The Coalescence Behavior of Two-Dimensional Materials Revealed by Multiscale In Situ Imaging during Chemical Vapor Deposition Growth

Zhu-Jun Wang,* Jichen Dong,△ Linfei Li,△ Guocai Dong, Yi Cui, Yang Yang, Wei Wei, Raoul Blume, Qing Li, Li Wang, Xiaozhi Xu, Kaihui Liu, Cédric Barroo, Joost W. M. Frenken, Qiang Fu, Xinhe Bao, Robert Schlögl, Feng Ding,* and Marc-Georg Willinger*

Cite This: ACS Nano 2020, 14, 1902−1918

ABSTRACT: Wafer-scale monocrystalline two-dimensional (2D) materials can theoretically be grown by seamless coalescence of individual domains into a large single crystal. Here we present a concise study of the coalescence behavior of crystalline 2D films using a combination of complementary in situ methods. Direct observation of overlayer growth from the atomic to the millimeter scale and under model- and industrially relevant growth conditions reveals the influence of the film−substrate interaction on the crystallinity of the 2D film. In the case of weakly interacting substrates, the coalescence behavior is dictated by the inherent growth kinetics of the 2D film. It is shown that the merging of coaligned domains leads to a distinct modification of the growth dynamics through the formation of fast-growing high-energy edges. The latter can be traced down to a reduced kink-creation energy at the interface between well-aligned domains. In the case of strongly interacting substrates, the lattice mismatch between film and substrate induces a pronounced moiré corrugation that determines the growth and coalescence behavior. It furthermore imposes additional criteria for seamless coalescence and determines the structure of grain boundaries. The experimental findings, obtained here for the case of graphene, are confirmed by theory-based growth simulations and can be generalized to other 2D materials that show 3- or 6-fold symmetry. Based on the gained understanding of the relation between film−substrate interaction, shape evolution, and coalescence behavior, conditions for seamless coalescence and, thus, for the optimization of large-scale production of monocrystalline 2D materials are established.

KEYWORDS: multiscale in situ imaging, seamless coalescence, 2D materials, complementary in situ methods, chemical vapor deposition, pressure gap

Large-scale application of two-dimensional (2D) materials in technology will only be possible once industrial-scale fabrication of high-quality, single-crystalline films becomes really feasible.1−3 Currently, chemical vapor deposition (CVD) is the most widely used method to grow 2D films onto various substrates.4−12 One promising strategy toward the fabrication of single-crystalline 2D films is based on the controlled coalescence of coaligned domains into a continuous, grain boundary (GB)-free film.13−15 Despite recent achievements, the role of the substrate and growth conditions on the growth and coalescence behavior of 2D films is not sufficiently understood, and consequently, possibilities of “seamless stitching” are not engaged.16 Using graphene as a prototype material, we present here a detailed study on the effect of the film−substrate interaction on the growth and coalescence behavior and demonstrate that the key findings can be generalized to other 2D materials.

Received: October 17, 2019
Accepted: February 7, 2020
Published: February 7, 2020

https://dx.doi.org/10.1021/acsnano.9b08221
ACS Nano 2020, 14, 1902−1918
To get a better understanding of the conditions required for seamless coalescence, the parameters that determine the growth behavior must be studied in detail. In situ methods that enable direct visualization of crystal growth and evolution are ideally suited to study the growth kinetics of 2D materials. However, surface science imaging techniques, such as low-energy electron microscopy (LEEM), photoemission electron microscopy (PEEM), and scanning tunneling microscopy (STM), are designed to work under pressures that are up to 10 orders of magnitude lower than those encountered in practical CVD conditions. This large pressure gap raises the question about the transferability of growth mechanisms derived on the basis of (ultra-high-vacuum) UHV observations to conditions applied in industrially relevant CVD processes.

By using a combination of complementary in situ tools, we are able to monitor details of the growth and coalescence behavior from the atomic to the millimeter scale and across the pressure gap between UHV and relevant CVD growth conditions. This unique combination of in situ real-space imaging and spectroscopic methods allows us to link atomistic details with macroscopic growth dynamics, including information about the chemical state. The results show that the coupling strength between film and substrate not only determines the growth behavior but also dictates conditions for seamless coalescence. In the case of a weak coupling, coalescing domains are able to slightly slide and rotate, enabling seamless stitching and GB-free merging without the requirement of perfect alignment. In the case of strongly coupling substrates, alternating adsorption sites induce a substantial periodic buckling in the form of a moiré corrugation. In this case, seamless coalescence requires, in addition to a coinciding orientation of the 2D film lattice, a coherence of the moiré corrugation of the respective domains.

Using theoretical analysis based on density functional theory (DFT) simulations and kinetic Wulff constructions (KWC), we are able to fully describe the coalescence process and show how atomistic processes are expressed on the macroscopic scale.
level. Based on the fundamental understanding of the coalescence behavior at different length scales, we present macroscopically observable growth features and shape evolution that can be used to identify GB-free coalescence. By extending the findings from graphene to other 2D films, we present a macroscopically observable criterion that can be used to identify GB-free coalescence in 2D materials that show 3- or 6-fold symmetry. Our findings thus set a general framework for the understanding of the role of film–substrate interactions during growth and provide guidelines for the controlled production of single-crystalline 2D films.

RESULTS AND DISCUSSION

In order to study the influence of the film–substrate interactions on the growth and coalescence behavior, in situ growth experiments were performed on (111) surfaces of Pt and Rh. The two substrates were chosen as representatives for materials that show a weak (Pt) and a strong coupling strength (Rh) with graphene, respectively.31,32

Bridging the Pressure Gap from UHV to Relevant CVD Conditions by a Multi-In Situ Approach. A set of complementary in situ imaging tools have been applied in order to trace effects related to the coupling strength from the atomic scale to the macroscopically observed growth behavior. Since these complementary in situ techniques operate at different pressures, we are able to bridge the pressure gap from UHV to relevant CVD conditions. While in situ environmental scanning electron microscopy (ESEM) and LEEM allow for the direct observation of the growth dynamics under pressures ranging from $\sim 10^{-7}$ to $\sim 100$ Pa at the micrometer to the nanometer length scale,33–37 in situ STM provides detailed information about graphene growth at the nanometer/atomic length scale under UHV conditions.38 In the case of growth on Rh(111), our growth experiments showed that graphene islands are generally terminated by the most stable zigzag edges and that the...
shape of single-crystalline graphene islands basically remains the same over the whole studied pressure range (Figure 1d,g,i). Only in the case of growth at very low pressure (∼10⁻⁷ Pa) and in the absence of H₂ (Figure 1a) do islands exhibit a lens-like shape, in agreement with previous observations. Due to the strong graphene–substrate interactions, the domains are aligned to the Rh(111) surface under all observed pressure conditions, as confirmed by low-energy electron diffraction (LEED) measurements of graphene grown inside the ESEM and LEEM chambers, respectively (see Figure 1).⁴⁰,⁴¹ As a consequence, only one type of periodicity in the moiré pattern is observed. In situ STM measurements of graphene grown in the ESEM/LEEM chamber show that the unit cell of the moiré lattice measures approximately 2.9 nm (see the rhombuses drawn in Figure 1c,f,i) and is caused by the lattice mismatch between graphene (2.46 Å) and Rh(111) (2.69 Å).²³,³²,⁴²

The chemical state of carbon during graphene formation on Rh(111) was monitored using in situ ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). The C₁s peak, which provides a chemical fingerprint of the carbon structure and is sensitive to changes in the graphene–substrate interaction,⁵⁰ was followed during growth under pressures ranging from ∼10⁻³ to 20 Pa (see Figure 1m–p). For growth in pure C₂H₄ at 10⁻⁵ Pa, the C₁s spectra exhibit two peaks centered at 284.72 and 284.3 eV, respectively. The two energetic positions reflect the modulation of the graphene–substrate interaction strength due to the moiré corrugation (see STM in Figure 1).³¹,³⁵

The composition of the C₁s signal is consistent across the observed pressure range and indicates that the stacking configuration and coupling strength of graphene on Rh does not change within the observed pressure range.

In the case of graphene growth on Pt, the extent to which the graphene–substrate interaction affects the growth depends weakly on the growth conditions. As shown in Figure 2a,b,c, growth under high vacuum (∼10⁻⁷ Pa) and in the absence of hydrogen results in the presence of two different in-plane orientations. Consequently, the LEED patterns of graphene grown inside the LEEM chamber show two spots due to the Pt(111) substrate (blue circles in Figure 2b) and two sets of six spots due to two sets of differently oriented graphene domains (highlighted as red and green circles in Figure 2b). The relative rotation angle between graphene domains and the substrate is either 19° (R19) or 11° (R11). These two orientations give rise to two distinct moiré superstructures that are rotated with respect to one another by 21° (see Figure 2b). In agreement with a strain-driven model proposed by Merino et al., the periods of these moiré superstructures measure 0.74 nm (R19.1°) and 1.13 nm (R10.9°), respectively.⁴⁴ The STM measurements of graphene grown inside the LEEM chamber confirm the coexistence of these two types of moiré patterns (Figure 2c). The different colored rhombuses in the STM image (Figure 2c) highlight the two types of moiré patterns, 1.1 nm (R11°) and 0.74 nm (R19°), with 21° rotation, in agreement with LEED observations (Figure 2b). Growth at slightly higher pressure (∼10⁻³ to ∼10⁻² Pa) and in the presence of H₂ and C₂H₄ results in the formation of only co-oriented graphene domains on Pt (see ESEM measurements in Figure 2d,g). LEED measurements (Figure 2f,j) show that the graphene lattice is rotated with respect to the Pt(111) by 19°. The dominance of only one orientation is a consequence of an increased nucleation barrier and the competition between hydrogen etching and growth in the presence of H₂. It reflects a slight difference in stability between the R19.1° and R10.9° configurations.⁴⁴,⁴⁵ Further increase of the H₂–C₂H₄ pressure to 25 Pa results in a higher growth rate. The slight energetic
difference between different moiré superstructures is no longer a discriminating factor for the selection of a dominant (low-energy) orientation of graphene islands. As a consequence, domains with a wide variety of rotational moiré variants can be observed by in situ ESEM/LEED/STM (Figure 2j–l). The dependence of the growth behavior on the growth conditions reflects the weak coupling strength on Pt and is in accordance with previous observations. However, except for the selection or preference of different rotational configurations, no influence of the growth conditions on the inherent growth behavior of graphene was found. Indeed, a comparison of the in situ ESEM/LEEM, LEED, and STM data shows similar behavior of graphene was found. Indeed, a comparison of the in situ ESEM/LEEM, LEED, and STM data shows similar shape evolutions across the whole observed parameter space.

Again, the evolution of the C1s peak was monitored during growth under different pressure and growth conditions by NAP-XPS in order to assess the influence of growth conditions on the chemical fingerprint of the formed graphene.

Growth at 3 × 10−3 Pa of C2H4 leads to a peak located at 284.76 eV with a shoulder at 285.2 eV. The latter can be assigned to the presence of sp3 bonds (Figure 2m), either due to C–H bonds at graphene edges or due to defects that can exist on the edges or inside of the graphene plane. Defects are likely to be present due to the lack of H2 etching during graphene growth. By increasing the pressure to 2 × 10−2 Pa and adding H2 into the chamber (i.e., under H2/C2H4 gas mixtures), the dominance of the 284.76 eV component is maintained up to pressures of ~8 Pa (Figure 2n,o). Further pressure increase to 20 Pa induces a small shift of ~0.5 eV toward lower binding energy (Figure 2p). Here, the graphene growth starts with the appearance of a peak at 284.25 eV, which is shifted toward the peak at 284.68 eV with longer growth time (Figure 2p). We attribute the change in binding energy to the presence of randomly rotated graphene islands on Pt (111) based on the growth observed by in situ ESEM, LEED, and STM (Figure 2j–l). Indeed, the substrate–overlayer interactions change with the rotational angle and are lower for randomly oriented islands.

The in situ NAP-XPS experiments prove that a comparison between high-vacuum in situ STM/LEEM and near-ambient-pressure in situ ESEM is legitimate and that one can draw a consistent picture from UHV to relevant CVD conditions (Figures 1 and 2).

Coalescence and GB Formation on Weakly Interacting Substrates. The occurrence of graphene domains with different in-plane orientations offers a practical way to compare the coalescence behavior of aligned and misaligned domains under identical growth conditions.

We first analyze the case of misaligned domains:

Due to the 6-fold symmetry of graphene, the rotational misalignment between adjacent grains can only vary between 0 and 30°. In Figure 3a, the 94° angle between the two zigzag edges at the concave corner shows that the neighboring domains are misaligned by 26°. The propagation of the adjacent growth fronts and, respectively, the trajectory of the concave corner are indicated by arrows and a dotted line in Figure 3 (see also Supporting Movie 1). During the coalescence, the angle between the growth fronts remains unchanged (see Figure 3a–c and Supporting Movie 1). The propagation of the concave corner during growth depicts the position of the resulting GB, as suggested by theory. It can be visualized by simply switching from growth conditions to hydrogen etching. As shown in Figure 3d–f and Supporting Movie 2, exposure to pure hydrogen at 900 °C leads to preferential etching at defects and, eventually, the formation of a chain of vacancy islands that are terminated by zigzag edges. The orientation and individual shape of the vacancy islands are shown in Figure 3d–f. The angles between the zigzag edges confirm that all the observed vacancy islands indeed originate from the line defined by the motion of the concave corner (Figure 3g,h). It should be pointed out here that GBs between growing domains do not necessarily form straight lines. Slight variations in the growth speed of the respective edges can result in a curved GB (Figure 3f), in agreement with previous visualizations of GBs in CVD graphene.
In the case of well-aligned domains, the concave angle between the respective zigzag growth fronts can measure only either 60° or 120°. In the frame of our experiments, both cases have been observed (see Figure 4, Supporting Movie 3, and Figure 5a,b).

When two zigzag edges of aligned neighboring domains meet, fast attachment of growth species at the concave corner leads to the formation of new growth fronts (Figure 5c–f). These growth fronts are tilted with respect to the zigzag edges by an angle of approximately 19° (Figure 5e). They expand rapidly and replace the original zigzag edges. Due to their high growth speed, they lead to a quick filling of the area between adjacent domains until either a straight zigzag edge or 120° vertexes between two zigzag edges are established (refer to the corner highlighted by red lines in Figure 4f and Figure 5b).

Figure 5. ESEM imaging of graphene growth on Pt(111) at 900 °C and KWC simulation of the shape evolution during the coalescence process. (a) Shape evolution of the graphene domains during coalescence, reproduced as color-coded superposition of outlines that were abstracted from images recorded during a 6300 s interval (Supporting Movie 3). The scale bar measures 5 μm. (b) Representation of the graphene GBs after coalescence. The blue dashed lines in (a) and (b) indicate the motion trajectory of the intersection point of misaligned graphene domains, which are responsible for GB formation during coalescence. The orange color-coded domains in (b) highlight the shape of graphene at the beginning of the recording. (c–f) Sequence of images showing the appearance of new edges at the concave corner during coalescence (the initial angle of the concave corner is highlighted by red lines, whereas the new edge angle is depicted in green). (g) Atomistic model of the growth process of a concave corner with an angle of 120° and zigzag edges in the case of well-aligned graphene domains. (h–k) KWC simulation of the shape evolution of well-aligned domains that coalesce from different directions and present a concave corner with an angle of either 120° (h) or 60° (i–k). (l) Superposition capturing the area of coalescence from three aligned domains marked by red arrows in (b). The outlines of growing domains are color-coded according to the growth time provided in the color legend. (n) Shape evolution of the graphene, reproduced as color-coded superposition of outlines that were abstracted from a sequence of in situ ESEM images (c–f). The corresponding coalescing processes shown in (l) and (n) are simulated by our modified KWC and presented in (m) and (o).
In order to rationalize the experimental findings, we first recall that the growth rate along different directions depends on the energy of the respective edge and is determined by the concentration of kinks.\textsuperscript{50} Kink creation, which is the rate-limiting step during growth, should be energetically favorable at the concave corner if the adjacent domains are well-aligned.\textsuperscript{42} Fast creation of new kinks at the concave corner is presumably the reason for the observed smoothening of the concave corner and formation of the fast growing edge (see Figure 5a,c−f).

In order to confirm that the fast growth at the concave corner between well-aligned domains is due to a reduced kink-creation energy, we performed KWC simulations of the shape evolution (refer to Supporting Note 1).\textsuperscript{57} Figure 5g−k show the simulated growth process at the concave corner between well-aligned domains for the case of domains that coalesce from different directions and present concave corners of either 120° (Figure 5h) or 60° (Figure 5i−k). For the simulation, hexagonal-shaped graphene domains were used, although experimentally observed domains generally deviate from ideal hexagons due to growth speed modulation by steps on the substrate surface. Due to the hexagonal geometry of the honeycomb lattice of graphene, the formation of kinks is easiest at concave corners presenting an angle of 60° or 120°, as confirmed by DFT simulations (refer to Supporting Note 2).

After attachment of carbon atoms at the concave corner, a sequence of new low-energy attachment sites is generated, as shown in Figure 5g. The sequential filling of low-energy sites leads to the formation of a new growth edge. This edge is tilted with respect to the zigzag edge by approximately 19.1°. It is characterized by having the highest possible kink density and is thus the fastest growing edge during attachment-limited growth. The simulations clearly show that the sequence of preferential attachment is the explanation for the observed rounding of the concave corner during the coalescence of aligned domains. Since the conditions for the formation of a 19.1° edge are only met if the carbon rings at the concave corner are not distorted, their appearance can be used to identify GB-free coalescence.

To validate the above discussion, we performed additional KWC simulations in order to reproduce the experimentally observed shape evolution of coalescing graphene domains (refer to Supporting Note 3 for simulation details).\textsuperscript{57} A single frame from the \textit{in situ} recorded movie was used as a starting point (Figure S1n). Besides the shape and position of the initial domains, only the growth speed of the zigzag edges was used as parameters for the simulation of the coalescence behavior. (The growth rate profile is provided in Figure S1 3.)

The striking consistency between the experimental coalescence of well-aligned graphene and the simulated evolution validates our above proposed coalescence mechanism.

One notable point is that the appearance of 19.1° edges at the concave corner does in fact not require a perfect alignment between the coalescing domains. As exemplified in the area marked by a white square in Figure 4b and Figure SI 4, we observe that the growth behavior of graphene domains follows that of well-aligned grains during merging as long as the angle of misalignment is less than ∼3°. We assume that the in-plane strain, which is generated during the coalescence, induces a correction of the misalignment through a slight rotation of one of the domains. Indeed, graphene rotation has been observed on other weak interaction substrates during annealing at growth temperature.\textsuperscript{58} Alternatively, during coalescence, the in-plane strain can induce a continuous rearrangement of the graphene lattice at the GB in order to decrease the orientation-dependent energy.\textsuperscript{59} In this case, the GB will be pushed through the grain with the higher energy. The misaligned grain thus in effect shrinks during the coalescence process.

It should be mentioned here that there are cases in which the 19.1° edges do not evolve, even though two grains are perfectly co-oriented.\textsuperscript{60−63} One such case is shown in Figure 6.

Close inspection by real-time imaging revealed that the attachment of carbon atoms at the concave corner is prevented by a surface impurity (highlighted by red arrow in Figure 6). This observation not only highlights the importance of growing on surfaces that are free of impurities but also provides an indirect proof that the kink creation at the concave corner is responsible for the formation of the 19.1° edge. Finally, this also further validates the rationalities and efficiencies of the theoretical model.

\textbf{Coalescence and GB Formation on Strongly Interacting Substrates.} In the case of a strong film−substrate interaction, the graphene layer will present a preferential in-plane orientation. Unlike the coalescence behavior on Pt, the most distinctive feature of graphene coalescence on Rh is that, even though the domains are well-aligned, the characteristic formation of 19.1° edges is not observed at the concave corner during coalescence. Instead, the angle of the concave corner remains unchanged with a value of 120° or 60° (Figure 7 and Supporting Movies 4 and 5).

A series of STM images capturing the growth and coalescence of graphene on Rh(111) at 700 °C is presented in Figure 8. It is revealed that the kink creation at the growth front occurs in units of the moiré lattice. Following the kink creation, C adatoms rapidly attach to this kink site and an
entire row of moiré pattern progresses along the edge. Similarly to the in situ ESEM observations, the 60° angle of the concave corner remains unchanged during the coalescence process observed in the STM (Figure 7). Furthermore, a GB that follows the trajectory of the concave corner is seen in the STM images (Figure 8 and Figure SI 5), even though the 60° or 120° angle indicates alignment of the two graphene lattices. The domains on either side of the boundary are aligned to each other, but the respective moiré pattern and associated height corrugations at the edge do not coincide (Figure 8e,f). This observation shows that the seamless coalescence on substrates with a strong film—substrate interaction requires both orientation alignment of the lattice and coincidence of the respective moiré pattern.

At higher pressure, multi-moiré-kink (MMK) nucleation can occur at the growth front. This can be observed by in situ ESEM (Figure 9 and Supporting Movie 5). The new kink that is created is coherent with the moiré lattice of the grain. The 120° angle at the kink site of a single crystalline grain can, in principle, be regarded as a representative for a concave corner between two co-oriented domains. The fact that formation of 19.1° edges is not observed at the 120° concave angle of a

Figure 7. Sequence of in situ ESEM images recorded during the coalescence of aligned domains on Rh(111). The green and red lines highlight the intersection corner with angles of 60°. Conditions of growth: 900 °C on Rh(111) at a total pressure of 4.2 × 10⁻² Pa (C₂H₄/H₂ = 1:10). Note that the angle of the concave corners remains the same during coalescence.

Figure 8. (a–e) In situ STM images recorded during graphene growth on Rh(111) at 700 °C with a C₂H₄ pressure of 5.7 × 10⁻⁷ Pa. The STM images have been taken at a sample voltage of Vₛ = −1.84 V and a tunneling current of Iₜ = 0.05 nA. (f) Schematic representation of the time-dependent changes of the domain shown in (a)–(e). The superimposed colored dots correspond to protrusion areas (weak adsorption region) in the moiré supercell and were extracted from the black window present on frames (b)–(e). The dashed lines indicate the graphene GBs.
single crystal during the growth process is a consequence of the growth in moiré units and, thus, associated with a strong film–substrate interaction.

We also performed STM postgrowth characterization of graphene films that were grown at 25 Pa in the ESEM. Figure 10a presents a stepped GB with steps in the height of a single moiré supercell. A portion of it is shown at higher magnification in Figure 10b. A schematic view of the coalescence process between aligned domains is provided in Figure 10c. It shows how kink creation in units of moiré cells...
can result in the formation of a GB with a stair-step shape in the case of noncoinciding moiré lattices. The postgrowth STM observation confirms that the modulated growth process in unit cells of the moiré pattern, which was first observed by in situ STM at UHV conditions (Figure 8), also occurs during growth at relevant CVD conditions.

In the following, we address the atomic structure of graphene GBs on the Rh substrate. In general, two types of GBs can stitch graphene domains together. In the case of rotated domains, the GB consists of a series of pentagon and heptagon carbon rings. In the case of well-aligned domains, the GB structure consists of octagons that are separated by pairs of pentagons. Such a GB zipping of aligned domains has been documented for the case of graphene growth on Ni(111), for example. As mentioned above, due to the strong interfacial interactions, the graphene domains are aligned on the Rh substrate. Therefore, the structure of graphene GBs on Rh should follow the GB zipping process and contain sections of pentagons and octagons. The high-resolution STM image in Figure 10b shows that the GB structure is composed of a linear chain of alternating pentagon pairs—octagon—pentagon pairs—heptagon pairs. The relationship between the graphene domains, the S5−8−S5−77 boundary structure, and the moiré pattern disrupted by shear dislocations of the honeycomb network at the intersection of two shifted moiré patterns.

The S5−8−S5−77 structure consists of a straight section of S5−8−S5 units and an offset bridge of 77, which links two parallel S5−8−S5 sections. This results in a zigzag GB, as shown in Figure 10c. Similar boundary structures have been
observed in silica films grown on Ru. Considering that the graphene is terminated by smooth zigzag edges during the growth in the attachment-limited regime, we can deduce that the most prevalent feature of a GB connecting aligned domains with zigzag edges should be a straight chain of pentagon pairs with an octagon unit (55−8). As shown in Figure 10f,g, a 55−8 GB interfaces the two domains, featuring half of the moiré spots on each side. While the row of 55−8 units is the typical structure forming at straight GBs between aligned zigzag edges, the 55−8−55−77 GB forms at stepped GBs.

**Generalization to Other 2D Materials and Substrates.** In the following, we generalize the findings obtained for graphene grown on Pt and Rh to other substrates and 2D materials.

![Figure 12](image)

**Figure 12.** Shape of concave corners between merging domains growing under the influence of a strong film–substrate interaction. (a−f) Sequence of in situ PEEM images recorded during hBN growth on Ni(111) at 640 °C under a total pressure of 4.7 × 10−6 Pa (BH3NH3) showing MMK creation on zigzag edges of hBN. The inset in (a) shows a low-energy electron diffraction (LEED) (50 eV) pattern recorded from the observed region. Rhombuses with different colors: purple, hBN; green, Ni(111); yellow, moiré superstructure. The different direction of zigzag edges is highlighted by a different color. Note that the angles at MMK sites, which are highlighted in (a)−(f) by blue arrows, measure 120° and remain unchanged during growing. The growth behavior of hBN on Ni is similar to the one of graphene on Rh (refer to Figure 9). (g−k) In situ STM images recorded during hBN growth on Rh(111) at 700 °C at a pressure of 1.2 × 10−7 Pa using borazine as precursor. The STM images were recorded at a sample voltage of Vb = 1.0 V and a tunneling current of It = 0.05 nA. The green and black grids in (k) indicate the lattice of the moiré pattern formed between hBN and the Rh(111). Note that red and blue dots in (k) highlight depression areas (strong adsorption region) in the moiré supercell. The arrangement of the two lattices shows that the adjacent domains are aligned but incoherent in the respective moiré corrugation. The purple arrows highlight the concave corner at which a GB is formed. The green arrows highlight a concave corner where coalescence is seamless. (l) Schematic representation of the time-dependent changes of the domain shown in (g)−(k). The superimposed colored dots correspond to depression areas in the moiré supercell and were extracted from the area indicated by a white square in frames (g)−(k). The dashed line in (l) indicates the position of the GB. Note that the growth behavior of hBN is similar to graphene on Rh (the kink creation at the edge occurs in units of the moiré lattice) and the angle of the concave corners remains the same during coalescence.
We start with copper, which is presently the most popular substrate for graphene growth and shows a weak coupling strength with graphene. In the literature, there are several cases where the formation of rounded concave corners during the coalescence of aligned graphene domains is evident from provided images. In some cases, it was either not noticed or commented; in others it was interpreted as a result of new nucleation events between adjacent domains at carbon defects. In order to confirm that the rounding at concave corners is related to seamless coalescence, we repeated CVD growth of graphene on copper (see Figure 11a).

Switching from graphene to hexagonal-boron-nitride (hBN), which also shows a weak film–substrate interaction when grown on copper, we confirm that rounded concave corners are observed during coalescence of aligned domains (see Figure 11b). Rounded concave corners with 19.1° edges also appear during the coalescence of transition metal dichalcogenides. As shown in our previous work, the frequent appearance of 19.1° edges can also be found during the growth–etching–regrowth processes of monolayer GaSe domains. Thus, the appearance of 19.1° edges and associated reduction of the angle at the concave corner seems to be general features of seamless coalescence of 2D materials on substrates that show a weak film–substrate interaction. To provide an additional case, we performed CVD growth of MoS₂ on SiO₂. The CVD growth was performed in a S-rich atmosphere. Under such conditions, the triangular-shaped MoS₂ domains are terminated by S at zigzag edges. As shown in Figure 11c,d, the formation of rounded concave corners is observed during the coalescence of aligned MoS₂ domains. At higher magnification, SEM imaging clearly reveals the ~19° tilted edges (highlighted by yellow arrows in Figure 11e). The atomic structure of each MoS₂ edge is directly correlated with the mesoscopic edge orientation, and we thus can reproduce the detailed structure of the MoS₂ edges at the rounded concave corner with 19.1° edges (see Figure 11f). The coalescence behavior of MoS₂ domains is thus very similar to the case of graphene islands that coalesce by seamless stitching. In view of the similar growth mechanism of 2D materials, we propose that the coalescence mechanism derived in this work can guide the growth of crystalline 2D materials such as semiconducting transition metal dichalcogenides. We also suggest that macroscopic growth features, such as the rounded concave corners, can be used as a convenient indicator for a judgment of the interaction strength between film and substrate. Overall, the appearance of rounded concave corners with 19.1° edges is just a macroscopic expression of the fact that attachment of new atoms and thus, kink creation, are energetically favorable at an unstrained concave corner. It is independent of the material type, as long as the film–substrate interaction is weak and can be used as a simple criterion for the judgment of seamless coalescence in weak film–substrate interactions.

In the case of growth on substrates that show a strong film–substrate interaction, the lattice mismatch between film and substrate induces a buckling of the film. Modulation of the adsorption energy on the atomic scale leads to a growth in units of the moiré cells. The seamless coalescence of two adjacent domains thus requires, in addition to the orientation alignment, also a coincidence of the respective moiré pattern. Because of the growth modulation in moiré units, the edges with highest kink density (i.e., the 19.1° edges) do not form. Therefore, the angle of the concave corners remains unchanged during coalescence, even if the coalescence is seamless. A coalescence behavior similar to the case of graphene grown on Rh should be observed in the case of other 2D materials that grow under the influence of a strong film–substrate interaction. Indeed, the MMKs forming at the growth front in hBN during growth on Ni(111) are indicative of a strong interaction. The observation that the angle between multi-moiré-kink sites remains unchanged during growth, as shown in Figure 12a–f, is a further confirmation of a strong film–substrate interaction. Further in situ STM imaging of aligned hBN domains growing on Rh reveals cases of seamless and nonseamless coalescence under identical conditions (highlighted by green and purple arrows in Figure 12g–k, respectively). In both cases, the angle of the concave corner remains unchanged (see Figure 12g–l). Similar coalescence behaviors of hBN have been observed on Re, Ni, and Co and on Ni–Cu substrates, each characterized by strong interactions. Overall, we find that in the case of growth on strongly interacting substrates there is no macroscopically observable growth feature that can be used to identify GB-free coalescence.

CONCLUSIONS

In summary, we studied the growth and coalescence behavior of 2D materials. Real-time multiscale observation of 2D film growth dynamics at different length scales, from the atomic to micrometer scale, provides the missing clues for unravelling the influence of interfacial interaction strength on the coalescence processes. We demonstrate that atomistic processes can be traced in the dynamics that are observed at the micrometer scale. Furthermore, it is shown that insights about factors that determine growth and coalescence under UHV conditions are valid for growth under relevant CVD conditions. Finally, by combining in situ experiments with theoretical calculations, it is shown that the experimental observations are in line with theoretical descriptions of mechanisms that determine 2D growth and coalescence.

In view of the similar growth mechanism of 2D materials, we propose that the coalescence mechanism derived in this work can guide the growth of crystalline 2D materials such as semiconducting transition metal dichalcogenides. We also suggest that macroscopic growth features, such as the rounded concave corners, can be used as a convenient indicator for a judgment of the interaction strength between film and substrate. Most importantly, this work highlights the importance of correlative in situ experiments for a better understanding of 2D growth processes.

The broader significance of this work lies in the demonstration that a combination of complementary in situ methods can lead to a consistent picture of growth from the atomic to the millimeter scale and across the pressure gap between surface-science UHV methods and industrially relevant CVD growth conditions.
METHODS

In Situ ESEM. In situ CVD growth experiments were performed inside the chamber of a modified commercial ESEM (FEI Quantum 200). The vacuum system of the ESEM was modified and upgraded with oil-free prevacuum pumps. The instrument is equipped with a homemade laser heating stage, a gas supply unit (mass flow controllers from Bronkhorst), and a mass spectrometer (Pfeiffer OmniStar) for the analysis of the chamber atmosphere. Owing to the use of rubber O-rings for the sealing and the fact that the chamber cannot be baked out, the base pressure of the instrument is around 2 × 10⁻⁵ Pa, with a residual gas composition mostly comprising water, N₂, and O₂. After each sample loading, the chamber was pumped out to around 10⁻⁴ Pa, purged with pure nitrogen, and pumped again to 10⁻³ Pa successively for several times. Under CVD growth conditions, the pressure is 6 orders of magnitude higher than the base pressure and constitutes mostly H₂ (99.9995% purity) and C₂H₄ (99.95% purity). Samples of sizes ranging from 4 × 4 to 5 × 5 mm are extracted from a 0.5 mm thick single-crystalline Pt and Rh (99.999% purity). Prior to all CVD growth experiments, the chamber of the ESEM was plasma cleaned. The crystals were annealed at 1000 °C under a hydrogen flow of 10 sccm at 25 Pa for more than 48 h inside the chamber. The temperature was measured via a B-type thermocouple that was spot-welded directly onto the sample, which simultaneously served to ground the sample. CVD growth was performed at temperatures ranging from 700 to 1000 °C, with a pressure in the chamber ranging from 10⁻³ to 25 Pa. Hydrogen etching was performed under 10 sccm H₂ at 900 °C at 25 Pa. During the experiments, the microscope was operated at an acceleration voltage of 5.0–7.5 kV. Images were recorded by an Everhart Thornley detector/a large field detector during CVD growth and etching under high-vacuum and low-vacuum conditions, respectively. No influence of the electron beam on the growth and etching process could be observed. The imaged regions and their respective surroundings showed similar behavior, as evidenced by changing the magnification or by moving the sample under the beam. Furthermore, no electron beam induced contamination was observed at elevated temperatures.

In Situ LEEM/LEED. Graphene growth under UHV was conducted in a SPECS LEEM system, which is connected to the Vacuum Interconnected Nanotech Workstation (NANO-X) of Suzhou Institute of Nano-Tech and Nano-Bionics, the Chinese Academy of Sciences, which is installed with a preparation chamber and a main chamber. For imaging for graphene domain growth on Rh/Pt(111), incident electron beam energies are chosen as 7 eV. In this system, LEED can also be performed to investigate surface structure after graphene growth. The incident electron beam energies are always kept at 50 eV during LEED measurements.

In Situ STM. In situ STM observations were performed on Rh(111) under low-vacuum conditions within an STM that can be operated under pressures ranging from UHV up to 10⁻⁵ Pa and at elevated pressures. Temperatures were measured using a K-type thermocouple that was spot-welded directly onto the sample. Gas pressures were measured by an ionization gauge that was calibrated following the Levenberg–Marquardt algorithm to minimize the χ². Peak shapes were modeled by using asymmetric Doniach–Sunjic functions convoluted with Gaussian profiles. The accuracy of the fitted peak positions is ∼0.05 eV.

DFT Calculations. All DFT calculations are performed by using the Vienna ab initio simulation package (VASP).86 Local density approximation (LDA) is used for the exchange–correlation functional.87 The electron–ion interaction is treated by the projected augmented wave (PAW) method.88 An energy cutoff of 400 eV is used for the plan wave basis. To calculate the growth behaviors of graphene coalescence in the presence of two neighboring graphene domains with a misorientation angle, a graphene flake with a concave structure and a GB, with a misorientation angle of 21.8°, is constructed. The graphene flake is modeled in an orthorhombic unit cell that is large enough to avoid interactions between repetitive images. Its growth process is shown in Figure S1a. C atoms are attached to the concave structure consecutively. A GB-free graphene flake, with a concave corner of 120°, is also constructed to study the growth of coalesced graphene domains that are well-aligned (Figure S1b). All these structures are fully optimized until the force on each atom is less than 0.01 eV/Å by the conjugate gradient method. Only the gamma point is used for the Monkhorst–Pack k-point sampling.

The formation energy change, ΔEf, during the growth of concave structures formed by coalescence of neighboring graphene domains is defined by

\[ ΔEf = E_f - E_{f,i} - N_C × ε_C - N_H × μ_H \]

where \( E_f \) is the energy of the structure at the ith growth step, \( E_{f,i} \) is the energy of the initial structure for growth calculation, \( N_C \) and \( N_H \) are the number of C and H atoms attached to the initial structure, \( ε_C \) is the energy of a C atom in a perfect monolayer graphene, and \( μ_H \) is the chemical potential of H atoms. \( μ_H \) is determined by setting the ΔEf of the final growth structure in Figure S1a to be 0, because this structure recovers to the concave structure of the initial growth configuration.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.9b08221.

Detailed simulation for kinetic Wulff construction of coalescence process; DFT calculations of graphene coalescence; simulation of MoS₂ coalescence process with the phase field model; structures used for the calculation of growth of coalesced graphene domains. (PDF)

Supporting Movie 1. In situ ESEM movie showing the coalescence of two misaligned domains on Pt (111) in a flow of 10 sccm H₂ and 0.1 sccm of C₂H₄ at 25 Pa and a substrate temperature of 900 °C. Images for this movie...
were recorded at a scan rate of one frame per 90 s, the movie is running at 25 frames per second. Movie size: 10 μm × 20 μm; Recording time: 1h 43min 47s. Note the angle of the concave corner of two merging edges remains unchanged during whole coalescence. (AVI)

Supporting Movie 2. In situ ESEM movie recorded at 900 °C, 25 Pa during H2 etching showing the evolution of etch pits on graphene GB. Images for this movie were recorded at a scan rate of one frame per 36 s, the movie is running at 4 frames per second. Movie size: 15 μm × 20 μm; Recording time: 1h 22min 51s. (AVI)

Supporting Movie 3. In situ ESEM movie showing the coalescence of graphene on Pt (111) in a flow of 10 sccm H2 and 0.1 sccm of C2H4 at 25 Pa and a substrate temperature of 900 °C. Images for this movie were recorded at a scan rate of one frame per 36 s, the movie is running at 17 frames per second. Movie size: 30 μm × 30 μm; Recording time: 1h 36min 26s. (AVI)

Supporting Movie 4. In situ ESEM movie showing the coalescence of aligned domains on Rh (111) in a flow of 4 sccm H2 and 0.4 sccm of C2H4 at 4.2 × 10⁻² Pa and a substrate temperature of 900 °C. Images for this movie were recorded at a scan rate of one frame per 95 s, the movie is running at 4 frames per second. Movie size: 2 μm × 3 μm; Recording time: 9min 33s. (AVI)

Supporting Movie 5. In situ ESEM movie showing the coalescence of aligned domains on Rh (111) in a flow of 10 sccm H2 and 0.1 sccm of C2H4 at 25 Pa and a substrate temperature of 900 °C. Images for this movie were recorded at a scan rate of one frame per 90 s, the movie is running at 4 frames per second. Movie size: 2 μm × 2 μm; Recording time: 1h 18min 21s. (AVI)

AUTHOR INFORMATION

Corresponding Authors

Zhu-Jun Wang — Scientific Center for Optical and Electron Microscopy, ETH Zürich, 8093 Zürich, Switzerland; Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin-Dahlem D-14195, Germany; orcid.org/0000-0002-8227-7323; Email: zhujun.wang@scopem.ethz.ch

Marc-Georg Willinger — Scientific Center for Optical and Electron Microscopy, ETH Zürich, 8093 Zürich, Switzerland; Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin-Dahlem D-14195, Germany; Email: marc.willinger@scopem.ethz.ch

Authors

Jichen Dong — School of Materials Science and Engineering and Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

Linfei Li — Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States; orcid.org/0000-0002-5217-3005

Guocai Dong — Kamerlingh Onnes Laboratory, Leiden University, 2300 RA Leiden, The Netherlands

Yi Cui — Vacuum Interconnected Nanotech Workstation, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China; orcid.org/0000-0002-9182-9038

Yang Yang — State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Wei Wei — Vacuum Interconnected Nanotech Workstation, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China; State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Raoul Blume — Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin-Dahlem D-14195, Germany

Qing Li — Institute of Functional Nano & Soft Materials (FUNSOM), Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, Jiangsu, China; orcid.org/0000-0002-6281-6342

Li Wang — State Key Laboratory for Mesoscopic Physics, Collaborative Innovation Centre of Quantum Matter, School of Physics, Peking University, Beijing 100871, China

Xiaohui Xu — State Key Laboratory for Mesoscopic Physics, Collaborative Innovation Centre of Quantum Matter, School of Physics, Peking University, Beijing 100871, China

Kaihui Liu — State Key Laboratory for Mesoscopic Physics, Collaborative Innovation Centre of Quantum Matter, School of Physics, Peking University, Beijing 100871, China; orcid.org/0000-0002-8781-2495

Cédric Barroo — Chemical Physics of Materials and Catalysis,Faculty of Sciences, Universite Libre de Bruxelles, 1050 Brussels, Belgium; orcid.org/0000-0002-3085-4934

Joost W. M. Frenken — Kamerlingh Onnes Laboratory, Leiden University, 2300 RA Leiden, The Netherlands

Qiang Fu — State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; orcid.org/0000-0001-5316-6758

Xinhe Bao — State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; orcid.org/0000-0001-9404-6429

Robert Schloegl — Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin-Dahlem D-14195, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.9b08221

Author Contributions

△Z.-J. Wang, J. Dong, and L. Li contributed equally to this work.

Author Contributions

Z.-J.W. and M.-G.W. modified the ESEM, planned and conducted the in situ growth and etching experiments, and wrote the manuscript. Z.-J.W. did most of the ESEM and STM data analysis; theoretical simulations and implementation of the obtained results were done by J.D. and F.D.; ex situ STM measurements were performed by L.L., Y.C., Q.F., Q.L., and Z.-J.W.; G.D. and J.W.M.F. conducted the in situ STM measurements; R.B. and Z.-J.W. conducted the in situ NAP-XPS measurement; Y.Y., W.W., and B.X. conducted the in situ PEEM measurement. Important contributions to the interpretation of the results, conception, and writing of the manuscript were made by Z.-J.W., F.D., and M.-G.W. All the authors discussed the results and commented on the manuscript.

https://dx.doi.org/10.1021/acsnano.9b08221
ACS Nano 2020, 14, 1902–1918


**ACKNOWLEDGMENTS**

The authors acknowledge Dr. Jun Cai and Prof. Zhi Liu for recording the NAP-XPS, and ShanghaiTech University for the use of the equipment. J.D. and F.D. acknowledge the support of Institute for Basic Science (IBS-R019-D1) of South Korea. The computational resource from Center for Multidimensional Carbon Materials, Institute for Basic Science, is also acknowledged. Y.C. is grateful for support from the NANO-X Workstation in Suzhou, Jiangsu Province Science Foundation for Youths (No. BK20170426) and Thousand Young Talents Program in China. C.B. thanks the Fonds de la Recherche Scientifique (F.R.S.-FNRS) and the Wallonie-Bruxelles International (Excellence Grant WBIWORLD) for financial support. The contribution to this work by G.D. was supported by the National Key Research and Development Program of China (Grant Nos. 2016YFE0125200 and 2016YFC0101100).

**REFERENCES**


