Single-layer CrI₃ grown by molecular beam epitaxy

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Abstract

Single- and few-layer chromium triiodide (CrI₃), which has been intensively investigated as a promising platform for two-dimensional magnetism, is usually prepared by the mechanical exfoliation. Here, we report direct growth of single-layer CrI₃ using molecular beam epitaxy in ultrahigh vacuum. Scanning tunneling microscopy (STM), together with density functional theory (DFT) calculation, revealed that the iodine trimers, each of which consists of three I atoms surrounding a three-fold Cr honeycomb center, are the basic units of the topmost I layer. Different superstructures of single-layer CrI₃ with periodicity around 2–4 nm were obtained on Au(1 1 1), while only the 1 × 1 structure was observed on the graphite substrate. At an elevated temperature of 423 K, single-layer CrI₃ began to decompose and transformed into single-layer chromium diiodide. Our bias-dependent STM images suggest that the unoccupied and occupied states are spatial-separately distributed, consistent with the results of our DFT calculation. We also discussed the role of charge distribution in the super-exchange interactions among Cr atoms in single-layer CrI₃.

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1. Introduction

Two-dimensional (2D) magnetic materials had been sought for a long time, since they were believed to be ideal platforms for investigating spin-related emergent phenomena at reduced dimensions and exhibit potential applications in optoelectronics and spintronics [1,2]. Mermin-Wagner theorem says that long-range magnetic order in 2D systems without anisotropy is, however, thermodynamically instable at finite temperatures owing to enhanced thermal fluctuations [3]. By introducing magnetic anisotropy, on the other hand, 2D magnetism may exist in a number of layered van der Waals (vdW) materials, for example, transition metal chalcogenides and halides [4–6]. Among them, single- and bi-layer chromium triiodide (CrI₃) was recently confirmed with long-range magnetic orders [16–21]. As a matured film growth technique, molecular beam epitaxy (MBE) was widely used in fundamental research and industry for preparing high-quality films and heterostructures with atomic-level structural controllability. Scanning tunneling microscopy (STM) was well adopted in in-situ investigating local structural and magnetic properties of MBE-prepared 2D magnetic materials at the atomic level [23,24]. Here, we prepared single-layer CrI₃ on Au(1 1 1) and graphite substrates, respectively, using MBE in ultrahigh vacuum. Surface geometry of epitaxial CrI₃ was revealed with atomic resolution using STM. According to our STM measurements and DFT calculations, we found that the distribution of the unoccupied state is concentrated upon the three-fold Cr

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honeycomb centers, while the occupied states are mainly located around the Cr-Cr bridge sites. In addition, we also successfully prepared single-layer chromium diiodide (CrIₓ) after removing iodine atoms partially from CrI₃ at elevated temperatures.

2. Experimental and calculation details

2.1. Experimental details

All experiments were conducted on a home-built low-temperature STM-MBE system designed by Dr. Kehui Wu, Institute of Physics, Chinese Academy of Sciences. Single-layer CrI₃ and CrI₂ were grown on both Au(1 1 1) and highly oriented pyrolytic graphite (HOPG) (Mateck GmbH) substrates, respectively in UHV with a base pressure of 8 × 10⁻¹⁰ mbar. The Au(1 1 1) surface was cleaned by cycles of sputtering and annealing under UHV condition. HOPG was cleaved in air and immediately transferred into a separate UHV system (Thermo Fisher) for X-ray photoelectron spectroscopy (XPS) measurement with a monochromatic Al Kα X-ray source (1486.6 eV). The sample was inserted into the UHV system designed by Dr. Kehui Wu, Institute of Physics, Chinese Academy of Sciences. Single-layer CrI₃ films with sub-monolayer coverage were prepared by co-deposition of chromium and iodine for 30 min onto the Au(1 1 1) substrate. The temperature of the surface was kept fixed at 425 K. If the Au surface temperature increases to 450 K, we could have CrI₂ films on the Au(1 1 1) substrate. In terms of the HOPG substrate, a two-step procedure was adopted, namely co-deposition of chromium and iodine at room temperature for 40 min followed by annealing to 463 K. A high iodine pressure was maintained during the whole annealing process, in order to suppress its desorption from the HOPG surface. CrI₂ films were grown by co-depositing of chromium and iodine onto the HOPG substrate for 60 min with the substrate temperature being kept at 463 K. Samples were transferred into the analysis chamber for STM measurement. All STM experiments were performed in a constant current mode at 78 K using a chemically etched tungsten tip. The CrI₃/Au(1 1 1) sample with monolayer coverage was transferred into a separate UHV system (Thermo Fisher) for X-ray photoelectron spectroscopy (XPS) measurement with a monochromatic Al Kα X-ray source (1486.6 eV). The sample was exposed in atmosphere for about 2 min during the transfer procedure.

2.2. Calculation details

Our DFT calculations were performed using the generalized gradient approximation and the projector augmented wave method [25] as implemented in the Vienna ab-initio simulation package (VASP) [26]. A uniform 15 × 15 × 1 Monkhorst-Pack k mesh was adopted for integration over the first Brillouin zone. A plane-wave kinetic energy cutoff of 700 eV was used during structural relaxations. A sufficiently large distance of c > 20 Å along the out-of-plane direction of CrI₃ was adopted to eliminate interactions among image layers. Dispersion correction was made at the van der Waals density functional (vdW-DF) level [27–29], with the optB86b functional for the exchange potential, which was proved to be accurate in describing the structural properties of layered materials [30–35]. During structural relaxation, all atoms and the shape of the supercell were allowed to relax until the residual force per atom was less than 0.01 eV/Å. On-site Coulomb interaction to the Cr d orbitals was self-consistently calculated based on a linear-response method [36], which gives U = 3.9 eV and J = 1.1 eV, as adopted in a previous calculation [37].

3. Results and discussion

Fig. 1a shows a large-scale STM image of single-layer CrI₃ on the Au(1 1 1) surface with sub-monolayer coverage. Those CrI₃ islands are initially nucleated at the step edges of Au(1 1 1). Their sizes range from several tens nm to 100 nm in irregular or proximately round shape. At sub-monolayer coverage, the areas without CrI₃ are covered with a layer of iodine. Samples fully covered by the CrI₃ monolayer were also prepared (Fig. S1 online). Our XPS spectra of the monolayer coverage indicate a Cr:1 ratio close to 1:4.4 (Table S1 online), implying the existence of an iodine buffer layer between CrI₃ and Au(1 1 1). The apparent height of the single-layer CrI₃ islands is about 6.8 Å (see inset of Fig. 1a), which is consistent with the thickness of the samples prepared by mechanical exfoliation (7 Å) [7]. In a zoom-in image (Fig. 1b), a hexagonal superstructure appears with a height oscillation about 30 pm, superposing on the periodic atomic structure of CrI₃. Fig. 1c is the Fourier transform image of Fig. 1b, containing three sets of hexagonal patterns. The spots marked by yellow, red and white circles correspond to the approximately closed-packed iodine atoms of the topmost layer, the Bravais lattice of CrI₃ and the superstructure, respectively. The superstructure exhibits a periodicity of 2.93 nm, 4.26 times the CrI₃ lattice constant (6.867 Å) [38] and 18.6° rotated with respect to the CrI₃ lattice. The relationship between the supercell and the primitive CrI₃ lattice can be described as

\[
\begin{pmatrix}
  a_{\text{dot}} \\
  b_{\text{dot}}
\end{pmatrix} = \begin{pmatrix}
  4.83 \\
  1.57
\end{pmatrix} \begin{pmatrix}
  a_{\text{crI3}} \\
  b_{\text{crI3}}
\end{pmatrix}.
\]

In some islands, there is more than one domain of such “dotted” superstructure separated by the domain boundary, as illustrated in Fig. 1d where the domain boundary was marked by the white dashed lines. These two domains (red and blue arrows) are 19° rotated with each other. However, the whole CrI₃ lattice (green arrows) is continuous at the domain boundaries (Fig. S2 online). The atomic-resolution STM images of single-layer CrI₃ were shown in Fig. 1e and f. The bright protrusions exhibit a nearly close-packed hexagonal lattice, corresponding to individual I atoms from the topmost layer. However, they are not uniformly arranged, resulting in an unambiguous feature of the triangle-shaped I trimer, in which three I atoms are slightly aggregated together. The I trimers form a larger hexagonal lattice with a periodicity of 6.95 Å, which is consistent with the lattice constant of the CrI₃ layer [11,38]. Given the three-fold symmetry and lattice constant, one can infer that these bright dots are I atoms and three of them in each trimer surround a honeycomb center of the Cr layer underneath, as illustrated by the structural model superposed on the STM image in Fig. 1f.

Besides the dominant dotted phase described above, minor superstructures of single-layer CrI₃ were also observed on Au(1 1 1). As shown in Fig. 2a, three different phases coexist: the dotted phase, the striped phase and the pristine phase. Note that all of them appear with the feature of I trimers. Fig. 2b and c show zoomed STM images of the pristine and striped phases, respectively. No superstructure exists in the pristine CrI₃ layer, while a rectangle supercell (1.83 nm × 1.88 nm) with the basic vectors written as

\[
\begin{pmatrix}
  a_{\text{stripe}} \\
  b_{\text{stripe}}
\end{pmatrix} = \begin{pmatrix}
  3.08 \\
  0
\end{pmatrix} \begin{pmatrix}
  a_{\text{crI3}} \\
  b_{\text{crI3}}
\end{pmatrix} \quad \text{appears in the striped phase, containing ~ 8 primitive cells. A new striped phase (type II striped phase, see Fig. 2d and e) emerges after annealing at 433 K for 30 min. The type II phase exhibits an even larger parallelogram supercell (3.83 nm × 2.32 nm, 100°) with the basic vectors written as}
\]

\[
\begin{pmatrix}
  a_{\text{spell}} \\
  b_{\text{spell}}
\end{pmatrix} = \begin{pmatrix}
  4.55 \\
  -2.24
\end{pmatrix} \begin{pmatrix}
  a_{\text{crI3}} \\
  b_{\text{crI3}}
\end{pmatrix}, \quad \text{containing roughly 21 primitive cells.}
\]

Continuous heating the samples at even higher temperatures (>423 K) could partially decompose CrI₃, forming single-layer chromium diiodide (CrI₂) which was previously predicted in a likely
AFM order and with a Type-II Dirac cone [4]. Fig. 3a shows a zigzag CrI2 phase together with the dotted phase. This zigzag phase can also be obtained by growing the sample at a high temperature of 450 K (Fig. S3 online). The apparent height of the zigzag phase is 0.34 Å smaller than that of the dotted phase (inset of Fig. 3a). Fig. 3b and c show the atoms of the topmost layer are close-packed with a hexagonal lattice (lattice constant 4.08 Å) in the zigzag phase. Lack of neither the 6.867 Å periodicity nor the iconic I trimer rules out the possibility of this phase being CrI3, but the observed lattice constant of 4.08 Å is well consistent with that of CrI2, i.e., 3.92–3.99 Å [39,40]. The reduced thickness compared with CrI3 also implies the formation of single-layer CrI2 (interlayer distance, 6.77 Å) [39,40].

Fig. 3c shows the atomic-resolution STM image of single-layer CrI2, in which the topmost atoms in two symmetric directions are uniformly arranged, while the atomic arrangement in the third direction is wavy. This implies that the zigzag superstructure may originate from a mismatched CrI2/Au(1 1 1) interface. If we further anneal the sample to 456 K, CrI3 completely converts into CrI2 and then to ordered iodine adlayer and disordered clusters (probably residual Cr) at 482 K. The iodine adlayer has a periodicity of 5 Å, which is the same as that of the iodine-adsorbed Au(1 1 1) surface [41].

Single-layer CrI2 and CrI3 were grown on graphite using similar growth procedures (see experimental details). Fig. 4a shows a large-scale STM image of single-layer CrI2 islands on graphite. The islands are strip-shaped with an apparent height of 7.5 Å (sample bias, 3.3 V) (Fig. S4 online). Fig. 4b shows an atomic-resolution STM image of single-layer CrI2 on graphite. Differently from the zigzag phase of CrI2 on Au(1 1 1), an apparent (1 × 6) striped superstructure was observed to superpose on a 3.98 Å hexagonal atomic lattice of CrI2. The lattice constant is consistent with that of bulk CrI2 [39,40]. Due to the inert graphite surface, it is difficult to obtain an excessive iodine environment, which is of importance to CrI3 growth. However, a two-step procedure, i.e., low-temperature co-deposition followed by annealing at elevated temperatures, was used to obtain CrI3 on graphite (see experimental details). Fig. 4c shows a fractal-shaped CrI3 island while increasing I and Cr deposition results in a larger domain size (Fig. S5 online). The measured height of the island is 7.9 Å (sample bias, 4 V) (Fig. S4 online), slightly larger than that of the CrI3 islands (6.8 Å) on Au(1 1 1); this is, most likely, due to the higher density of states (DOS) on Au(1 1 1). Similar trimers feature and the lattice constant of 6.84 Å were also observed on the fractal island (Fig. 4d). Detailed structural parameters were listed in Table S2 (online). In different with the Au(1 1 1) case, no superstructure was observed for CrI3 on graphite, ascribed to the weaker CrI3-substrate interaction on graphite.

The substrate effect is crucial to the formation of superstructures in single-layer CrI2. A likely formation mechanism may relate to the surface reconstruction of substrate, the intrinsic structural transition of CrI3 itself or moiré pattern between CrI3 and Au. The Au(1 1 1) herringbone reconstruction is still visible on NaCl bilayer covered Au(1 1 1) [42], however, our CrI3 superstructures are quite dissimilar to usual Au(1 1 1) herringbone patterns. The solely CrI3 phase on HOPG excludes the likely explanation by the intrinsic structure of CrI3 for the superlattice pattern. Therefore, the
superstructure is, most likely, a result of moiré pattern. Our XPS data indicates the presence of an iodine buffer layer between CrI₃ and Au(1 1 1), which means that the moiré pattern is caused by the lattice mismatch between CrI₃ and the I layer underneath. Fig. S6 (online) shows a tentative model of the dotted phase, which is qualitatively in agreement with the experimental results. It was reported that iodine adlayers on Au(1 1 1) exhibit different structures [41], which may lead to the formation of different CrI₃/Au superstructures observed in this work. Nevertheless, it is still an open question whether the magnetic properties of single-layer CrI₃ are modulated by the superstructures.

We also performed bias-dependent STM imaging on single-layer CrI₃, unveiling the spatial distribution of the occupied and unoccupied DOSs near the Fermi energy. The dI/dV spectrum (Fig. S7 online) acquired on the dotted CrI₃ phase (at ~77 K) shows the valence band maximum (VBM) and conduction band minimum
The measured bandgap $\Delta = 1.25$ eV is consistent with the previous experiments and calculations \[9,43\]. Fig. 5a and c show the STM images of single-layer CrI$_3$ at the bias voltage ($V_s$) of 1 and $-1$ V, respectively. At $V_s = 1$ V, the image displays the typical trimer feature, indicating that the unoccupied local density of states (LDOS) of the topmost I layer is distributed around the Cr honeycomb centers (marked by yellow triangles). When $V_s$ switches to $-1$ V, the sites of the Cr centers darken (dark triangular holes, marked by black triangles) associated with the much brighter surrounding edges (Fig. 5c). Such bias-dependent contrast difference was repeatedly observable when switching the bias between 1 and $-1$ V (Figs. 5e and S8 (online)), manifesting that it is not an artefact of accidentally changing the tip electronic states. Importantly, our simulated STM images for both positive and negative biases well resemble the experiment (Fig. 5b and d). Our results indicate that the distribution of the unoccupied states is concentrated around the Cr-I bond direction as the $x$ and $y$ axes while the direction perpendicular to the Cr-I plane as the $z$ axis (black arrows in Fig. 6a). We found that significant charge transfer occurs from Cr $e_g$ orbitals to the bonding regions of Cr-I covalent $r_b$ bonds, suggesting that the Cr $e_g$ orbitals hybridize with I $p$ orbitals. Meanwhile, there are three Cr $d$ electrons filling in the Cr $t_{2g}$ states with parallel spin orientation, which shows a local magnetic moment of 3.28 $\mu_B$ on each Cr atom. Decomposed spin-polarized band structures shown in Fig. S10 (online) also confirm this picture. While spin-up Cr $t_{2g}$ states exhibit the local moments, the valence band states near the bandgap of CrI$_3$ is mainly comprised of spin-up $I p_{x,y}$ orbitals and the conduction band is primarily contributed by the spin-up Cr-$e_g$ and $I p_{x,y}$ states.

Such band-decomposition is highly consistent with the spin charge density plotted in Fig. 6b where the spin up density (red) is mostly around Cr atoms with a minor portion at the $p_z$ states of adjacent I atoms, while the opposite spin density (blue) is observable for $l-p_{x,y}$ orbitals. This particularly spatial distribution of valence and conduction states were indeed observed in STM images. Since STM is a surface sensitive measuring technique, we focus on the I trimer of the topmost layer. The conduction band states, detectable in positive biases, is around $I p_{x,y}$ states (denoted by red arrows). These states extend toward the vacuum and the Cr honeycomb center, giving rise to a bright and diffuse trimer-like appearance in the positively biased STM images (Fig. 5a and b). In terms of negatively biased images, the valence band states mainly reside at the $I p_z$ orbitals (marked by blue arrows). The $I p_z$ orbital points to the center of two neighboring Cr atoms being bridged by this I atom, exhibiting a bright protrusion sitting at the Cr-Cr center, as depicted in Fig. 5c and d.
Fig. 5. Distribution of unoccupied and occupied states at single-layer CrI$_3$ surface. (a), (b) Experimental and simulated STM images at $V_s = 1\,\text{V}$ ($I_t = 300\,\text{pA}$), showing the brighter I trimer feature upon the Cr honeycomb centers. (c), (d) Experimental and simulated STM images at $V_s = -1\,\text{V}$ ($I_t = -200\,\text{pA}$), showing dark triangular holes upon the Cr honeycomb centers. (e) STM image with repeated bias switching between 1 and -1 V. Green dashed lines represent $V_s$ switching from 1 to -1 V while the blue dashed line from -1 to 1 V. Yellow and black triangles correspond to the I trimers and dark triangular holes upon the Cr honeycomb centers.

Fig. 6. Electronic structure of single-layer CrI$_3$ with FM order. (a) Atomic differential charge density. Pink and green isosurfaces correspond to the charge accumulation and reduction after Cr and I atoms bonding together, respectively. (b) Top view of spin charge density of single-layer CrI$_3$ with FM order. Red and blue isosurfaces correspond to the charge with spin component up and down, respectively. (c) Schematic of the FM super-exchange mechanism for nearest spin-exchange bridged by two I atoms (denoted $J_1$), in which red up-oriented and blue down-oriented arrows represent electrons with different spins.
The electronic structure of monolayer CrI₃ indicates an FM super-exchange mechanism between Cr atoms bridged by two intermediated 1 atoms with a Cr-I-Cr bond angle of 93° (denoted as $f_j$). Cation Cr$^{3+}$ takes a sp$^3$d$^2$ hybridization where six orbitals orient towards the corners of the Cr-I octahedrons, with 3/2 e$^-$ in each orbital and each I-p orbital is filled by 5/3 e$^-$. The super-exchange interaction involves four Cr orbitals from two Cr cations and four I $p_{xy}$ orbitals from two bridging I atoms, which are totally filled with 38/3 e$^-$ from Cr and 20/3 e$^-$ from I, as illustrated in Fig. 6c. Such filling motifs offers roughly three channels for virtual hopping of spin-up electrons sitting on Cr sites. Moreover, the I $p_z$ orbital also plays a certain role in enhancing the FM super-exchange as that a portion of spin-up electrons does transfer to the I $p_z$ orbital (Fig. 6a and b), which may open an additional exchange chancel for the FM interaction.

4. Conclusions

In summary, we successfully synthesized single-layer CrI₃ on Au(1 1 1) and graphite using MBE in UHV. A trimer is identified as the basic unit of the topmost I layer. Different superstructures of single-layer CrI₃ were obtained on Au(1 1 1) while only the pristine structure was found on graphite. We also prepared single-layer CrI₂ on Au(1 1 1) by annealing the CrI₃ sample or directly growing at an elevated temperature. Joint experiment and theory investigations revealed that the different appearance of unoccupied and occupied STM images are ascribed to particularly spatial distributions of the $p_{xy}$ and $p_z$ orbitals of the topmost I layer. A detailed FM super-exchange mechanism of the Cr-I-Cr channel was unveiled and discussed, which is useful for understanding the strong out-of-plane FM and highlights the role of I $p_z$ orbitals in tuning magnetism of single- and few-layer CrI₃.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Peigen Li and Dingyong Zhong conceived the research and designed the experiments. Peigen Li, Jiuhao Zhang and Shenwei Chen performed the STM/STS and KPFM experiments. Cong Wang and Wei Ji proposed the theoretical model and performed the theoretical calculations. Peigen Li, Jiuhao Zhang, Donghui Guo, Dingyong Zhong, Cong Wang and Wei Ji analyzed and interpreted the results. Peigen Li, Dingyong Zhong, Cong Wang and Wei Ji wrote the manuscript with contributions from all authors.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2020.03.031.

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