domains merging with each other. However, the vdW epitaxy of h-BN and TMDC whose lattices have threefold symmetry always results in antiparallel domains and thus the twin boundaries when the domains stick with each other, which may degrade the film performance.\textsuperscript{[115,119]} The antiparallel domains formation is due to the binding energy degeneracy and only when it is broken can the unidirectionally aligned domains be grown. According to density functional theory (DFT) results (Figure 4i), the binding energy differences between two inversion orientations of MoS\(_2\) triangles on h-BN with interstitial B vacancy and Mo adatom at the center can reach 0.5 eV, totally different from the much weaker variation in the binding energy of the same MoS\(_2\) flake on h-BN without defects, where the center of the flake lies above a B atom (red squares), N atom (blue diamonds), or hollow site (green triangles) as the flake is rotated.\textsuperscript{[121]} This defect-induced orientational preference has also been demonstrated experimentally. As show in Figure 4j, ∼90% of the MoS\(_2\) domains grown on h-BN by physical vapor transport (PVT) method that prioritizes the initial heterogeneous nucleation of metal species at the boron vacancy have the same orientation.\textsuperscript{[121]} The authors also realized the orientation as well nucleation density control by the h-BN surface defects density and achieved well aligned WSe\(_2\) domains with a single preferred orientation (84%) using metal organic CVD (MOCVD) method.\textsuperscript{[122]} Similarly, dot defects with W dangling bonds produced by a focused laser irradiation can induce a fully oriented VSe\(_2\) nucleation and growth on the WSe\(_2\) (Figure 4k,l).\textsuperscript{[123]} The introduction of point or dot defects to the single-crystal substrate can not only contribute to the controllable nucleation of 2D materials, but also modulate their interaction with the substrate and further realize the unidirectional epitaxial growth. This strategy may provide an efficient way to prepare large-area single-crystal vertical stacking heterostructures.

The lack of strong covalent bonds at vdW interface significantly reduces the rigorous requirements for lattice matching in conventional epitaxy, which extremely extends heteroepitaxial systems. However, due to the weak van der Waals interactions, multiple preferential orientations are easily formed in the growth of low-symmetry 2D materials, such as TMDC materials with threefold symmetry.\textsuperscript{[106]} In addition, no dangling bonds will lead to difficulties in nucleation of 2D domains on the substrate.

### 3.2. Edge Epitaxy

The surface of 2D materials is free of dangling bonds, while there are inevitable dangling bonds at the edge. When growing 2D materials on some chemically active substrates, such as metal substrate, which serves as both catalyst and substrate to promote the dissociation of precursors and the synthesis of 2D materials,\textsuperscript{[124]} the edge atoms of 2D materials will interact with the metal substrate strongly and form chemical bonds.\textsuperscript{[125–122]} In the nucleation stage, the number of atoms in the domain varies from a few to a few dozen\textsuperscript{[126]} and the proportion of edge atoms is relatively large. Therefore, the chemical interaction between the edge atoms and the substrate is much stronger than the intralayer vdW interaction,\textsuperscript{[127]} and the orientation of nucleus is determined by the edge interactions. In this case, the epitaxial growth is called “edge epitaxy.”\textsuperscript{[127]}

The most typical edge epitaxial growth systems are the growth of graphene and h-BN on metal substrates. It is worth mentioning that the edge of the graphene or h-BN can also be passivated by active atoms from the environment of its growth, such as H or OH groups, where there is only the weak vdW interaction between the 2D material and the substrate, and the law to control the 2D domains orientations follows the vdW epitaxy as discussed in Section 3.1.\textsuperscript{[111,116]} The theory calculation results give the conditions for the edge C atoms of graphene being passivated by hydrogen on Cu(111), which are determined jointly by the growth temperature and H\(_2\) partial pressure (Figure 5a).\textsuperscript{[133]} The conditions for hydrogen passivation of 2D edges are varied with different metals.\textsuperscript{[134]} Therefore, only under proper growth conditions and on proper substrates the edge epitaxy can be realized. Although the interfacial interactions between graphene and different metal substrates change significantly, the unsaturated graphene edge can always bend to the metal surface and form chemical bonds during the growth.\textsuperscript{[125–135]} Given this interaction of their edges, dome-shaped carbon nanoslands would form on the metal surface which can be regarded as the intermediate between carbide clusters and quasi-freestanding graphene.\textsuperscript{[125]} As shown in Figure 5b is an atomic model of a carbon dome on Ir(111).\textsuperscript{[125]} Consequently, the interactions between graphene and metals consist of strong chemical bonding at the edges and
weak vdW forces between the layers. According to the correlation between the bonding interaction of the cluster and the number of atoms at the periphery, the effect of edge interactions on binding energy decreases with cluster size (Figure 5c). Thus at the infancy of growth the orientations of domains are determined by edge interactions and such orientations can be inherited by the matured graphene due to the higher rotation barrier of larger graphene domains. Similar to graphene on metal surface, the strong interactions between the h-BN edges and underlying metal atoms also lead to the formation of dome-like geometries.

To elucidate how edge interactions determine the orientation of graphene and h-BN on metal surface, we focus on their edge epitaxial growth on low-index single-crystal Cu substrates, namely Cu(100), Cu(110), and Cu(111). Graphene and h-BN have the same lattice structures and similar lattice constants (graphene: 2.46 Å; h-BN: 2.50 Å) and thus exhibit almost the same growth behaviors in the CVD growth. By theoretical calculation, it has been demonstrated that the zigzag (ZZ) edge of graphene and the nitrogen terminated ZZ (N-ZZ) edge of h-BN are generally the slowest propagating edges because of their highest propagation barriers. Graphene has a C_{6v} symmetry and the single-crystal graphene domain always is perfect hexagonal with ZZ edges, while h-BN has a C_{3v} symmetry and the single-crystal h-BN domain always is triangle with N-ZZ edges. The ZZ (N-ZZ) edge of graphene (h-BN) tends to bond with Cu surface and when it is along the Cu<110> direction, the binding energy has the maximum. The strongest bonding of the ZZ (N-ZZ) edge of graphene (h-BN) along the Cu<110> direction mainly lies in two aspects: i) The atoms are close-packed (with high symmetry) and thus the electron density fluctuation is lowest with alternative ridges and valleys of uniform height along <110> direction, leading to the preferential formation of a straight edge. ii) The lattice mismatch is minimum along <110> direction. The <110> direction varies depending on the Cu crystal surface and thus the alignment of graphene and h-BN is different on three low-index Cu surface (Figure 5d). Theoretically, unidirectional alignment of graphene domains can be achieved on both Cu(111) and Cu(110), while two identical orientations along perpendicular directions on Cu(100). Experimental
observations are consistent with this theoretical prediction ideally.\[44,141,142\] Due to a relatively low surface energy, large-size single-crystal Cu(111) can be achieved by abnormal grain growth from commercial polycrystal Cu and thus the most feasible synthesis method of large graphene single crystal is to epitaxially grow graphene on Cu(111) currently.\[44\] Figure 5e is an optical image of aligned graphene domains on single-crystal Cu(111) substrate.\[44\] Actually, above alignment theory is also applicable to the epitypse of graphene on other FCC metal substrate. For example, graphene grows with a single orientation on the Ge(110) substrate with graphene edges along $<110>$ direction resulting from the Ge-C covalent bonds at the early stage of growth.\[53\]

The edge epitaxy of h-BN follows the same alignment rules as that of graphene. However, due to the lower symmetry of h-BN ($C_{3v}$), the inversion triangle h-BN domains (of 60° rotation) with degenerated energy have different crystallographic directions, and when they merge together twin boundaries would form. Therefore, even on Cu(111) and Cu(110) single-crystal h-BN film can hardly be achieved and the domains on Cu(100) have four different orientations.\[45–47\] Although the energy degeneration can be broken when the influences from subsurface Cu layer are also taken into consideration, the energy difference of two orientations are so small (several meV) that both orientations appear during the high-temperature CVD process (Figure 5f, inversion h-BN domains with 60° rotation grown on Cu(111) substrate).\[46\]

In addition, that the slowest propagating edges of a 2D material tend to align along high symmetry directions of the substrate also appears in the vdW epitaxial mode, such as the ZZ edge of TMDC domains along $<1120>$ or $<1100>$ direction of Al$_2$O$_3$(0001).\[67–69\] $<1100>$ direction of Al$_2$O$_3$(1120)\[71\] and $<1100>$ direction of GaN (m-plane).\[111,143\] This means the domain alignment rule in edge epitaxy also works for vdW epitaxy. That is to say, no matter the edge is passivated by functional groups in the growth environment or by the metal surface, 2D domains would have the same orientation distribution theoretically on metal substrate.\[46–48\] On the other hand, due to the strong chemical bonding between the edge and the metal surface, the edge epitaxial growth of 2D materials on the metal substrate is more robust compared with the vdW epitaxy.

### 3.3. Step-Guided Epitaxy

The aligned growth of 2D materials on different single-crystal substrates can be realized by vdW or edge epitaxy. Nevertheless, only graphene with sixfold lattice symmetry can have unidirectional domains, which can further seamlessly stitch into single-crystal films. Most of other 2D materials, including h-BN and TMDC, have lower symmetry and thus always have antiparallel domains, resulting in twin boundaries which greatly degrade the electronic properties on most substrates.\[70,119\] Tremendous efforts have been made to obtain unidirectional alignment of h-BN and TMDC. In 2019, Wang et al. successfully demonstrated the ~99% unidirectional alignment of h-BN domains on single-crystal vicinal Cu(110) substrate with Cu step edges along $<211>$ direction (Figure 6a).\[49\] Unlike previous reports, the unidirectional alignment clearly reveals the presence of one and only configuration of h-BN/vicinal Cu(110). The DFT calculation revealed that the N-ZZ edge of h-BN domains bonding with $<211>$ step edge is the exclusive minimum-energy state (Figure 6b,c).\[49\] This suggests that the inversion degeneracy of h-BN domains can be lifted by the atomic $<211>$ step on the vicinal Cu(110) surface.\[144\] Combining the experimental observation and theoretical calculation, the “step-guided epitaxy” was first proposed definitely that the steps edge along the specific direction would guide the unidirectional alignment of 2D materials. In the wake of this work step-guide epitaxial growth of different 2D materials on different substrates has been springing up.\[145\]

On a vicinal low-index surface or high-index surface, the steps trend only up or down across the entire surface, while on a low-index surface, for example, Cu(111) surface, the steps can trend both up and down (Figure 6d).\[52\] It is plausible that the edge-guided h-BN domains on such low-index surface can have both orientations of 0° and 60°. The DFT calculation of binding energy for 6 kinds of stacking configuration of h-BN cluster on Cu(111) surface demonstrates the existence of steps amplifies the bonding energy difference between the two most stable configurations (N$_i$B$_{ii}$ and N$_i$B$_{iii}$), enabling easily achieving the unidirectional alignment of the h-BN lattice (Figure 6d,e).\[52\] Virtually the experimental observations are well consistent with the theoretical calculation that unidirectionally aligned h-BN domains can be obtained on a wafer-scale single-crystal Cu(111) substrate (Figure 6f).\[52\] Additionally, the step-guided epitaxy is also applicable to the unidirectional growth of graphene. Figure 6g displays the unidirectionally aligned graphene nanoislands on the 12° miscut Ge(001) surface.\[146\]

The step-guided epitaxy of single-crystal 2D materials is universal and can also realize the growth of unidirectional domains of TMDC materials. Because Cu is highly reactive with chalcogen atoms,\[147\] growing TMDC materials generally employs the Au substrate in view of its chemical inertness toward the chalcogen precursor in the traditional CVD process.\[177,148\] In 2020, Yang et al. first proposed the step-guided epitaxial growth of MoS$_2$ and obtained wafer-scale single-crystal MoS$_2$ film on the single-crystal Au(111) which was prepared by the melting and resolidifying technique.\[79\] The MoS$_2$ nucleates and aligns at the step edges along $<110>$ direction of Au(111) substrate and then grows up, producing unidirectionally aligned domains (Figure 6h).\[79\] Some domains have trapezoid shapes, characteristic of the step-guided growth.\[149,146\] Similar to Cu(111), there are both step-up and step-down edges along the $<110>$ direction on Au(111), named as A-step and B-step in Figure 6i.\[79\] The DFT calculation indicates that Mo terminated ZZ (Mo-ZZ) edge attaching to B-step has the minimum contact energy, 0.16 eV/formula unit) lower than that of Mo-ZZ edge attaching to A-step, meaning Mo-ZZ edge attaching to B-step is energetically more favorable, which thus facilitates unidirectional growth of MoS$_2$ domains (Figure 6j).\[79\] Additionally, the binding energy maximum of step contact is almost twice as that of the surface contact, indicating that the interaction between step and Mo-ZZ edges plays a decisive role in the oriented nucleation and growth of MoS$_2$ domains. In 2021 Choi et al. successfully grew several TMDC single-crystal monolayers on various high-index Au surface, demonstrating the universality of this step-guided epitaxial growth of TMDC.\[81\] It was also confirmed that the orientation of domains is independent of surface index but step direction, consistent with the above analysis on the mechanism of step-guided growth. This strategy
provides a general avenue for the single-crystal growth of 2D materials.

Actually, as early as 2015, the aligned growth of 2D WSe₂ on c-plane sapphire guided by the steps has been observed (Figure 7a). When the growth temperature is above 950 °C, parallel atomic steps along <11̅20> direction are formed due to surface reconstruction of sapphire substrate and can guide the nucleation and growth of aligned WSe₂ domains. However, in their experiments the uphill WSe₂ domains cannot stitch with the downhill ones but overlap on them when propagating across the step edge (Figure 7b). Thus they could not achieve the continuous single-crystal WSe₂ film. This year the WS₂ monolayers on c-plane sapphire with well-defined <11̅20> steps were synthesized using MOCVD growth. By designing a multi-step variable-temperature growth process, high nucleation density and small unidirectionally aligned WS₂ domains were obtained (Figure 7c). In this case, the small domains could stitch with each other, forming a continuous film. However, the STEM image reveals the existence of translational boundaries that may arise from a slight lattice offset between coalescing aligned domains (Figure 7d), which are rarely observed in the single-crystal films grown on the metal substrate. This is because the high stability of the sapphire at the growth temperature makes the surface atoms movement extremely hard and thus it is difficult to offset lattice translational mismatch between neighboring WS₂ domains by sapphire surface atoms movement, which is a common
phenomenon for metal substrates. \cite{79,81} Therefore, it requires more careful control of the growth kinetics to achieve perfect domains stitching and further high-quality single-crystal films on sapphire substrate. Recently, Li et al. realized the epitaxial growth of wafer-scale single-crystal MoS$_2$ on c-plane sapphire with steps along <1100> direction under S-rich condition. \cite{73} Their experimental results demonstrated that unidirectionally aligned MoS$_2$ domains can only be grown on the surface with <1100> steps, in contrast with those of inversion orientations on the surface with <1120> steps (Figure 7c,f). \cite{73} The first-principles calculation results reveal that under S-rich condition, the Mo-ZZ edge with a $100\%$ S coverage (ZZ-MoS$_2$) bonding with <1100> step edge is the most stable configuration, with formation energy of 0.1 eV Å$^{-1}$ lower than that of the inversion domain (ZZ-S$_2$), while the two orientations domains bonding with <1120> step edge have comparable formation energies (Figure 7g,h). \cite{73} Thus it should be noted here that only the steps that can lift the energy degeneracy of inversion orientations could guide the unidirectional alignment of nucleation and growth of the 2D domains. The aligned domains could merge into a continuous single-crystal film perfectly, demonstrated by both the atomic resolved STEM image and polarized second harmonic generation mapping, and the film exhibits excellent uniformity and electronic performance. Based on above experimental observations and theoretical calculations, we can obtain almost complete understanding toward the step-guided epitaxial growth. Generally, the step edges on the substrate surfaces could act as preferential nucleation sites and 2D materials tend to nucleate at step edges by the formation of energetically stable chemical bonds with edge atoms. \cite{126,145} Thus lattice match between the step edges and 2D edges is needed and the step direction and the 2D edge configuration concurrently determine the alignment of the 2D materials. \cite{144,149}

High-index surfaces ideally with parallel step along specific directions provide abundant surface structures to investigate the epitaxial growth of 2D materials. Traditionally a high-index surface can be prepared by cutting a low-index single crystal along a specific direction. The cutting plane is the high-index facet with step direction along the line intersecting the low-index surface and step density is determined by the cutting angle ($\theta_{CA}$) between the cutting plane and its nearest low-index facet (Figure 8a,b). \cite{149} We take Cu as an example for detailed analysis. According to crystallography step orientations of FCC metal could be along <100>, <110>, and <211> directions. If the cutting direction is along one of them, straight steps will be produced, otherwise tilted steps (step with kinks) may form. For example, Cu(111) sertial high-index surfaces (the one with the terrace of (111) facet) have two types of straight steps along <110> or <211> directions and two types of tilted steps consisting of two different components of straight steps (Figure 8c). \cite{149} A straight 2D edge attaching to a straight step edge i) and a tilted 2D edge attaching to a tilted step edge ii) are two energetically favorable interfaces (Figure 8d). \cite{149} For the case (i), once the lattice match between the step edge and 2D edge is met, unidirectional alignment of 2D domains can be achieved. For the case (ii), the larger step edges would determine the primary direction of the domain, while the
Figure 8. Atomic steps on metal surfaces. a,b) schematic diagram showing cutting of a single crystal with a high-index surface where $\theta_{\text{CA}}$ denotes the cutting angle. c) Different possible types of step edges on Cu(111) surface. d) Interfaces between h-BN and step edges. Reproduced with permission. Copyright 2021, Wiley-VCH. e) Complementarity of kinks at the h-BN edge (red B, blue N) to the steps of the metal surface. $\delta_k$ indicates the mismatch in kink height. Reproduced with permission. Copyright 2019, American Chemical Society. f) Color-false dark field low energy electron microscopy (LEEM) image (left) and low energy electron diffraction (LEED) patterns (right) of h-BN on Cu. The colors of h-BN triangles are assigned according to the diffraction patterns, and the white dashed arrows represent the step directions. Reproduced with permission. Copyright 2019, Wiley-VCH.

matching degree between metal kinks ($k$) and 2D kinks ($k_{2D}$) also affect the primary direction. Only when the kinks complement each other, that is, the offset $\delta_k = k_{\text{Cu}} - k_{2D}$ is small (<0.1 Å), the primary orientation of the domains can be preserved in the presence of the kink (Figure 8e).\(^{144}\)

Ideally, the high-index surface is consisted of parallel and evenly spaced straight or tilted steps, while in the real growth condition, surface roughening is inevitable which would lead to step meandering. This step direction change can also alter the orientation of the attached 2D domains as shown in Figure 8f.\(^{190}\) Theoretical calculations revealed that the high-index surface with a large cutting angle was more robust to surface roughness and thus to achieve unidirectionally aligned 2D domains.\(^{51,144}\) Additionally, cutting angle also determines the step density and further the epitaxial growth behaviors of 2D domains.\(^{148}\) For instance, graphene nanoribbons of high aspect ratios can be grown on Ge(001) by edge epitaxy and the two dominant orientations with same proportions (perpendicular to each other) were ascribed to the surface atomic reconstruction on the terrace.\(^{146}\) However, the growth behaviors of graphene nanoribbons change as the cutting angle (cutting toward the $<111>$ direction of Ge(001) substrate) increases. With the increment of cutting angle, step density increases so that step-induced epitaxial growth predominates, resulting in unidirectional growth of nanoribbons when the cutting angle is larger than 10°. Thus by rational design of step direction and step density, it could be robust to achieve the step-guided epitaxy and further realize the fabrication of high-quality single-crystal 2D materials films.

3.4. In-Plane Epitaxy

In-plane epitaxy means the epitaxial growth of one 2D material from the edge of the other one, forming a lateral heterojunction with covalently bonded interface. Unlike vertical heterojunctions, which can be prepared by physical stacking, lateral heterojunctions can only be achieved by direct growth. In 2012, Levendorf et al. first reported the graphene/h-BN lateral heterostructure by a patterned regrowth strategy and demonstrated the mechanical continuity of the junction, and the conductivity of graphene and insulativity of h-BN in the patterned film maintained excellently.\(^{150}\) Liu et al. gave the explicit experimental results to show the epitaxial growth of h-BN from the edge of graphene domain on Cu substrate. They utilized hydrogen to etch graphene to obtain fresh edges, where h-BN nucleated and grew (Figure 9a).\(^{151}\) The atomic-resolved scanning tunneling microscope (STM) image shows the stitching boundaries and lattice coherency between graphene and h-BN (Figure 9b).\(^{152}\) Also it can be observed that at the stitching boundaries h-BN has B/N-zigzag terminations. The h-BN lattice adopts the orientation of the graphene independent of the underlying Cu lattice as proven by LEED (Figure 9c,d), because the in-plane bonding is much stronger than and thus overrides the out-of-plane vdW interaction with the Cu.\(^{151}\) Also graphene can be epitaxially grown from h-BN edge.\(^{153–155}\) Liu et al. used photolithographically patterned h-BN monolayers as templates to grow graphene to produce patterned heterojunctions.\(^{156}\) And in-plane superlattices of alternating graphene and h-BN could be achieved directly via a
CVD process by feeding alternating streams of C and B, N pre-cursor gases.\cite{157} The dangling bonds make the nucleation barrier at the 2D edge lower than on the 2D surface, and so nucleation is preferred at the edge under lower growth temperature or lower precursor concentrations.\cite{158,159} On the other hand, nucleation rates at edge or on the surface become comparable under high temperature or high precursor concentration.\cite{158} Gao et al. developed a temperature-triggered reaction route in CVD process to achieve the selective growth of h-BN/graphene lateral and vertical heterostructures on Cu foils.\cite{160} Such an atomic-scale seamless stitching in the h-BN/graphene lateral heterojunction is because the same lattice structure and small lattice mismatch (1.7%) between graphene and h-BN, which could be accommodated via in-plane bond length variations. Besides, that h-BN and graphene have comparable interactions with the metal substrate, giving a consistent overlayer-substrate distance and a highly comparable surface corrugation, is of great significance to achieve the perfect stitching during the growth.

In-plane epitaxy of 2D materials requires the matching of the crystal structure and this is what we associate with conventional epitaxy, where the difference is simply the bonding of 2D and 1D interfaces. The similar lattice structure of TMDC provides a
prerequisite for in-plane epitaxial growth. In 2014, Gong et al. successfully prepared high-quality in-plane heterostructures of WS$_2$/MoS$_2$ in a one-step growth where the sequential growth of MoS$_2$ and WS$_2$ was achieved due to their nucleation and growth rates difference (Figure 9e). They found at low temperature WS$_2$ could epitaxially grow from MoS$_2$ edges, resulted from the advantage of low nucleation potential at the edge due to dangling bonds. The high-resolution STEM images show the atomic structures of heterojunction interface where MoS$_2$ and WS$_2$ stitch seamlessly into a single hexagonal lattice and share the same orientation (Figure 9f,g). Atomically sharp zigzag interface with metal-terminated and chalcogen-terminated zigzag edges joined by covalent bonds, was preferred in such heterostructures. This interface is common in TMDC heterogeneous interfaces, which means that this interface is the most stable in terms of energy. Whereas, armchair interface was also observed with slight interdiffusion of metal elements, possibly due to the low stability of the armchair edge during the growth. Meantime Duan et al. designed a CVD system that allowed in situ switching of the solid source (WS$_2$ and WSe$_2$) into and out of the hot zone to enable the sequential growth of single- or few-layer WS$_2$/WSe$_2$ lateral heterostructures. One-step growth strategy could guarantee the fresh edge during the growth, which is beneficial to achieve the coherent stitching interface, while it also makes the alloying inevitable, resulting in the inhomogeneous composition and properties of the lateral heterojunction. To tackle the alloying problems, researchers have developed various techniques. Li et al. applied two-step growth method where they grew WSe$_2$ at a higher temperature first and then grew MoS$_2$ in a separate furnace at a lower temperature to avoid any alloy reaction. They also could achieve high-quality lateral heterojunction with atomically sharp interface. Furthermore, as-grown TMDC monolayers can be patterned and the exposed edges serve as the seeds for growing a second TMDC material to form desired lateral heterostructures with arbitrary layouts. It is worth mentioning that Zhang et al. introduced a reverse flow during the temperature swing between the successive growth stages to cool down the as-grown 2D domains to avoid the excessive thermal degradation or uncontrolled nucleation. By this trick, they could realize the robust preparation of a wide range of multi-heterostructures and superlattices with precisely controlled structure and atomically sharp interface. Figure 9h is the Raman mapping of WS$_2$/WSe$_2$/MoS$_2$ multi-heterostructure. Due to the covalent bonding at the interface in in-plane epitaxy, the difference in lattice constants between the two materials can introduce stress at the interface. When the lattice mismatch is small, the stress can be released by in-plane bond length variations (lattice strain), as the case of h-BN/graphene heterojunction. But when the mismatch is large, dislocation at the interface or out-of-plane ripple may form. The ADF-STEM image of a lateral WSe$_2$/MoS$_2$ heterojunction (lattice mismatch of 3.8%) with dashed red line indicating the atomic plane clearly shows the formation of misfit dislocation at the interface (Figure 9i). More interestingly, Han et al. found the dislocation at the interface of WSe$_2$/MoS$_2$ could induce the growth of sub-nanometer-wide 1D MoS$_2$ into the WSe$_2$ monolayers and the edge of MoS$_2$ is perfectly stitched with WSe$_2$, forming a coherent interface (Figure 9j). The higher reactivity in the core of the dislocations allows the Mo and S to be inserted into the dislocation core, thus pushing the dislocations away from the original interface, forming 1D MoS$_2$ channels. Actually, this dislocation-guided 1D channel epitaxial growth can not only occur at the heterojunction interface, but also at the grain boundaries of 2D film with a periodic distribution of dislocations. This opens a new path for the synthesis of 1D superlattices in 2D monolayers. In a coherent WSe$_2$/WS$_2$ superlattice (lattice mismatch of 4%), the compressive strain in WSe$_2$ with width smaller than 320 nm could be released by out-of-plane rippling, as shown in Figure 9k, while when the width of WSe$_2$ is larger than 320 nm, the rippling is not continuous anymore and other strain-release path may form, such as the misfit dislocations. Therefore, tuning the supercell dimensions would engineer the epitaxial strain in the superlattices, and further the performances, which is unique in 2D in-plane epitaxy.

The lattice match requirement makes the in-plane epitaxy of 2D materials can only achieved for the ones with same crystal lattice. For example, TMDC materials can also nucleate at the edge of graphene, but only form an overlap junction with graphene rather than a stitching and coherent interface. Although there are no one-to-one chemical bonds formation, the vdW interaction between the overlapped edges of graphene and TMDC materials could also guide the TMDC orientations under well-controlled conditions.

4. Conclusion and Outlook

After more than 10 years’ intense study, the CVD growth of single-crystal 2D materials has achieved great improvement, from the micrometer-scale single domain to wafer-scale single-crystal film. Although the single nucleus method can also obtain inch-size single crystal, the epitaxial growth of 2D single crystals on single-crystal substrates is more simple, economical and practical to realize the large-scale manufacturing. The four epitaxial growth modes discussed in this review, vdW epitaxy, edge epitaxy, step-guided epitaxy and in-plane epitaxy, feature distinct interactions between 2D materials and substrates and the epitaxy mechanisms. In vdW epitaxy, the interaction is weak vdW or quasi vdW force, and the epitaxy follows rotation-alignment behavior where the nuclei with random orientations could rotate to the aligned ones driven by binding energy difference between different rotation angles. But the energy difference is small due to the weak vdW interaction, thus the growth window for vdW epitaxy is narrow in practice. Generally, the epitaxial growth of vertical 2D heterojunctions or 2D materials on nonmetal substrates follows vdW epitaxy. The commonly used transitional metal substrates could interact with the edge of the 2D materials due to their catalytic activities, thus resulting in the edge epitaxy or step-guided epitaxy. In edge epitaxy, the epitaxial relation between the 2D material and substrate is the same with that in vdW epitaxy, while due to the strong chemical bonding between 2D edge and metal, the 2D lattice orientation is determined when nucleation begins. And this is also true for step-guided epitaxy. The strong interactions between the 2D domains and metal substrates in the case of edge epitaxy and step-guided epitaxy also lead to much lower formation energy of the nuclei with preferred orientation, making the edge and step-guided epitaxy are more robust. For 2D materials with lower symmetry like h-BN and TMDCs, there always exist two preferred orientations (0° and 60°) due to their
small energy differences in the vdW and edge epitaxy, while the steps on the substrate surface could lift off the energy difference and induce the unidirectional alignment in step-guided epitaxy. Furthermore, the energy difference is much larger in the case of high-index metal substrates with steps trending only down on the entire surface than that in the case of low-index metal substrates with steps trending both up and down. That means the unidirectional alignment is more feasible on the high-index metal substrate. In addition, sapphire substrates can also be applied to achieve the step-guided epitaxial growth of TMDC materials. But the high stability of sapphire at growth temperature makes the stitching of TMDC domains more difficult than that on the metal substrates, requiring very careful control of the growth kinetics. In-plane epitaxy is actually more like conventional one, requiring restrict lattice match, but with 1D coherent interface. In general, the experimental window for achieving in-plane epitaxial growth is large due to the strong chemical bonding at the epitaxial interface. By the delicate design and careful control, in-plane epitaxy can even realize in-plane multi-heterostructure and superlattice. In fact, in-plane epitaxy is the only technique to prepare in-plane heterojunctions.

Up to now, meter-scale graphene and h-BN and wafer-scale TMDC monolayer single crystals have been successfully prepared on single-crystal metal or sapphire substrates by the CVD method. The large-scale fabrication and applications of 2D single crystals seem to be at the corner. But the growth behaviors especially the nucleation of 2D materials has not been understood thoroughly, which makes the precise and controllable growth difficult. Besides, the growth of multilayer or the vertical heterojunction of 2D materials is still faced with many problems, like the layer number control, stacking angle control and lateral continuity control. The prerequisite of controllable growth of multilayer or the vertical heterojunction is the understanding of growth mechanism, but it is still very limited at the present because of the more complex processes. At the early days, most of understanding to the growth mechanism was gained by inferring from the ex-situ experimental results. But we know the best way to figure out what happens is to “see” what is happening. Thus, the in situ growth and characterization technologies have attracted more and more attentions nowadays. MOCVD and molecule beam evaporation (MBE), which could realize more accurate control over the growth process and have been demonstrated to have potential to prepare high-quality 2D single-crystal films. always possess in situ characterization capability and thus are very important techniques to explore the growth mechanism in the future. Besides, thanks to the quick technology advances, currently some in situ technologies, such as in situ TEM and STM, can achieve atomic-scale spatial resolution and femtosecond-scale time resolution. We believe by combining in situ growth and characterization technologies with theoretical calculations, deeper insight in 2D materials growth would be achieved in the near future, and precise and controllable growth of monolayer, multilayer and heterojunctions of 2D single crystals would be realized. This will greatly promote the high-end industrial application of 2D materials and also provide new opportunities for the growth of many other materials on 2D single crystals.

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Conflict of Interest

The authors declare no conflict of interest.

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2D materials, epitaxy, interaction, lattice symmetry, single crystal

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