Role of Buffer Layer and Building Unit in the Monolayer CrI₃ Growth: A First-Principles Perspective

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ABSTRACT: CrI₃, a two-dimensional layered material, has recently attracted a lot of research interest due to its exotic magnetic property. However, the synthesis of a CrI₃ monolayer (ML) by vapor-phase deposition has not been achieved by current experimental endeavors, which require a better understanding of the vapor-phase growth mechanism involved. In this study, we theoretically simulate the growth of the CrI₃ ML on the Si(111) surface by using a first-principles calculation. Our key finding is that an iodine buffer layer on the Si surface is crucial to the formation of the CrI₃ ML by stabilizing the precursor and also reacting with the precursor. Moreover, our simulation reveals that the CrI₂ cluster as the growth building unit, which can be formed by controlling the chemical potential of the I source, is preferred for the formation of CrI₃ ML. We think that our work will provide insightful guidance for the experimental synthesis of CrI₃ ML in the future.

Layered CrI₃, one of the most studied two-dimensional (2D) magnetic materials, has been experimentally demonstrated to be ferromagnetic (FM) in the intralayer and antiferromagnetic (AFM) in the interlayer.¹ This exotic magnetic property confers great potential to CrI₃ layers for the use as magnetoresistive memories² and magnetic tunnel junctions^{3,4} in spintronic devices. Consequently, it is of paramount importance to achieve the mass production of CrI₃ layers with consistent and controllable quality. Currently, the most frequently adopted method of producing CrI₃ layers is mechanical exfoliation from its bulk.^{1,5} However, the high throughput of CrI₃ ML, especially with size up to the micrometer scale, is challenging due to its low chemical stability toward water molecules under ambient conditions. Vapor-phase deposition (VPD) is a widely utilized method in industry that allows for precise control of the atmosphere in the reaction chamber.⁶ For example, VPD has been demonstrated to be an efficient strategy for producing 2D materials with large sizes, such as graphene of centimeter size⁷ and the MoSe₂ monolayer of millimeter size.⁸ However, the production of CrI₃ ML through the VPD method seems to be a daunting task. We think that an understanding of its growth mechanism is lacking, which is a prerequisite for achieving the successful production of CrI₃ ML via VPD.

The first-principles calculation based on density functional theory (DFT) is a powerful theoretical tool for understanding the growth behaviors of various 2D materials including graphene, silicene, borophene, and phosphorene on various substrates.^{9–19} The building unit is considered to be a determining factor in graphene growth on metal substrates in the chemical vapor deposition process.^{20–23} For example, the carbon dimer as the building unit is reported to be an

important factor in graphene growth on the Cu(111) surface due to the spontaneous formation and low migration energy of its unit.²⁰ A five-atom carbon cluster is suggested to be the attachment unit that is responsible for the nonlinear growth of graphene on the Ru(0001) substrate.²¹ Chen et al. find that the building units can be carbon dimers, carbon rectangles, and zigzag-like and armchair-like chains at different growth stages of graphene, whose saturation on the Cu(111) surface results in defective graphene.²² The building unit directly affects the subsequent nucleation and crystallization quality of a material. Hence, the ascertaining of building unit is of great importance in understanding the growth mechanism of 2D materials. Moreover, a buffer layer on the substrate plays an important role in 2D material growth.^{24–28} In the growth of a silicon layer on the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag template at 200 °C, the Ag buffer layer helps to realize the formation of a multilayer silicene rather than a diamondlike silicon layer.²⁸ A germanium buffer layer is necessary to make the $\sqrt{7} \times \sqrt{7}$ germanene supercell match the $4 \times 2\sqrt{3}$ Au(111) supercell during growth.²⁶ Overall, the introduction of a proper buffer layer onto the substrate could improve the quality of the as-grown 2D materials.

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In this letter, we describe a first-principles calculation prediction of the growth of CrI₃ ML on the Si(111) substrate with an iodine buffer layer (Figure 1a). We investigated the

Figure 1. (a) Schematic diagram of CrI₃ ML growth by the VPD method. (b) Gibbs free energies of CrI_x ($x = 1-6$) clusters versus $\Delta\mu_I$. Insets exhibit the atomic configurations of CrI_x clusters.

formation of the iodine buffer layer, the building unit for CrI₃ growth, the aggregation of CrI₂/CrI₄ clusters, and the atomic structure of the obtained CrI₃ edge. The key finding of our study is the dominant role of the iodine buffer layer and the CrI₂ cluster as the building unit in the synthesis of single-layer CrI₃. We hope that our theoretical results could provide the scientific basis for further experimental efforts toward the production of CrI₃ ML and even other 2D binary materials via VPD methods.

All calculations were performed with the Vienna ab initio simulation package (VASP)²⁹ using the generalized gradient approximation (GGA) and projector-augmented wave (PAW)³⁰ method. The cutoff energy was set to 450 eV. The convergence criteria of energy and force for structure optimization are 10^{-4} eV and 0.02 eV/Å, respectively. The length of vacuum in the direction perpendicular to the substrate is larger than 11 Å to eliminate the interaction between periodic images. We use GaAs(111), Ir(111), Cu(111), Si(111), SiC(111), GaSe(0001), and SnSe₂(0001) as model substrates. Each substrate consists of three atomic or van der Waals layers, as shown in Figure S1 of the Supporting Information (SI). To describe the interaction between CrI₃ layer and the above substrates, we employ the nonlocal correlation functional optB86b.³¹ This method gives a closer calculated lattice parameter and bond length of the CrI₃ bulk with respect to the experimental values³² than other methods, such as DFT-D2,³³ DFT-D3,³⁴ original vdW-DF,³⁵ and modified vdW-DF with more accurate exchange functionals optB88-vdW^{36,37} and rPW86 (vdW-DF2).³⁸ The comparison of data is shown in Figure S2 in the SI. The bottoms of SiC, GaAs, and Si substrates are hydrogenated to eliminate the effects of broken bonds. After structure optimization, the bottom atomic layer and H atoms of the substrate are fixed during further calculations. A $\sqrt{3} \times \sqrt{3} \times 1$ Si(111) supercell slab is used in the iodized substrate models with a uniform $6 \times 6 \times 1$ Monkhorst–Pack k mesh. A larger $3\sqrt{3} \times 3\sqrt{3} \times 1$ Si(111) supercell slab model is chosen for the cluster-related calculations with a $2 \times 2 \times 1$ k mesh. Four types of stacking between CrI₃ ML and Si(111) are tested as shown in Figure S3 of the SI. The total energy difference of any two of these structures is found to be less than 0.105 eV per CrI₃ formula unit, and the most stable one (Figure S3a) is used in this work.

Formation and Adsorption of CrI_x on the Si Substrate. The first stage in a typical VPD growth is the formation of precursors (i.e., CrI_x ($x = 1-6$) clusters in this case). The stability of the cluster precursor is evaluated by its Gibbs free energy (ΔG) defined by eq 1

$$\Delta G = E_{\text{tot}}^{\text{cluster}} - E_{\text{Cr}} - N_I \times (E_I + \Delta\mu_I) \quad (1)$$

Figure 2. (a) CrI, (b) CrI₂, (c) CrI₃, and (d) CrI₄ clusters decompose after being adsorbed on the exposed Si surface. The decomposed I atom is highlighted in green. (e) Phase diagram of the iodized Si surface. Insets show top and side views of the I buffer layer.

where $E_{\text{tot}}^{\text{cluster}}$, E_{Cr} , E_{I} are the energies of the cluster, one Cr atom in the Cr bulk, and one I atom in the I_2 molecule, respectively. $\Delta\mu_1$ is the energy difference between the chemical potential of the I source (μ_1) and E_{I} . N_{I} is the atomic number of I. A lower ΔG indicates the easier formation of the CrI_x cluster. As plotted in Figure 1b, CrI_x clusters with $x = 1-4$ are relatively easy to form with different $\Delta\mu_1$ values, while CrI_5 and CrI_6 are relatively difficult to form due to the higher ΔG . Therefore, we consider only the dominant clusters under each $\Delta\mu_1$ in the following investigations (e.g., CrI , CrI_2 , CrI_3 , and CrI_4). The critical transition points of $\Delta\mu_1$ for the formation of CrI_x ($x = 1-4$) clusters are -1.721 , -1.386 , and -1.042 eV, respectively.

The second stage of VPD growth is the adsorption of the formed precursors on substrate. We considered Si(111) surface as the substrate because of the current mature Si-based electronic industry. The lattice mismatch between CrI_3 ML and Si(111) substrates is 4.8%, indicating the growth to be experimentally feasible. Diagrams of the adsorption of CrI_x ($x = 1-4$) clusters on Si substrate are shown in top panels of Figure 2a-d. The bottom panels of Figure 2a-d show that the I atom in CrI_x cluster prefers to dissociate from Cr and then adsorb onto the surface. The total energies of the decomposed clusters are 1.129, 0.201, 0.483, and 1.575 eV lower than those of the adsorbed CrI , CrI_2 , CrI_3 , and CrI_4 clusters, respectively, suggesting an instability of these clusters on the exposed Si substrate. A larger cluster, namely, Cr_2I_6 , was also examined, and a similar event was predicted, indicating a decomposition of Cr_2I_6 on the Si substrate with an energy reduction of 2.126 eV (not shown). We also notice that the ion relaxation calculation predicts that an I_2 molecule on the exposed Si surface could decompose directly into two I atoms with a formation energy of -2.772 eV/I, indicating the strong oxidizing ability of I_2 . We postulate the decomposition of precursors to be due to the oxidation of I atoms and the reduction of Si atoms on the surface. The decomposition of these clusters impedes the formation of building units and also the nucleation of CrI_3 . Hence, the growth mechanism of CrI_3 ML on the exposed Si surface is more complicated than the growth mechanisms of other single-element 2D materials.⁹⁻¹²

Formation of an Iodine Buffer Layer. During the growth of 2D materials, a thin transition region known as a buffer layer is commonly used to cover the substrate.^{25-27,39} The role of the buffer layer is crucial because it could modify the chemical activity of the substrate and affect the lattice mismatch between 2D materials and the substrate.^{25-27,39} Here, we anticipate that a buffer layer on the Si surface would solve the issue of CrI_x decomposition and facilitate the subsequent growth of the CrI_3 ML.

In a VPD process, I_2 molecules sublime easily in the initial stage to generate I_2 vapor that is transported onto the substrate before the formation of CrI_x species. The exposed Si surface could thus be easily iodized before the adsorption of CrI_x clusters. The saturation of the broken Si bonds on the surface by iodine atoms weakens the reduction ability of the Si substrate and forms a layer that could be referred as the I buffer layer (insets in Figure 2e). The corresponding experimental conditions under which this I buffer layer forms could be determined by a thermodynamic evaluation through eq 2

$$\Delta G^{\text{surf}} = \frac{1}{A} [E_{\text{tot}} - E_{\text{sub}} - N_{\text{I}} \times \mu_1(T, P_{\text{I}_2})] \quad (2)$$

where ΔG^{surf} is the surface Gibbs free energy of the iodized Si substrate. E_{tot} and E_{sub} are the energies of the whole structure and the Si substrate, respectively. A , T , and P_{I_2} are the surface area of the supercell and the temperature and pressure of I_2 vapor, respectively. $\mu_1(T, P_{\text{I}_2})$ is expressed in eq 3

$$\mu_1(T, P_{\text{I}_2}) = \frac{1}{2} [E_{\text{I}_2} + \Delta\mu_1(T, P_{\text{I}_2})] = \frac{1}{2} \left[E_{\text{I}_2} + H^0(T) - H^0(0) - TS^0(T) + k_{\text{B}} T \ln \left(\frac{P_{\text{I}_2}}{P^0} \right) \right] \quad (3)$$

where E_{I_2} is the energy of I_2 vapor. k_{B} is the Boltzmann's constant. $H^0(T)$, $H^0(0)$, and $S^0(T)$ of gaseous I_2 can be obtained from the JANAF thermodynamic tables.⁴⁰ Note that I_2 vapor is the source of iodine forming the I buffer layer in the VPD process. Hence, the energy and chemical potential of the I_2 molecule are used in the current work as a reference to investigate the stability of the I buffer layer. On the basis of eq 2 and previous studies,^{41,42} one could plot the 2D (T , P_{I_2}) phase diagram of the iodized Si substrate versus the degree of iodization, which is defined by the multiple of the I atom number in the I buffer layer in Figure 2e. For example, 0.3 ML means that the number of covered I atoms is 0.3 times the number of I atoms in the I buffer layer. Clearly, the iodization degree of the Si surface is reduced with the increase in T and the reduction in P_{I_2} . The diagonally shaded area represents the conditions suitable for the formation of the I buffer layer (labeled by 1 ML), most of which (T and P_{I_2}) are experimentally achievable. Moreover, the large area of the I buffer layer implies a broad controllable range of experimental conditions. We also considered the iodized reconstructed Si(111)-2 $\times$ 1 surface. Its energy level is calculated to be 0.591 eV/supercell higher than that of the iodized pristine Si surface. Hence, the substrate model we used is receivable, and its stability is further confirmed by the molecular dynamics simulations at 825 K for 10 ps as shown in Figure S4 of the SI.

Building Unit for CrI_3 ML Growth. Though we identified possible CrI_x clusters, it remains unknown which is the building unit for the formation of CrI_3 ML. We then proceeded to examine the adsorption of CrI_x clusters on an Si surface containing an I buffer layer. The total energies of adsorbed CrI_x clusters are 1.255, 1.870, 1.325, and 0.857 eV lower than the corresponding decomposed clusters with $x = 1-4$, indicating the structural stability of the adsorbed CrI_x clusters. Consequently, the introduction of an I buffer layer on the exposed Si surface could effectively prevent the decomposition of CrI_x clusters. Furthermore, the adsorption energy (E_{ads}) is calculated to evaluate the interaction between the CrI_x cluster and the iodized Si surface. The equations for the calculations of E_{ads} and other adsorption or formation energies mentioned below are all presented in SI. The values of E_{ads} for CrI_x ($x = 1-4$) clusters are calculated to be 1.916, 1.960, 1.785, and 0.918 eV, respectively. The similar E_{ads} values of CrI , CrI_2 , and CrI_3 clusters are attributed to the bonding between the Cr atom in the CrI_x cluster and the I atom in the buffer layer, as shown in Figure 3a. With respect to the CrI_4 cluster, the weak van der Waals interaction between the CrI_4 cluster and the substrate results in a relative low E_{ads} value. Nevertheless, this E_{ads} value of 0.918 eV is large enough to stabilize the CrI_4 cluster on an iodized Si substrate.¹⁴

Figure 3. (a) Side views of atomic configurations of CrI_x ($x = 1-4$) clusters adsorbed on the iodized Si substrate. Diffusion energy barriers of (b) CrI, (c) CrI₂, (d) CrI₃, and (e) CrI₄ clusters on the iodized Si substrate. The highlighted I atom in green is taken as a positional reference.

We next evaluated the diffusion kinetics of CrI_x on the iodized Si surface. Figure 3b–e exhibit the diffusion energy barriers (E_{barr}) of CrI_x calculated by the climbing nudged elastic band (CI-NEB) method.⁴³ The E_{barr} values of CrI_x clusters are 0.563, 0.187, 0.721, and 0.026 eV for $x = 1, 2, 3$, and 4, respectively. The low E_{barr} values of CrI₂ and CrI₄ suggest their possible diffusion on the iodized Si surface. The diffusion coefficient (D) of the cluster on the substrate could be calculated via eq 4⁴⁴

$$D = a^2 \nu e^{-E_{\text{barr}}/k_B T} \quad (4)$$

where a and ν are the in-plane lattice parameter and vibrational frequency, respectively. At a typical experimental temperature of 550 °C⁵ for CrI₃ crystal growth, the diffusion coefficient ratio among CrI, CrI₂, CrI₃, and CrI₄ clusters is determined to be $5 \times 10^{-3}:1:5 \times 10^{-4}:10$, suggesting the much higher diffusion rates of CrI₂ and CrI₄ clusters compared to those of CrI and CrI₃ clusters. On the basis of the previous results, we postulate that on the iodized Si substrate, CrI₂ and CrI₄

clusters should be the building units for the subsequent growth of the CrI₃ ML.

Initial Growth of CrI₃ ML on the Iodine Buffer Layer. Given the crucial role of the I buffer layer and CrI₂/CrI₄ clusters as building units, we further investigated the subsequent growth procedure of the CrI₃ ML. Previous studies have established for 2D elemental monolayers that the growth is normally achieved through the aggregation of building units to form 2D networks on the substrate.⁴⁵ Consequently, we plot the formation energies (E_{form}) of (CrI_{2/4})_m aggregates versus m but with different aggregation patterns in Figure 4. Several other possible configurations of the aggregates are also considered and given in Figure S5 of the SI but with higher energies. In the case of CrI₂ as the building unit (Figure 4a), when $m \geq 3$, the aggregates of (CrI₂)_m could be formed as two different patterns: one is the sharing of two I atoms to form the CrI₃ domain (orange line), and the other is the sharing of three I atoms to form the CrI₂ domain (blue line). The two pink stars represent the E_{form} value of dispersed (CrI₂)_m clusters for $m = 3$ and 4, clearly indicating that the formation of (CrI₂)_m aggregates on the iodized Si surface is thermodynamically favored.

It is informative to compare the difference between the two aggregation patterns. Figure 4a shows that in the initial growth stage for $3 \leq m \leq 5$ the CrI₂ domain is more favored than the CrI₃ domain. With the increase in m to 6 and 7, the CrI₃ domain becomes more favorable, probably due to less structural strain. The average magnetic moment on the Cr atom of each domain is in the range of 3.351–3.460 μ_B/Cr . Moreover, our calculated results in Figure S6 of SI show that the lattice mismatch between the CrI₂ ML and the Si(111) substrate is 6.2%, which is greater than that (4.8%) between the CrI₃ ML and the substrate. Another calculation reveals that the formation energy of the CrI₃ ML (−0.247 eV/atom) is much smaller than that of the CrI₂ ML (0.231 eV/atom). The negative value suggests that the formation of the CrI₃ ML on the iodized Si substrate is exothermic. These results imply that small CrI₂ domains could be observed in the initial growth stage in an experiment, but a large CrI₃ domain or ML should dominate in the subsequent growth on the iodized Si substrate. Note that, similar to the free-standing case,⁴⁶ the compressed CrI₃ ML on the Si(111) substrate turns to be AFM with an energy that is 36 meV lower than that of the FM CrI₃ ML. To obtain the FM CrI₃ ML, one can use a substrate with a smaller lattice mismatch to the CrI₃ ML or apply an extra tensile stress to the prepared CrI₃ ML on the Si substrate.

We continued to consider CrI₄ as a building unit for the growth of CrI₃ ML. Figure 4b shows that there are also two aggregation patterns for CrI₄ clusters, very similar to the situation for CrI₂ with the same transition point at $m = 6$ but with an opposite evolution trend in E_{form} for the CrI₂ domain. For CrI₄ as the building unit, E_{form} of the CrI₂ domain decreases with m to a minimum at $m = 6$ and then increases with the further increase in m . The average magnetic moment on the Cr atom of each domain varies from 2.833 to 2.998 μ_B/Cr . The overall E_{form} values of (CrI₄)_m aggregates are larger than those of the corresponding (CrI₂)_m aggregates, presumably because of the weak van der Waals interaction between (CrI₄)_m and the substrate instead of the strong covalent bonding between (CrI₂)_m and the substrate (Figure 3a). Interestingly, the two different interactions lead to different chemical environments for the final formed CrI₃ ML provided by the substrate. For CrI₂ as the building unit, the CrI₃ ML is

Figure 4. Two aggregation evolutions for (a) CrI₂ and (b) CrI₄ building units versus the cluster number (m) on the iodized Si surface. The blue (orange) line represents E_{form} of the CrI₂ (CrI₃) domain. The pink stars represent E_{form} of the dispersed clusters with $m = 3$ and 4. The substrate is not shown to emphasize the CrI₂/CrI₃ domain. The top views of ZZ and AC CrI₃ ribbons with widths of (c) 18 and (d) 24 Å. (e) E_{ads} of the first and second CrI₃ layers on different substrates.

directly supported by the exposed Si surface because the I buffer layer becomes part of the CrI₃ ML. However, for CrI₄ as the building unit, the CrI₃ ML is physically adsorbed on the iodized Si surface.

Furthermore, the subsequent growth of a second CrI₃ layer in both situations was considered (i.e., without and with the I layer between CrI₃ and the Si substrate). We calculated the adsorption energies of the first (E_{ads}^1) and second (E_{ads}^2) CrI₃ layers on exposed Si substrates to be 0.203 and 0.090 eV/atom and those on the iodized Si surface to be 0.027 and 0.137 eV/atom. A larger E_{ads} value suggests a stronger interaction between the CrI₃ layer and the substrate. Consequently, the CrI₃ ML prefers to sit on the exposed Si surface compared to the iodized surface. The further adsorption of a second CrI₃ layer on the exposed Si surface is unfavored due to a dramatic energy reduction of 0.113 eV/atom, suggesting that CrI₃ ML is preferred on the exposed Si surface. With respect to the iodized Si substrate, E_{ads}^2 is much higher than E_{ads}^1 , indicating the favored growth of the CrI₃ bilayer. These results suggest that the growth mechanism involving CrI₂ as a building unit consumed the I buffer layer, leaving the direct contact of CrI₃ with the exposed Si surface that facilitates the formation of the CrI₃ ML.

With further growth of the large CrI₃ domain, various edges emerge due to the edge formation energy and growth rate. It is important to examine the final edge structure of the formed CrI₃ ML supported by the Si substrate. We consider two

possible ribbons with different edges shown in Figure 4c,d (i.e. zigzag (ZZ) or armchair (AC) edges) which are mostly seen in hexagonal structures. The edge formation energy (E_{edge}) is defined by eq 5

$$E_{\text{edge}} = \frac{E_{\text{tot}} - E_{\text{sub}}^{\text{iodized}} - N_{\text{Cr}} \times E_{\text{CrI}_{1.5}} - \Delta N_{\text{I}}^{\text{top}} \times E_{\text{I}}}{L} \quad (5)$$

where $E_{\text{CrI}_{1.5}} = (E_{\text{tot}} - E_{\text{sub}}^{\text{iodized}}) / N_{\text{Cr}}$ is the energy per CrI_{1.5} formula unit for the model having a CrI₃ ML on an exposed Si(111) substrate, which can be also regarded as a CrI_{1.5} ML on an iodized Si(111) surface. $\Delta N_{\text{I}}^{\text{top}}$ is the difference between the atomic number of top I atoms in the ribbon and $1.5N_{\text{Cr}}$. L is the unit length of the simulated superstructure along the CrI₃ ribbon. Our calculated results show that for the same ribbon width of ca. 18 Å, E_{edge} of the ZZ edge is −0.254 eV/Å, while E_{edge} of the AC edge is −0.266 eV/Å. With respect to the ribbon width of ca. 24 Å, the E_{edge} values are −0.243 and −0.251 eV/Å for ZZ and AC, respectively. The lower value for E_{edge} of AC in both situations suggests that the AC edge is thermodynamically more stable than the ZZ edge, which is analogous to the free CrI₃ nanoribbons.⁴⁷ We thus conclude that the AC edge should be the dominant type in the CrI₃ ML formed on the Si(111) substrate.

Extension of the Growth Mechanism. In the end, we extended the above growth mechanism of CrI₃ ML to other substrates, including SiC, GaAs, Ir, Cu, GaSe, and SnSe₂, by evaluating

their values of E_{ads}^1 and E_{ads}^2 during growth. Figure 4e shows that for van der Waals substrates such as GaSe and SnSe₂, E_{ads}^1 values are much lower than those for the Si substrate, suggesting a low chemical activity and a weak interaction with CrI₃. Moreover, E_{ads}^1 is slightly lower than E_{ads}^2 for each substrate and unfavorable to the formation of the CrI₃ ML. However, with respect to SiC, GaAs, Ir, and Cu substrates, E_{ads}^1 values are higher than those for the Si substrate, suggesting a high chemical activity and a strong interaction with CrI₃. Meanwhile, E_{ads}^2 is much lower than E_{ads}^1 for each substrate, implying the favorable formation of the CrI₃ ML. Here we conclude that a chemically inert substrate is favorable to the synthesis of multilayer CrI₃, while a chemically active substrate could be easily iodized and is favorable to the formation of the CrI₃ ML with CrI₂ as a building unit growth mechanism.

In conclusion, we described a first-principles calculation study to predict the growth of CrI₃ ML on the Si(111) surface with an I buffer layer. Interestingly, we identified the key role of the I buffer layer not only to stabilize the precursors but also to participate in the formation of CrI₃ ML by forming covalent bonds. We also revealed that it is crucial to the CrI₂ cluster, whose formation is controlled by the chemical potential of the I source, to be the building unit for the formation of the CrI₃ ML. We then extended our growth mechanism of CrI₃ ML to other substrates and expect our study to provide a theoretical basis for the future experimental synthesis of the CrI₃ ML and even provide insights for the preparation of other binary 2D materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02717>.

Atomic structures of CrI₃ MLs on various substrates, lattice and bond length comparison between calculated and experimental data, structures of four types of stacking of the CrI₃ ML on the Si substrate, structures of the iodized Si substrate before and after molecular dynamics simulations, structures of (CrI₂)_m aggregates on the iodized Si surface, the CrI₂ ML on the Si surface, and equations for the calculation of adsorption and formation energies mentioned in the main text (PDF)

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Notes

The authors declare no competing financial interest.

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