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Visualizing Van der Waals Epitaxial Growth of 2D Heterostructures

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Understanding the growth mechanisms of 2D van der Waals (vdW) heterostructures is of great importance in exploring their functionalities and device applications. A custom-built system integrating physical vapor deposition and optical microscopy/Raman spectroscopy is employed to study the dynamic growth processes of 2D vdW heterostructures in situ. This allows the identification of a new growth mode with a distinctly different growth rate and morphology from those of the conventional linear growth mode. A model that explains the difference in morphologies and quantifies the growth rates of the two modes by taking the role of surface diffusion into account is proposed. A range of material combinations including CdI₂/WS₂, CdI₂/MoS₂, CdI₂/WSe₂, PbI₂/WS₂, PbI₂/MoS₂, PbI₂/WSe₂, and Bi₂Se₃/WS₂ is systematically investigated. These findings may be generalized to the synthesis of many other 2D heterostructures with controlled morphologies and physical properties, benefiting future device applications.

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1. Introduction

Atomically thin 2D van der Waals (vdW) heterostructures provide a new material platform for fundamental research and applications in electronics, optoelectronics, spintronics, and valleytronics, etc. Most vdW heterostructures are obtained by transferring and stacking individual layers. However, using this method, it is challenging to precisely control the size, shape, layer thickness, and interface properties of the heterostructures, along with being ill-suited for the scale-up needed for device applications. Although considerable work has been done in the past few years for the direct synthesis of vdW heterostructures using physical vapor deposition and chemical vapor deposition (CVD), the growth mechanisms are not well understood. This is partly due to the fact that most studies on growth mechanisms relied on ex situ characterizations and often drew similarities to the growth of a single 2D vdW material (e.g., graphene or transition metal dichalcogenides (TMD)) on non-vdW substrates. It has been found that in typical growth of vdW 2D materials, the 2D domains tend to evolve into regular shapes (e.g., triangular or hexagonal) under equilibrium conditions, following the Wulff construction (diffusion dominating over adhesion) whereas they can yield dendritic or fractal shapes under conditions away from equilibrium. In situ electron, atomic force and optical microscopy and spectroscopy allow the capture of the growth dynamics. A range of 2D materials have been studied by these in situ techniques, including graphene, TMDs, organic crystals, and MXenes. Most of such studies focused on single materials grown on conventional metal or covalent substrates, and rarely have in situ imaging and spectroscopy been used on the investigation of epitaxial growth of 2D vdW heterostructures. For such heterostructures, a second 2D material nucleates and grows on the top surface of an existing vdW layer. Compared with conventional non-vdW substrates such as SiO₂, sapphire, and metals, the atomically smooth vdW surface lacks steps and dangling bonds. The precursor molecules can diffuse nearly freely due to their weak interactions with the underlying vdW layer. This diffusion strongly modifies the growth dynamics of the vdW heterostructures. Therefore, clear differences exist in the growth mechanisms between vdW heterostructures and
single 2D materials. The lack of detailed knowledge of growth dynamics may hinder the progress in the synthesis of novel 2D vdW heterostructures with precisely controlled morphology, stacking order, twisting angles, and thus their applications.

In this work, we report the development of a system that integrates physical vapor deposition with in situ optical microscopy/Raman spectroscopy, and the application of such technique to characterize the growth dynamics of 2D vdW heterostructures in real-time. We have grown a series of vdW heterostructures as prototype material systems, including CdI$_2$/WS$_2$, CdI$_2$/MoS$_2$, CdI$_2$/WSe$_2$, PbI$_2$/WS$_2$, PbI$_2$/MoS$_2$, and PbI$_2$/WSe$_2$ to demonstrate the universality of this system to reveal 2D heterostructure growth dynamics in situ. Our studies found that 2D materials preferentially nucleate on the vdW templates (rather than non-vdW substrates such as sapphire). We discovered two different growth modes which may be universal for 2D vdW heterostructures: one growth mode is characterized by its constant growth rate, resulting in regular shaped domains; the other has its growth rate inversely proportional to the domain size, leading to a suborbicular crystal shape. Using density functional theory (DFT) calculations, we replicated the two growth modes and explained their origins as the significant surface diffusion and edge adsorption effects. Based on this understanding, we designed experiments to synthesize other 2D vdW heterostructures (such as Bi$_2$Se$_3$/WS$_2$) and demonstrated the characteristic peaks of MX$_2$, but also show those of YI$_2$ (A$_1$ of CdI$_2$; E$_{2g}$, A$_{1g}$, and 2LA(M) of PbI$_2$). Meanwhile, the 2LA(M) mode of WS$_2$, A$_{1g}$ mode of MoS$_2$, and E$^{1/2}_g$ mode of WSe$_2$ soften by ~1–1.5 cm$^{-1}$ after the YI$_2$ was grown on the MX$_2$ layers, which can be attributed to the interlayer coupling between YI$_2$ and MX$_2$ layers, as shown in Figure S3, Supporting Information.

2. Results and Discussion

2.1. In Situ, Real-Time Monitoring of the Growth Dynamics of 2D vdW Heterostructures

A system was built which integrates a temperature and environment-controlled stage for 2D material growth and a Raman microscope accessed through an optical window for optical microscopy and Raman spectroscopy/mapping for in situ monitoring of the growth dynamics (see Section 4). Monolayer MX$_2$ (WS$_2$, MoS$_2$, WSe$_2$) flakes were pre-grown on double-side polished sapphire substrates by conventional CVD. YI$_2$ (CdI$_2$, PbI$_2$) was thermally evaporated in the home-built system for growing YI$_2$/MX$_2$ heterostructures, as sketched in Figure 1a and Figure S1, Supporting Information. The X-ray diffraction (XRD) patterns shown in Figure S2, Supporting Information, indicate the grown CdI$_2$ and PbI$_2$ have high crystalline quality. The XRD pattern of CdI$_2$ matches well with standard PDF#12-0574, while that of PbI$_2$ matches with PDF#80-1000. Both are of hexagonal structure with a space group of P3$_1$m1, and they show a strong (001) orientation expected for 2D CdI$_2$ and PbI$_2$. Six kinds of YI$_2$/MX$_2$ vdW heterostructures with different combinations of Y and M were fabricated and their growth processes were recorded in real-time.

Figure 1b–g$_1$ shows the optical microscopy images of the pre-grown single-layer TMD flakes on sapphire substrates. Figure 1b$_2$–g$_2$ shows the images of as-grown CdI$_2$/WS$_2$, CdI$_2$/MoS$_2$, CdI$_2$/WSe$_2$, PbI$_2$/WS$_2$, PbI$_2$/MoS$_2$, and PbI$_2$/WSe$_2$ heterostructures, respectively. It can be seen that in all of these cases, isolated single microcrystals with triangular or hexagonal shapes are observed, thus reflecting the shapes of the underlying TMD flakes. Raman mapping is used to reveal the size and shape of individual YI$_2$ and TMD layers in the heterostructure. Raman mappings using the A mode (A$_1$ or A$_{1g}$) of CdI$_2$ or PbI$_2$ are shown in Figure 1b$_1$–g$_1$, and those with the E$^{1/2}_g$ and E$^g$ modes of TMD are shown in Figure 1b$_2$–g$_2$. It can be seen clearly that the two sets of images match well with each other, showing identical size and shape of YI$_2$ crystals with the underlying monolayer TMDs. This suggests that the YI$_2$ crystals grew selectively on the vdW TMD monolayers and covered the entire flakes, while no material was deposited on the sapphire substrate. The typical Raman spectra of single-layer MX$_2$, bilayer YI$_2$/MX$_2$, and multilayer YI$_2$/MX$_2$ heterostructures are presented as black, red, and blue curves in Figure 1b$_1$–g$_1$, respectively. The Raman spectra of YI$_2$/MX$_2$ heterostructures not only demonstrate the characteristic peaks of MX$_2$, but also show those of YI$_2$ (A$_1$ of CdI$_2$; E$_{2g}$, A$_{1g}$, and 2LA(M) of PbI$_2$). Meanwhile, the 2LA(M) mode of WS$_2$, A$_{1g}$ mode of MoS$_2$, and E$^{1/2}_g$ mode of WSe$_2$ soften by ~1–1.5 cm$^{-1}$ after the YI$_2$ was grown on the MX$_2$ layers, which can be attributed to the interlayer coupling between YI$_2$ and MX$_2$ layers, as shown in Figure S3, Supporting Information.

2.2. Growth Dynamics of the 2D vdW Heterostructures

In situ, time-lapse optical microscopy images reveal the growth dynamics and give deeper insights into the growth mechanisms of the 2D vdW heterostructures. Figure 2a shows the time-lapse images of the growth processes of CdI$_2$/WS$_2$ heterostructures at 285 °C (Movie S1, Supporting Information). For CdI$_2$ on WS$_2$ at 10 s, it can be seen that a nucleus was formed at the top right corner with no well-defined facets. With increasing time to 30 s, the nucleus grew and evolved into a hexagonal shaped crystal. With further increasing time, the domain grew isotropically in all directions, keeping the hexagonal shape unchanged. This process continued until the CdI$_2$ crystal reached one of the edges of WS$_2$. The edge shape of CdI$_2$ then conformed to that of WS$_2$, and the growth in that direction ceased, while the other edges of the CdI$_2$ crystal continued to grow. Interestingly, no growth of CdI$_2$ was observed beyond the boundaries of WS$_2$. In this particular example, a second CdI$_2$ nucleation event was observed at the lower-left corner at 30 s; the growth continued in a similar fashion. Atomic force microscopy (AFM) images clearly show that the growth edges remain flat and smooth during the growth process. The growth front can consist of either monolayer or step edges with different layer thicknesses, as shown in Figure 2b,c. Figure 2f (tetragonal points) shows the size evolution of the CdI$_2$ domains as a function of time. By fitting this data, we can obtain a linear relationship between the domain size and the growth time. The growth rate $R$, as measured by the side length of the domains as a function of time, is found to be 0.41 µm s$^{-1}$ for CdI$_2$. The Pearson
correlation coefficients of the linear fitting are 0.995, indicating excellent linearity. Moreover, we found that multiple islands can nucleate on a single TMD flake and exhibit similar growth rates (Figure S4, Supporting Information). We suggest that the number of nuclei on each TMD flake is related to the surface defect density, as the precursor molecules prefer to nucleate at energetically favorable defect sites.\cite{45}

Surprisingly, by lowering the growth temperature, a different growth mode is observed (termed as sublinear growth mode). Figure 2d (Movie S2, Supporting Information) shows the time-lapse images of the growth process of a CdI$_2$/WS$_2$ heterostructure at 260°C. It can be seen that the nucleated pattern has a suborbicular shape with no clearly defined facets. A magnified AFM image shows that the pattern exhibits irregular sawtooth...
edges instead of smooth ones (Figure 2e; Figure S5, Supporting Information). Figure 2f gives a comparison of the size evolution process between sublinear and linear growth modes. Different from the linear growth mode that shows a constant growth rate, the size of the low temperature grown YI₂ increases with time in a sublinear fashion. This suggests that the growth rate decreases with time. The clear differences in the growth rates and morphologies between linear and sublinear modes suggest distinct growth mechanisms of the 2D vdW heterostructures that require further elucidation.

2.3. Modeling of the Growth Mechanisms of 2D vdW Heterostructures

The growth of YI₂ on TMD monolayers to form 2D vdW heterostructures is the result of a dynamic balance between precursor adsorption, desorption, and surface diffusion. Calculating the energetics of these processes will help us to understand first and foremost, why YI₂ prefers 2D over 3D growth on TMDs, and second, why YI₂ prefers to grow on top of TMDs versus the sapphire surface. The adsorption energies for CdI₂ molecules over WS₂ (001), CdI₂ (001), and edges of CdI₂/WS₂ heterostructure were calculated by the Vienna ab initio simulation package (VASP). The adsorption energy for the CdI₂ molecules on the growth edges of the heterostructure (CdI₂/WS₂) is about 0.82 eV (Figure 3a). However, the adsorption energies for CdI₂ molecules over WS₂ (001) and CdI₂ (001) are lower, at 0.3 and 0.55 eV, respectively (Figure 3b,c). It has been shown in recent work that there is strong fluctuation in the sizes of the nuclei at the early crystal nucleation stage, and a nucleus will only continue to grow when a critical size is reached. For the growth of YI₂ on TMDs, once the nucleus reaches the critical size, the growth will proceed by the attachment of precursor molecules at the edges, as the rate of adsorption there far exceeds the rate of desorption. On the top surfaces of YI₂ and WS₂, due to the much lower adsorption energies, the rate of adsorption and desorption is balanced at the optimized growth temperatures, and thus a nucleus is unable to grow beyond the critical size and eventually completely evaporates. Therefore, the 2D growth mode of YI₂ is a consequence of the differential adsorption energies of the edges and top surfaces. The absence of growth on the sapphire substrate can be understood similarly. The adsorption energy of CdI₂ on sapphire is found to be

Figure 2. Growth dynamics of 2D CdI₂/WS₂ vdW heterostructures. a) In situ real-time images of the dynamic growth process of CdI₂/WS₂ heterostructure at the growth temperature of 285 °C. b,c) AFM images of the boundaries of CdI₂/WS₂ heterostructure samples grown at 285 °C. d) In situ real-time images of the dynamic growth process of CdI₂/WS₂ heterostructure at the growth temperature of 260 °C. e) AFM image showing the morphology of the boundaries of CdI₂/WS₂ heterostructure grown at 260 °C. f) Domain size as a function of time for CdI₂/WS₂ heterostructures grown at 285 and 260 °C, respectively. The dots are measured data and the lines are fitting curves using Equations (1) and (3), respectively. Scale bars: 20 µm (a,d); 2 µm (b,c,e).
0.31 eV (Figure S6a, Supporting Information). While the diffusion energy barrier is found to be 4.5 eV (Figure S6b, Supporting Information). Thus, it is difficult for CdI₂ molecules to aggregate to form nuclei above the critical size for their further growth on sapphire. As shown by the images and movies, Yi₂ crystals grow selectively on TMDs instead of on sapphire substrates.

With the understanding of the selective 2D growth, we next focus on the two observed growth modes with different time dependences at different temperatures. As has been discussed above, the 2D growth is dictated by initial nucleation followed by edge growth through the competition between adsorption and desorption of precursor molecules at growth edges. Precursor molecules can arrive at the growth edges mainly in two ways: first, precursor molecules can directly attach to the growth edges from the vapor phase; second, molecules can diffuse along the vdW surfaces and then attach to the growth edges (Figure 3e). At a relatively high temperature (higher than 285 °C), the weak adsorption energies of CdI₂ molecules on CdI₂ and WS₂ top surfaces (0.3 and 0.55 eV, respectively) are readily overcome by thermal energy, resulting in facile desorption of CdI₂ molecules from the surface of 2D layers. These precursor molecules thus do not contribute to the growth rate of CdI₂ 2D crystals. Since the adsorption energy of 0.82 eV at the growth edges is much larger than those at top surfaces, the CdI₂ molecules attach to the growth edges mainly by direct adsorption from the vapor phase. At sufficiently high growth temperatures, the edge shape is an outcome of the
competition between adsorption and desorption. The morphology of the early stage nucleus likely possesses irregular sawtooth edges. These concave edges are thermodynamically favorable sites for adsorption due to the higher adsorption energy (see calculated values for Figure S7, Supporting Information). The precursor molecules that go deep into the concave edge sites are also more likely to be trapped and adsorbed due to the increased probability of multiple collisions. On the other hand, the CdI\(_2\) molecules adsorbed at the convex edge sites have a higher probability of desorption since the direction of diffusion is random, which decreases the chance of re-adsorption. Hence, the concave sites are preferentially filled, resulting in flat edges (Figure 3f, red dash). The overall triangular or hexagonal shape of the 2D CdI\(_2\) crystal is dictated by the underlying hexagonal crystal symmetry. Our calculation further shows that the edge shape is not determined by edge diffusion, as the energy barrier of CdI\(_2\) molecule diffusion is prohibitively high (≈1.25 eV as shown in Figure S8, Supporting Information). The growth rate (R) of a 2D domain is the result of the competition between edge adsorption and desorption, which can be presented as:

\[ R = \frac{dL}{dt} = \left( c_1 \frac{e_{\lambda_1}}{kT} - c_2 \frac{e_{\lambda_2}}{kT} \right) s_0 \]  

where \(c_1\) is the linear density of the precursor molecules in the vapor phase; \(c_2\) is the linear density of the molecules adsorbed at the growth edge; \(f = kT/h\) is the attachment/detachment frequency; \(E_{ba}\) and \(E_{bd}\) are energy barriers of source molecules/atoms attaching to the growth edge and detaching from the growth edge (not calculated here); \(k\) is the Boltzmann constant; \(h\) is the Planck constant; \(T\) is the growth temperature; \(s_0\) is the unit cell area of the 2D material; \(L\) is the diameter of the 2D domain; and \(t\) is the growth time. As mentioned earlier, at relatively high temperatures (higher than 285 °C), the CdI\(_2\) molecules attach to the growth edges mainly from the vapor phase by direct adsorption. At equilibrium for a given temperature, both \(c_1\) and \(c_2\) are constants. Therefore, a constant \(R\) of CdI\(_2\) is expected because all the parameters in Equation (1) are constants, resulting in a size dependence of the CdI\(_2\) linear in time. Our setup allows for precise measurement of the growth rate of the 2D crystals. For CdI\(_2\) crystals, \(R\) is found to be in the range of 0.41–0.48 μm s\(^{-1}\).

With decreasing growth temperatures (below 260 °C), the main difference is that the desorption rate of CdI\(_2\) molecules landing on the top surface decreases. Meanwhile, the low diffusion energy barrier (0.15 eV on WS\(_2\) and 0.22 eV on CdI\(_2\)) suggests fast diffusion of CdI\(_2\) molecules on WS\(_2\) and CdI\(_2\) layers (Figure 3d). Therefore, the CdI\(_2\) molecules within the mean-free-path of the edges can arrive and get adsorbed at the edges (Figure 3g). This results in a growth rate that is time-dependent, which will be derived below. The second difference is that the desorption rate of CdI\(_2\) molecules at the growth edges also decreases dramatically with decreasing temperature. Therefore, the edge shape is kinetically controlled. This leads to a suborbicular shape of the as-grown CdI\(_2\) 2D crystals since the surface diffusion is isotropic. The edge shapes are irregular due to the fast growth rate, with the edge voids unable to be filled before new growth.

Compared with the linear mode, the sublinear growth mode exhibits a higher growth rate due to the higher precursor density near the growth edges and decreased desorption rate. The concentration of precursor CdI\(_2\) molecules (\(c\)) near the growth edge is now composed of three parts: the CdI\(_2\) molecules in the vapor phase (\(c_0\)), and those adsorbed on the top surfaces of WS\(_2\) and CdI\(_2\) within the mean free paths \(\lambda_1\) and \(\lambda_2\), respectively (\(c_1\)). Assume the growing CdI\(_2\) to be of a circular shape, and the CdI\(_2\) molecules adsorbed on the surfaces of WS\(_2\) and CdI\(_2\) within the mean free paths to the edges (of the shape of two circular rings with widths of \(\lambda_1\) and \(\lambda_2\), respectively, as shown in Figure S9, Supporting Information) can diffuse and get adsorbed at the edges. \(c\) can be presented as:

\[ c = c_1 + c_2 = c_0 + \frac{c_{51} S_1 + c_{52} S_2}{\pi L} = c_0 + c_1 \lambda_1 + c_2 \lambda_2 + \frac{c_{51} \lambda_1^2 - c_{52} \lambda_2^2}{L} \]  

where \(c_{51}\) and \(c_{52}\) are the areal concentrations of the precursor molecules adsorbed on WS\(_2\) and CdI\(_2\) layers, respectively; \(S_1\) and \(S_2\) are the effective adsorption areas for CdI\(_2\) molecules over WS\(_2\) and CdI\(_2\) layers within the mean free paths \(\lambda_1\) and \(\lambda_2\), respectively; and \(L\) is the diameter of the CdI\(_2\) layer.

The explicit expression of \(dL/dt\) is obtained by substituting the linear concentration of precursor \(c\) in Equation (1) by Equation (2):

\[ \frac{dL}{dt} = \frac{A}{L} + B \]  

where \(A = (c_{51} \lambda_1^2 - c_{52} \lambda_2^2) s_0 e_{\lambda_1}/kT\) and \(B = \left( c_0 + c_{51} \lambda_1 + c_{52} \lambda_2 \right) e_{\lambda_1}/kT - c_0 e_{\lambda_2}/kT \) are both constants independent of time. Equation (3) shows that the size of the CdI\(_2\) domains as a function of growth time exhibits a sublinear behavior. This sublinear behavior originates from the significant contribution of precursor molecules that arrive at growth edges via surface diffusion. The fitting curves by Equation (3) agree well with the experimental data, as shown in Figure 2f (pink line).

2.4. Universality of the Growth Models

While we used CdI\(_2\)/WS\(_2\) to illustrate the two different growth models at different growth temperatures, these models should be generally applicable to other vdW heterostructures. Based on the understanding of these two models, we designed experiments to synthesize other 2D vdW heterostructures with different morphologies, including CdI\(_2\) and PbI\(_2\) on different TMDs. It is found that PbI\(_2\) follows the behavior of CdI\(_2\) closely, with linear and sublinear growth modes at high and low temperatures, respectively. The critical temperature separating the two modes is found to be 330 °C. As shown in Figure 4a,b, the suborbicular and triangular PbI\(_2\)/WS\(_2\) can be controllably grown at 300 and 330 °C, respectively. As expected, the sublinear growth mode of PbI\(_2\) exhibits a higher growth rate, as shown in Figure 4c. Furthermore, the sublinear growth mode always arises regardless of the underlying vdW layers, as long as the growth temperature is sufficiently
low. Figure 4d,e shows the time-lapse images of the sublinear growth processes of CdI$_2$/MoS$_2$ and CdI$_2$/WSe$_2$ heterostructures at 260 °C (Movies S3 and S4, Supporting Information). The optical microscopy images of completed CdI$_2$/MoS$_2$ and CdI$_2$/WSe$_2$ heterostructures with growth times of 320 and 95 s in panels (d,e), respectively, h) Domain size of CdI$_2$/WS$_2$, CdI$_2$/MoS$_2$, and CdI$_2$/WSe$_2$ heterostructures as a function of time grown at 260 °C. The solid lines in (c) and (h) represent the fitting curves. Scale bars: 20 µm (a,d,f); 10 µm (b,e,g).

Figure 4. Dynamic growth process by in situ imaging of other 2D vdW heterostructures. a,b) In situ real-time images of growth dynamics of PbI$_2$/WS$_2$ heterostructure at temperatures of 300 and 330 °C, respectively. c) Domain size as a function of time for PbI$_2$/WS$_2$ heterostructures grown at 300 and 330 °C, respectively. d,e) In situ real-time imaging of growth dynamics of CdI$_2$/MoS$_2$ and CdI$_2$/WSe$_2$ heterostructures at the growth temperature of 260 °C. f,g) Optical microscopy images of completed CdI$_2$/MoS$_2$ and CdI$_2$/WSe$_2$ heterostructures with growth times of 320 and 95 s in panels (d,e), respectively. h) Domain size of CdI$_2$/WS$_2$, CdI$_2$/MoS$_2$, and CdI$_2$/WSe$_2$ heterostructures as a function of time grown at 260 °C. The solid lines in (c) and (h) represent the fitting curves. Scale bars: 20 µm (a,d,f); 10 µm (b,e,g).

We further synthesized 2D Bi$_2$Se$_3$, a topological insulator, with different morphologies, on WS$_2$ using conventional CVD methods. Figure 5a–d shows the AFM and Raman mapping of Bi$_2$Se$_3$/WS$_2$ vdW heterostructures grown at 600 and 505 °C, respectively, with identical growth time. It can be seen that the shapes of Bi$_2$Se$_3$ grown at 600 °C are triangular and hexagonal, with smooth edges; whereas those grown at 505 °C are sub-ornicular and possess irregular sawtooth edges (Figure 5a,c;
Figure S11, Supporting Information). Although both are grown for the same amount of time, the domain size of Bi$_2$Se$_3$ grown at 505 °C is clearly larger than that generated at 600 °C (Figure 5a,c; Figure S11, Supporting Information). This confirms the model predictions convincingly, even though the growth rates cannot be easily obtained in conventional CVD growth. To gain deeper insights into the differences between the 2D vdW heterostructures grown by the two modes, we used transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) to investigate possible epitaxial relationship between Bi$_2$Se$_3$ and WS$_2$. Figure 5e–n depicts the low-magnification TEM images and SAED patterns of Bi$_2$Se$_3$/WS$_2$ heterostructure samples grown by both modes. The SAED shows two different sets of hexagonal diffraction patterns (highlighted by green and red dashed lines), corresponding to the WS$_2$ lattice (0.27 nm) and the Bi$_2$Se$_3$ lattice (0.21 nm), respectively (Figure S12, Supporting Information). The two sets of SAED patterns are clearly aligned for the sample grown at 600 °C, as shown in Figure 5e,f. A total of 15 flakes were measured and 100% of them are aligned. On the other hand, for Bi$_2$Se$_3$ grown at 505 °C, while majority of the flakes (17 out of 20 tested) show SAED patterns aligned to that of WS$_2$, different twisting angles including 1.1°, 3.7°, and 30° are also observed (Figure 5g–n; Figure S13, Supporting Information). This can be understood as following: the higher growth temperature provides sufficient thermal energy for the Bi$_2$Se$_3$ islands initially nucleated on the WS$_2$ layer to relax into the most thermodynamically stable configuration. However, with decreasing growth temperature, the initially nucleated Bi$_2$Se$_3$ island with a twisted angle cannot overcome the high diffusion barrier to reorient itself. The interlayer twisted angle is an important parameter for 2D vdW heterostructures because it may create flat bands with localized states and enhanced electronic correlations that can lead to exotic many body physics such as superconductivity and ferromagnetism.[51–54] To date, most of the heterostructures with twisting angles were obtained by transferring and layer stacking, which could lead to potential issues of interface contamination. We suggest that our sublinear growth mode may provide a convenient method to grow 2D vdW heterostructures with variable interlayer twisting angles, allowing the investigation of new many body physics.

3. Conclusions

The dynamic growth processes of several 2D vdW heterostructures were systematically investigated by in situ imaging and Raman spectroscopy using a custom-built system. While a commonly known linear growth mode with a constant growth rate is confirmed by in situ studies, a new growth mode, namely the sublinear mode, is also identified. The two modes demonstrate substantially different growth rates and morphologies. This difference is mainly attributed to the contribution of surface
diffusion of adsorbed precursor molecules to the edge growth, which can be controlled by substrate temperature. While a limited number of vdW layer combinations were studied, it is expected that these models are applicable to the growth processes of a broad range of vdW heterostructures.

4. Experimental Section

Preparation of Monolayer WS$_2$, MoS$_2$, and WSe$_2$: The sapphire substrates (0.1 mm, double-sided polished) were placed in the center of a quartz tube furnace, and the WO$_3$ (or MoO$_3$) powder was dispersed on the sapphire substrates. Ar/H$_2$ with a flow rate of 30/10 sccm was used as the carrier gas and S source. The furnace was heated to 1000 °C (or 800 °C) and was held at that temperature for 2 min for the growth of monolayer WS$_2$ (or MoS$_2$). The WO$_3$ powder in an alumina boat was placed in the center of the quartz tube furnace, and sapphire substrates (0.1 mm, double-sided polished) were placed face down on top of the alumina boat. Another boat containing Se powder was placed further upstream at 300 °C. Ar/H$_2$ with a flow rate of 35/5 sccm was used as the carrier gas. The furnace was heated to 900 °C and was held at that temperature for 2 min for growing WSe$_2$. Growth of CdI$_2$/WS$_2$, CdI$_2$/MoS$_2$, CdI$_2$/WSe$_2$, PbI$_2$/WS$_2$, PbI$_2$/MoS$_2$, PbI$_2$/WSe$_2$. 2D vdW Heterostructures: The custom-made system consisted of a temperature and environment control stage (Linkam THMS600) and an in situ imaging system (invia Renishaw micro-Raman). The growth apparatus consisted of a heating stage and a water-cooler. An optical window made of quartz was used for in situ optical imaging and spectrum collection. The system was purged with high-purity Ar gas during the growth process. 1 mg precursor powder (CdI$_2$ or PbI$_2$) was dispersed on the heating stage. A sapphire substrate (with pre-grown TMD) was placed face down on top of the heating stage. The spacing between the substrate and the heating stage was set at 500 mm. The growth temperature was as follows: CdI$_2$/TMD heterostructures (260 °C for sublinear growth mode; 285 °C for linear growth mode), PbI$_2$/TMD heterostructures (300 °C for sublinear growth mode; 330 °C for linear growth mode).

Growth of Bi$_2$Se$_3$/WS$_2$. 2D vdW Heterostructures: The Bi$_2$Se$_3$/WS$_2$ heterostructure was grown by a CVD tube furnace. Bi$_2$Se$_3$ powder was placed in a quartz boat in the tube furnace. A sapphire substrate (with pre-grown WS$_2$) was placed downstream near the Bi$_2$Se$_3$ powder. The quartz tube was kept in an argon atmosphere for 40 min to remove oxygen. The furnace was heated to the target temperature (505–600 °C) for the growth of Bi$_2$Se$_3$/WS$_2$ heterostructures (505 °C for sublinear growth mode; 600 °C for linear growth mode).

Characterizations: In situ Raman measurements were performed using an invia Renishaw micro-Raman system with a 532 nm excitation laser. Raman spectra were calibrated by the Raman shift of single-crystal silicon at 520.4 cm$^{-1}$. The thicknesses of 2D heterostructures were measured by AFM (Dimension Icon, Bruker). TEM measurements were conducted in a JEOL 2100F. XRD patterns were recorded on a Bruker D8-Advance system.

DFT Calculations: All first-principles calculations were performed using the VASP based on DFT. The frozen-core projector augmented wave method was adopted to describe the interaction between the core and valence electrons and the Perdew–Burke–Ernzerhof exchange correlation functional was used to depict the interactions within the generalized gradient approximation framework. The vdW interactions for the CdI$_2$/WS$_2$ and Bi$_2$Se$_3$/WS$_2$ heterostructures were considered by adopting Grimme’s DFT-D3 method. In all calculations, 7×7×1 k-points were selected for the Monkhorst-Pack mesh to sample the 2D Brillouin Zone. The cutoff energy for the plane wave adopted in the present work was 500 eV. In the structural relaxation and other calculations, the convergence criteria were chosen to be $<10^{-3}$ eV for the total energy and 0.01 eV Å$^{-1}$ for the force on each atom. After testing, a vacuum zone of 15 Å was employed to prevent the interactions between the adjacent images.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

K.Z., L.Z., and S.H. designed the research. K.Z. and B.P. synthesized the materials and conducted optical microscope, AFM, XRD, Raman, TEM, and data analysis. C.D. carried out the first-principles calculation. K.Z. and H.Z. proposed the growth models and analyzed the data. K.Z., W.Z., A.M., H.Z., and S.H. wrote the paper with input from the other coauthors.

Data Availability Statement

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

Keywords

2D heterostructures, epitaxial growth, growth dynamics, van der Waals heterostructures

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