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A Kinetic Monte Carlo Study for Mono- and Bi-layer Growth of MoS₂ during Chemical Vapor Deposition

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Abstract: Controllable synthesis of MoS₂ with desired number of layers *via* chemical vapor deposition (CVD) remains challenging. Hence, it is highly desirable to develop a theoretical model that can be used to predict the single- and multilayer growth of MoS₂ quantitatively, and provide guidelines for experimental fabrication. Herein we have established a kinetic Monte Carlo (kMC) model to predict the CVD growth of mono- and bilayer MoS₂. First, we proposed that the growth rates of layer 1 and layer 2 were governed by the distribution of the adatom concentration, and the growth kinetics of compact triangular MoS₂ followed the kink nucleation-propagation mechanism. The adatom concentration was formulated in terms of adatom flux, effective lifetime of adatoms, growth temperature, binding energies, edge energies, and nucleation criterion. The kink nucleation and propagation were determined by energy barriers of the adatom attachments to the zigzag and armchair edges. We then employed an analytic thermodynamic criterion to extract these parameters. Using the calibrated model, we found that the growth rate of layer 2 strongly depended on the size of layer 1 and decreased monotonically with increasing size of layer 1, and might even become prohibited at the maximum size of layer 1. Furthermore, we analyzed the size and morphology evolutions of bilayer MoS₂ at different growth temperatures and adatom fluxes. Throughout the growth processes of bilayer MoS₂, the morphologies of layers 1 and 2 maintained triangular shapes with compact edges, consistent with the kink nucleation-propagation growth mechanism. Our simulations revealed that the growth of bilayer MoS₂ was promoted by increasing the growth temperature or decreasing the adatom flux, which corroborated the experimental observations. The increase in growth temperature led to reduced adatom concentration at the edge of layer 2 in accordance with the adatom concentration far from the edge of layer 2, resulting in a consistent difference in the adatom concentration to promote the growth of bilayer MoS₂. Similarly, the decrease in adatom flux lowered the difference between the adatom concentrations far from the edge and at the edge of layer 1, decelerating the growth of layer 1. The decelerated growth of layer 1 reduced the difference between the adatom concentrations far from the edge and at the edge of layer 2 to zero, permitting the growth of bilayer MoS₂. To guide the experimental synthesis, we constructed a phase diagram to delineate the permitted or prohibited growth of bilayer MoS₂ at different growth temperatures and adatom fluxes. Hence, this work not only unveils the conditions for the growth of mono- and bi-layer MoS₂, but also provides guidelines for controllable synthesis of MoS₂ with the desired number of layers.

Key Words: MoS₂; Monolayer growth; Bilayer growth; Chemical vapor deposition; Kinetic Monte Carlo

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单层和双层二硫化钼化学气相沉积生长的动力学蒙特卡罗模拟研究

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摘要: 通过化学气相沉积方法, 可控合成所需层数的二硫化钼仍然是一个挑战。因此, 建立一个能够定量预测单层和多层二硫化钼生长的理论模型, 并为实验制备提供指导, 是十分必要的。在本文中, 我们建立了一个动力学蒙特卡罗模型, 来预测单层和双层二硫化钼的化学气相沉积生长。首先, 我们提出了第一层和第二层的生长速率受吸附原子浓度分布的控制, 以及紧凑三角形二硫化钼的生长过程为扭结成核和传播。其中, 原子浓度是由吸附原子流量, 吸附原子的有效寿命, 生长温度, 边的单位长度能量, 单层和双层的单位面积结合能, 成核准则决定的。扭结成核和传播是由锯齿边和扶手边附加原子所需的能量势垒决定的。然后, 我们采用热力学理论准则对这些参数进行了标定。通过标定的动力学蒙特卡罗模型, 我们发现第二层的生长速率与第一层的尺寸有很强的依赖性。随着第一层尺寸增加, 第二层的生长速率呈单调递减趋势, 甚至在第一层达到某个尺寸时, 第二层的生长会被抑制。此外, 我们还分析了不同生长温度和吸附原子流量下, 双层二硫化钼的尺寸和形貌演化。在双层二硫化钼的整个生长过程中, 第一层和第二层的形貌保持紧凑三角形, 验证了扭结成核和传播模型的正确性。模拟结果表明, 生长温度的升高或吸附原子流量的降低, 促进了双层二硫化钼的生长, 这与已报导的实验结果相吻合。生长温度升高使得第二层二硫化钼边缘的吸附原子浓度, 随着远离第二层边缘的吸附原子浓度降低而相应降低, 促进了双层二硫化钼的生长。同样, 吸附原子流量降低减小了基体上的吸附原子浓度, 降低了第一层远离边缘和靠近边缘的吸附原子浓度差, 从而减缓了第一层的生长。第一层的生长减慢, 减缓了第二层远离边缘和靠近边缘的吸附原子浓度差减小到零, 从而促进双层二硫化钼的生长。为了更好地指导实验, 我们进一步构建了双层二硫化钼生长的相图, 可通过控制生长温度和吸附原子流量来实现或阻止双层二硫化钼的生长。因此, 本工作不仅揭示了单层和双层二硫化钼生长所需的实验条件, 而且为可控合成所需层数的二硫化钼提供了详细指导。

关键词: 二硫化钼; 单层生长; 双层生长; 化学气相沉积; 动力学蒙特卡罗

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1 Introduction

Two-dimensional (2D) materials, such as graphene, phosphorene, transition metal dichalcogenides (TMDs), have attracted a great deal of attention due to their fascinating lattice structures and unusual physical properties¹⁻⁴. 2D MoS₂, a member in the TMD family, is a semiconductor with a large band gap, high on/off ratio and high mobility⁵⁻⁷, promising for many interesting electronic and energy applications. However, layer number of 2D MoS₂ can drastically change its physical properties. For example, monolayer MoS₂ is a direct band gap semiconductor with a band gap of ~1.9 eV⁸; while bi-layer MoS₂ is an indirect band gap semiconductor with a reduced band gap of ~1.6 eV⁸. In addition, the change in layer number may also tune the charge mobility and photoelectric properties. Nowadays, monolayer and multilayer MoS₂ have been grown *via* chemical vapor deposition (CVD) experimentally⁹, but how to accurately and robustly control the number of layers remains a challenge. Clearly, addressing this issue would enable robust control of their physical properties and thus facilitate their applications⁹.

Fabrication techniques, such as mechanical exfoliation⁹⁻¹¹ and liquid exfoliation¹²⁻¹⁴, have been frequently used to produce layered MoS₂ samples. However, these fabrication techniques are limited by their scalability and lack of precise control of layer

number. CVD has the advantage of the controllable synthesis of large-area 2D MoS₂¹⁵⁻²⁰, and is widely recognized as a superior synthesis technique. However, CVD is well-known for its notorious difficulty in extending across reactors in different laboratories. Often, subtle changes in reactor parameters and growth conditions may confound reproducibility. To address this challenge, it is highly desirable to develop a theoretical tool that is able to make insightful predictions on the growth of MoS₂ and provide useful guidelines to control CVD synthesis.

We note that significant theoretical efforts have been made to understand the CVD growth of graphene²¹⁻³⁴. However, only a few studies have been performed to model TMDs growth due to their more complex compound structures³⁵⁻⁴⁰. Recently, Ye *et al.*³⁷ established an analytic thermodynamic criterion for the vertical growth (bilayer) *versus* in-plane lateral growth (monolayer) of MoS₂ with regard to the sizes of both layers, van der Waals (vdW) interaction energies, and edge energies of 2D layers, which provided useful guidelines for the growth of bilayer MoS₂. However, the conditions to permit or prohibit the growth of bilayer MoS₂ remain unclear. Hence, it is highly desirable to develop a phase diagram which is able to delineate the permitted or prohibited growth regime of bilayer MoS₂ in terms of growth temperature and adatom flux.

Usually, the second layer of MoS₂ starts to nucleate when the

first layer is sufficient large. Therefore, there is a need to develop a computational method that is able to reproduce the growth kinetics in large scale. It is well-known that kinetic Monte Carlo (kMC) method has the advantage of much longer time scale and larger length scale. Moreover, kMC simulations can be directly correlated with experimental growth conditions, such as growth temperature and adatom flux, to understand underlying growth mechanisms and predict growth phase diagrams. Hence, kMC simulations have been used to reproduce the experimental growth behaviors and further reveal the growth mechanism of 2D materials under different conditions, for example, the growth of monolayer graphene and monolayer TMDs^{38–40}. However, a detailed kMC model that is able to describe the mono- and bi-layer growth of MoS₂, currently, is still unavailable.

In this work, we aim to develop a kMC model to make insightful predictions on the mono- and bi-layer growth of MoS₂. First, we proposed and formulated our kMC model of bilayer MoS₂ growth, and then employed the analytic thermodynamic criterion³⁷ to calibrate the kMC model. With the calibrated model, the size and morphology evolutions of bilayer MoS₂ at different growth temperatures and adatom fluxes were analyzed. Then, the conditions for the permitted or prohibited growth of the bilayer MoS₂ in terms of growth temperature and adatom flux were revealed, which match well with the experimental observations. Lastly, a phase diagram on the permitted or prohibited growth of the bilayer MoS₂ was predicted. The present study not only unveils the growth conditions for mono- and bi-layer MoS₂ growth, but also provides guidelines for controllable growth of MoS₂ with desired number of layers.

2 Method

Our kMC simulation model is illustrated in Fig. 1a, in which hexagonal MoS₂ lattice (lattice constant $a = 0.318$ nm) with bilayer structures grown on a substrate is used⁴¹. An initial triangular domain of the first layer (layer 1) with an edge length of L_1 and a smaller triangular domain of the second layer (layer 2) with an edge length of L_2 are introduced at the center of the

Fig. 1 Schematic illustration of (a) the bilayer MoS₂ model and (b) growth procedures at MoS₂ edge.

The growth starts from a kink nucleation at the zigzag edge and proceeds with kink propagation in kMC simulation. Mo atoms at layer 1, Mo atoms at layer 2, and all S atoms are represented by the orange, purple and white spheres, respectively. Color online.

substrate surface. Starting from the bilayer nucleus, the growth of MoS₂ is made by the attachments of molybdenum and sulfur adatoms to the edges of both the layer 1 and layer 2. To form the triangular MoS₂ with S-terminated zigzag edge^{15,18}, in our simulation, we assume sulfur source is sufficient. Once the molybdenum adatom is attached to the edge, its neighboring sulfur sites are quickly filled. Our model is also applicable to simulate the conditions when molybdenum source is sufficient. In that case, once the sulfur adatom is attached to the edge, its neighboring molybdenum sites are quickly filled.

Ye *et al.*³⁷ reported that the growth of the MoS₂ is governed by the distribution of the adatom concentration. The growth of layer 1 is permitted when the adatom concentration on the substrate far from the edge of layer 1 (C_0) is larger than that at the edge of layer 1 (C_{1-}). However, if C_0 is not larger than C_{1-} , the growth of layer 1 is prohibited due to the lack of feeding stock. Similarly, the growth of layer 2 is permitted when the adatom concentration on layer 1 far from the edge of layer 2 (C_{1+}) is larger than that at the edge of layer 2 (C_2). Otherwise, the growth of layer 2 is prohibited. In our simulations, we assume that the Schwoebel barrier is absent. Therefore, the adatom concentration at the edge of layer 1 (C_{1-}) is equal to the adatom concentration on layer 1 far from the edge of layer 2 (C_{1+}), *i.e.*, $C_{1-} = C_{1+} = C_1$. Meanwhile, the occurrence for attachment to the edge is also determined by the energy barrier, whose rate can be calculated by the transition state theory. Therefore, we proposed the following occurrence rate for the growth of layer 1 when $C_0 > C_1$ and layer 2 when $C_1 > C_2$.

$$P_n = (C_{n-1} - C_n) \times \nu \times \exp\left(-\frac{E_n}{k_b T}\right) \quad (1)$$

The subscript $n = 1, 2$ refers to the layer 1 and layer 2, respectively. If the adatom concentration $C_{n-1} \leq C_n$, the occurrence rate $P_n = 0$. ν is the order of the frequency of atomic vibration (10^{12} s⁻¹). E_n is the energy barrier for the attachment to the edge of layer n . It has been reported that the attachment of W adatom is mainly determined by the bond energy of W-Se (2.38 eV), which is used to simulate the growth of WSe₂ on different substrates³⁸. Therefore, in our simulations, we assume $E_1 = E_2$. k_b is the Boltzmann constant, and T is the temperature.

Based on Ye *et al.*'s work³⁷, the adatom concentrations on the edge of layer 1 and layer 2 can be expressed as

$$C_1 = C_{\text{ref}} \times \exp\left(\frac{1}{k_b T \Omega} \left(-\varepsilon_1 + \eta \frac{\gamma_1}{L_1}\right)\right) \quad (2)$$

$$C_2 = C_{\text{ref}} \times \exp\left(\frac{1}{k_b T \Omega} \left(\varepsilon_2 - \varepsilon_1 + \eta \frac{\gamma_2}{L_2}\right)\right) \quad (3)$$

C_{ref} is the reference adatom concentration, which is taken to be $C_{\text{ref}} = F \times \Omega \times \tau$. F is the rate of adatom supply that accounts for the precursor decomposition and adsorption rate. It is a dimensionless number, often called adatom flux. Ω is the concentration of atomic sites in the 2D layer (10^{20} m⁻²), and τ is the effective lifetime of adatoms due to desorption. ε_1 and ε_2 are the binding energies per unit area of monolayer and bilayer,

respectively, accounting for both in-plane bonding within the formed layers and across-layer vdW interactions. γ_n is the edge energy per unit length, and η is the structural parameter determined by the shape of the domain. L_1 and L_2 are the edge lengths of layer 1 and layer 2, respectively.

Based on the adatom concentration at the edge of layer 1, we proposed the adatom concentration on the substrate far from the edge of layer 1 to be

$$C_0 = k_F \times C_{\text{ref}} \times \exp\left(\frac{1}{k_b T \Omega} \left(-\varepsilon_1 + \eta \frac{\gamma_1}{L_0}\right)\right) \quad (4)$$

k_F is a parameter which is determined by the system and $k_F < 1$ (more detailed discussion on this is given in Sections 3.1 and 3.3). L_0 is the edge length of the nucleus. Here, the adatom concentration on the substrate far from the edge of layer 1 should be lower than that required to induce new nucleation. If there exists a Schwoebel barrier at the edge of layer 1, the adatom concentration at the edge of layer 1 on substrate (C_{1-}) will be not equal to the adatom concentration on layer 1 far from the edge of layer 2 (C_{1+}), *i.e.* $C_{1-} > C_{1+}$ or $C_{1-} < C_{1+}$. In calibrating our kMC model with the analytic thermodynamic criterion, the parameter k_F could be tuned to change the value of C_0 to maintain the relative dominance between the adatom concentration differences for layer 1 and layer 2, *i.e.* $C_0 - C_{1-}$ and $C_{1+} - C_2$. Therefore, the assumption that the Schwoebel barrier is absent will only change the value of k_F but will not affect the conclusions.

It has been reported that the morphology of MoS₂ domain in experiments always maintains a triangular shape with compact edges^{15–17}. The underlying mechanism to achieve compact edges has been unveiled as fast kink propagation after kink nucleation²⁸. Based on the above analyses, we proposed the following growth process of a triangular shape with compact edges in our simulations: the growth starts from a kink nucleation at the zigzag edge and proceeds with kink propagation (*cf.* Fig. 1b). The kink is nucleated by the initial attachments of adatoms to the zigzag edge, while the kink is propagated by the further attachments of adatoms to the active armchair site near the kink. It was previously reported that the difference in the energy barriers for the attachment to the zigzag edge and the armchair edge was ~0.3 eV for graphene by first-principles calculations⁴². In addition, the difference in the energy barriers for the attachment to the zigzag edge and the armchair edge was 0.23 eV for WSe₂ by first-principles calculations⁴³. Therefore, in our kMC simulations, the difference in the energy barrier between the kink nucleation E_{K-N} and the kink propagation E_{K-P} is chosen as $E_{K-N} - E_{K-P} = 0.3$ eV. Thus, the overall growth rates are determined by the kink nucleation E_{K-N} . The value of E_{K-N} can be deduced from the experimental growth rate (more detailed discussion on this is given in Section 3.1). Because the energy barrier for the attachment of adatoms to the armchair edge is 0.2–0.3 eV lower than that to the zigzag edge^{42,43}, the fast growing armchair edges will lose out to the slow growing zigzag edges. The compact

triangular MoS₂ domains observed in experiments also indicate that the zigzag edge is dominated^{15–17}. In addition, many experimental and simulation studies have indicated that S source is always sufficient, resulting in the formation of S-terminated zigzag edge^{15,18}. Therefore, in our simulation, S-terminated zigzag edge is used. This kMC model can also be applied to other edges, such as Mo-terminated zigzag edge or armchair edge. In this scenario, the energy barrier of the kink nucleation should be chosen according to the edge type and edge structure.

3 Results and discussion

3.1 KMC model formulation and calibration based on analytic thermodynamic criterion

In Section 2, we proposed the occurrence rate for the growth of layer 1 and layer 2 in our kMC model. In this section, we made efforts to obtain the values of parameters in Eqs. 1 to 4. Fortunately, Ye *et al.*'s³⁷ reported the values of most parameters in our kMC model when proposing their analytic thermodynamic criterion, such as the adatom flux ($F = 1.0 \times 10^{-3}$), concentration of atomic sites $\Omega = 10^{20} \text{ m}^{-2}$, effective lifetime of adatoms ($\tau = 10$ s), growth temperature ($T = 1000$ K), binding energies ($\Delta\varepsilon = 500 \text{ meV} \cdot \text{nm}^{-2}$, $\varepsilon_1 = 20\Delta\varepsilon$, $\varepsilon_2 = 2\varepsilon_1 + \Delta\varepsilon$), structural parameter ($\eta = 2\sqrt{3}$ for an equilateral triangle), and edge energy ($\gamma_1 = \gamma_2 = 10 \text{ eV} \cdot \text{nm}^{-1}$). Up to now, the unknown parameters in our kMC model are the edge length of nucleus (L_0), initial edge lengths of layer 1 and layer 2 (L_1 and L_2), energy barrier of kink nucleation (E_{K-N}) and system parameter (k_F).

Xue *et al.*⁴⁴ studied the initial nucleation of Mo_xS_y clusters on the Au(111) surface by using first-principles calculations, and reported that the 2D three-atom-thick layer structures could be stabilized only after the number of Mo atoms exceeded 12. Since the edge length of MoS₂ flake is ~2 nm when the number of Mo atoms is 12, in our kMC simulation, the value of L_0 is set to be 2 nm. In Ye *et al.*'s³⁷ study, the initial edge length of layer 2 was fixed to be 50 nm and layer 1 was changed from 80 to 130 nm (*cf.* Fig. 2d). To calibrate our kMC Model based on Ye *et al.*'s analytic thermodynamic criterion³⁷, the initial edge length of layer 2 in our kMC model was also set to be 50 nm and layer 1 was varied from 80 to 130 nm (*cf.* Fig. 2a to 2c).

As above analyses, the growth occurs at layer 1 or layer 2 is governed by the adatom concentration difference ($C_0 - C_1$ versus $C_1 - C_2$) and energy barrier of kink nucleation (E_{K-N}), which can be described by Eq. 1 in our kMC model. When the above energetic data (binding energy, edge energy, *etc.*) and structure parameters (edge lengths of nucleus, layer 1 and layer 2) are chosen, the growths of layer 1 and layer 2 are determined by the parameter (k_F) and the energy barrier (E_{K-N}). With these in hands, we carried out a series of kMC simulations by tuning the values of k_F and E_{K-N} to compare the size evolutions in our simulations with those from Ye *et al.*'s calculations³⁷.

The results show that when the value of k_F is 0.155 and the value of E_{K-N} is 1.7 eV, the domain evolutions of layer 2 (*cf.* Fig. 2b) with different initial sizes of layer 1 ($L_1 = 80, 90, 100, 110$,

Fig. 2 Size evolution of layer 2 (L_2) with different initial sizes of layer 1 ($L_1 = 80$ nm, 90 nm, 100 nm, 110 nm, 120 nm and 130 nm) when (a) $k_F = 0.145$, (b) $k_F = 0.155$, and (c) $k_F = 0.165$. (d) Size evolution of layer 2 with different initial sizes of layer 1 in Ye *et al.*'s³⁷ calculations based on analytic thermodynamic criterion. Copyright from Ref. 37.

120, 130 nm) match well with those in Ye *et al.*'s calculations³⁷ (cf. Fig. 2d). This signifies that our kMC model with this set of parameters is capable to reproduce the growth of bilayer MoS₂. When the initial edge length of layer 1 is 80 to 100 nm, the growth of layer 2 is permitted and its domain continuously increases from 50 to 80 nm. When the initial edge length of layer 1 is from 110 to 130 nm, however, the growth of layer 2 is prohibited after initial growth. This indicates that the growth rate of layer 2 strongly depends on the size of layer 1 (L_1) for a given size of layer 2 (L_2). The growth of layer 2 monotonically decreases with increasing the size of layer 1 (L_1), and may even become prohibited at a maximum value of L_1 .

In our kMC simulations, the growth of layer 2 is determined by the competition between the adatom concentration difference of layer 1 and layer 2 ($C_0 - C_1$ versus $C_1 - C_2$). When the value of k_F decreases to 0.145, the adatom concentration difference of layer 1 ($C_0 - C_1$) is reduced because the value of C_0 decreases (cf. Eq. 4). Therefore, the adatom concentration difference of layer 2 ($C_1 - C_2$) is relatively superior to that of layer 1 ($C_0 - C_1$), leading to the acceleration on the growth of layer 2. Layer 2 continuously grows when the initial edge length of layer 1 is 80 to 130 nm (cf. Fig. 2a). When the value of k_F increases to 0.165, the adatom concentration gradient of layer 1 is increased because the value of C_0 increases (cf. Eq. 4). In this case, the adatom concentration difference of layer 2 ($C_1 - C_2$) is relatively inferior to that of layer 1 ($C_0 - C_1$), resulting in the prohibition of the growth of layer 2. The growth of layer 2 is prohibited when the initial edge length of layer 1 is from 90 to 130 nm (cf. Fig. 2c).

Clearly, the growth competition between layer 1 and layer 2 is

determined by the parameter (k_F), not the energy barrier of kink nucleation (E_{K-N}). The value of E_{K-N} only changes the overall time line, and thus does not affect the conclusion on whether the growth occurs at layer 1 or layer 2. The overall growth time increased with increasing the value of E_{K-N} . In our kMC simulations, the time line when E_{K-N} is 1.7 eV (cf. Fig. 2b) agrees well with that of Ye *et al.*'s calculations³⁷ (cf. Fig. 2d). Therefore, in the following simulations, the value of E_{K-N} is fixed at 1.7 eV and the value of k_F is set to 0.155 when the adatom flux is 1.0×10^{-3} .

3.2 Morphology evolution of bilayer MoS₂ in growth process

In Section 3.1, the size evolutions of layer 2 (L_2) with different initial sizes of layer 1 ($L_1 = 80$ nm, 90 nm, 100 nm, 110 nm, 120 nm and 130 nm) were analyzed and calibrated by Ye *et al.*'s calculations³⁷. As a result, our kMC model with this set of parameters is capable to reproduce the growth of bilayer MoS₂. In this section, more detailed analyses on the morphology evolutions of both layer 1 and layer 2 were carried out. The morphology evolutions of the bilayer MoS₂, when the initial size of layer 1 is 80 nm and 130 nm, are shown in Fig. 3a, b, separately. In the whole growth processes of bilayer MoS₂, the morphologies of layer 1 and layer 2 maintain triangular shapes with compact edges, which is consistent with the kink-nucleation-propagation mechanism in our kMC model. The evolutions on the sizes of the triangles marked in Fig. 3a, b indicate the effect of the initial sizes on the growth of bilayer MoS₂.

Fig. 3a shows that layer 1 grows dramatically from 80 to 259 nm with increasing the time from 0 to 2.4 s. Together with the

Fig. 3 Size and morphology evolutions of bilayer MoS₂ growth processes when the initial size of layer 2 is 50 nm and that of layer 1 is (a) 80 nm and (b) 130 nm.

Orange and purple domains represent layer 1 and layer 2, respectively. Color online.

growth of layer 1, layer 2 continuously increases from 50 nm to 80 nm, which indicates that the growth of layer 2 is permitted. This is corresponding to the experimental fabrication of bilayer MoS₂. When the initial size of layer 1 is 130 nm, however, it exhibits an opposite trend for layer 2. When layer 1 increases from 130 to 259 nm with the time increasing from 0 to 1.6 s, layer 2 grows only slightly, from 50 to 51 nm initially from 0 to 0.4 s and then ceased to grow after 0.4 s. This is corresponding to the experimental synthesis of monolayer MoS₂.

3.3 Permitted or prohibited growth affected by growth temperature and adatom flux

For the CVD synthesis method, subtle changes in the growth conditions may cause a huge difference in the growth of MoS₂ domain. To verify the robustness of our kMC model, more simulations with varying growth temperatures and adatom fluxes were carried out. The size evolutions of layer 2 at different growth temperatures (950, 975, 1000, 1025 and 1050 K) with initial layer 1 of 100 nm are shown in Fig. 4a. The results indicate that an increase in growth temperature promotes the growth of layer 2. The growth of layer 2 is permitted when the growth temperature is high (from 1000 to 1050 K), while the growth of layer 2 is prohibited when the growth temperature is low (from 950 to 975 K). These simulation results match well with Ye *et al.*'s experimental observations³⁷, where only monolayer MoS₂ was synthesized at the growth temperature of 973 K (*cf.* Fig. 4c); second layer of MoS₂ was formed at some places on top of the first layer when the growth temperature increased to 1023 K; and a complete bilayer MoS₂ was fabricated when the growth temperature further increased to 1073 K.

Experimental results³⁷ shown in Fig. 4d indicate that the adatom flux has larger influence on the adatom concentration gradient of layer 1 than that of layer 2. With decreasing the adatom flux, the adatom concentration gradient of layer 1

decreases more dramatically than that of layer 2. Therefore, in our simulations, the value of k_F is tuned to simulate the variation of the relative dominance between the adatom concentration gradient of layer 1 and that of layer 2 with the adatom flux. In the following simulations, the adatom flux F decreases from 1.8×10^{-3} to 0.6×10^{-3} , and the value of k_F is assumed to linearly decrease with decreasing the flux F ($k_F = 0.145 + k \times F$, $k = 10$). The size evolutions of layer 2 at different adatom fluxes (0.6×10^{-3} , 1.0×10^{-3} , 1.4×10^{-3} and 1.8×10^{-3}) when the initial size of layer 1 is 100 nm are shown in Fig. 4b. The simulation results indicate that the decrease of the adatom flux accelerates the growth of layer 2. The growth of layer 2 is prohibited when the adatom flux is high (1.4×10^{-3} to 1.8×10^{-3}), while the growth of layer 2 is permitted when the adatom flux is low (0.6×10^{-3} to 1.0×10^{-3}). These simulation results also match well with Ye *et al.*'s experimental observations³⁷. They discovered that at the Ar gas flow rate of 150 standard cubic centimeter per minute (sccm), only monolayer MoS₂ was synthesized (*cf.* Fig. 4d). When the Ar gas flow rate decreased to 70 sccm, however, layer 2 was formed at some positions on top of layer 1. When the Ar flow rate further decreased to 20 sccm, a complete bilayer MoS₂ was fabricated. These comparisons between our simulation results and Ye *et al.*'s experiments³⁷ further verify that our kMC model is capable to reproduce the CVD growth of monolayer and bilayer MoS₂.

3.4 Phase diagram on permitted or prohibited growth of bilayer MoS₂

To further provide guideline to the experimental synthesis of MoS₂ with desired number of layers, a phase diagram with varying growth temperatures and adatom fluxes is produced in Fig. 5. The red symbol "x" denotes the prohibited growth of layer 2 at the corresponding growth temperature and adatom flux, while the green symbol "o" denotes the permitted growth

Fig. 4 Size evolution of layer 2 at (a) different growth temperatures (950, 975, 1000, 1025 and 1050 K) and (b) different adatom fluxes (0.6×10^{-3} , 1.0×10^{-3} , 1.4×10^{-3} and 1.8×10^{-3}). Experimental observations of MoS₂ layers at (c) different growth temperatures (973, 1023 and 1073 K) and (d) different flow rates of Ar gas (150, 70 and 20 sccm).

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Fig. 5 Phase diagram on permitted or prohibited growth of bilayer MoS₂ with varying growth temperature (950, 975, 1000, 1025 and 1050 K) and adatom flux (0.2×10^{-3} , 0.6×10^{-3} , 1.0×10^{-3} , 1.4×10^{-3} and 1.8×10^{-3}).

of layer 2 at the corresponding experimental condition. For example, at the growth temperature of 950 K, MoS₂ always grows as monolayer. When the growth temperature increases to 1000 K, either monolayer or bilayer MoS₂ can be synthesized by

controlling the adatom flux (monolayer: 1.4×10^{-3} to 1.8×10^{-3} , bilayer: 0.2×10^{-3} to 1.0×10^{-3}). If the growth temperature is even higher (1025 or 1050 K), MoS₂ always grows in bilayer form without the need to adjust the adatom flux.

To unveil the underlying mechanism that the growth of bilayer MoS₂ is promoted by the increase of growth temperature or the decrease of adatom flux, variations of the adatom concentrations C_1 and C_2 with time at different growth temperatures (975 and 1000 K) and different adatom fluxes (1.0×10^{-3} and 0.6×10^{-3}) were further analyzed and plotted in Fig. 6. Fig. 6a indicates that the adatom concentration C_1 is larger than C_2 initially at both 975 K and 1000 K, promoting the growth of bilayer MoS₂. Then, both the adatom concentration C_1 and C_2 decreased as the bilayer MoS₂ grew. The difference between the adatom concentration C_1 (blue rhombus) and C_2 (blue triangle) decreased drastically to zero at the growth temperature of 975 K, prohibiting the growth of bilayer MoS₂. When the temperature increased to 1000 K, however, the difference between the adatom concentration C_1 (red rhombus) and C_2 (red triangle) maintained constant after 1 s, permitting the growth of bilayer MoS₂. Hence, the increase of

Fig. 6 Variations of adatom concentrations C_1 and C_2 with time (a) when the growth temperature is 975 K and 1000 K and the adatom flux is 1.0×10^{-3} , and (b) when the growth temperatures is 975 K and the adatom flux is 0.6×10^{-3} . Color online.

temperature enables the adatom concentration C_2 to decrease accordingly with the adatom concentration C_1 , resulting in a consistent difference in adatom concentration to promote the growth of bilayer MoS₂. This is the underlying mechanism that the growth of bilayer MoS₂ can be promoted by the increase of temperature. Similarly, the decrease of adatom flux from 1.0×10^{-3} (blue curves in Fig. 6a) to 0.6×10^{-3} (blue curve in Fig. 6b) lowers the value of k_F , resulting in the decrease of C_0 . Then, the decrease of C_0 lowers the concentration gradient of layer 1, decelerating the growth of layer 1. Furthermore, the decelerated growth of layer 1 reduces the difference between the adatom concentration C_1 (blue rhombus) and C_2 (blue triangle) to zero, permitting the growth of bilayer MoS₂.

Compared with Ye *et al.*'s research³⁷, our work has the following contributions: We presented a new kinetical Monte Carlo model for the CVD growth of MoS₂ and calibrated the model by using existing thermodynamic models and experimental results. We revealed the underlying mechanism that the growth of bilayer MoS₂ can be promoted by the increase of growth temperature or the decrease of adatom flux. Specifically, the growth temperature enables the adatom concentration C_2 to decrease with the adatom concentration C_1 , resulting in a consistent adatom concentration difference to promote the growth of bilayer MoS₂; while the decrease of adatom flux decelerated the difference between the adatom concentration C_1 and C_2 to zero, permitting the growth of bilayer MoS₂. Importantly, we presented a phase diagram (*cf.* Fig. 5) in the growth temperature and adatom flux space to predict the growth of bilayer MoS₂, which may guide the experimental CVD fabrication of mono- and bi-layer MoS₂.

4 Conclusions

In this work, we developed a kMC model to study the CVD growth kinetics and underlying mechanisms of mono- and bi-layer MoS₂. First, we formulated and calibrated our kMC model by an analytic thermodynamic criterion³⁷. With the calibrated model, we successfully reproduced the mono- and bi-layer growth of MoS₂ under different growth conditions. We found that the growth rate of layer 2 strongly depends on the size of layer 1 and monotonically decreases with increasing the size of layer 1, and may even become prohibited at a maximum size of layer 1. Then, the size and morphology evolutions of the bilayer MoS₂ growth processes were analyzed. In the whole growth processes of bilayer MoS₂, the morphologies of layer 1 and layer 2 maintained triangular shapes with compact edges. Furthermore, the permitted or prohibited growth of bilayer MoS₂ in terms of growth temperature and adatom flux was analyzed. The increase of the growth temperature or the decrease of the adatom flux promotes the growth of layer 2, which agrees well with experimental observation³⁷. Lastly, a phase diagram on permitted or prohibited growth of bilayer MoS₂ in terms of growth temperature and adatom flux was predicted. The underlying mechanism that the growth of bilayer MoS₂ can be

promoted by the increase of growth temperature or the decrease of adatom flux was further revealed. Hence, our study here not only unveils the conditions of the mono- and bi-layer growth of MoS₂, but also provides guidelines for the controllable growth of MoS₂ with desired number of layers.

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