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Monolayer transition metal dichalcogenides (TMDCs) in the 1T′ structural phase have drawn a great deal of attention due to the prediction of quantum spin Hall insulator states. The band inversion and the concomitant changes in the band topology induced by the structural distortion from 1T to 1T′ phases are well established. However, the bandgap opening due to the strong spin-orbit coupling (SOC) is only verified for 1T′-WTe$_2$ recently and still debated for other TMDCs. Here we report a successful growth of high-quality monolayer 1T′-MoTe$_2$ on a bilayer graphene substrate through molecular beam epitaxy. Using in situ angle-resolved photoemission spectroscopy (ARPES), we have investigated the low-energy electronic structure and Fermi surface topology. The SOC-induced breaking of the band degeneracy points between the valence and conduction bands is clearly observed by ARPES. However, the strength of SOC is found to be insufficient to open a bandgap, which makes monolayer 1T′-MoTe$_2$ on bilayer graphene a semimetal. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5004700

Two-dimensional (2D) transition metal dichalcogenide (TMDC) is a versatile material platform, in which electrical, optical, and topological properties can be controlled through thickness, strain, field, and other perturbations.$^{1-4}$ The most well-studied example is the 2H-MX$_2$ (M = Mo, W; X = S, Se) semiconductor that makes a transition from indirect bandgap to direct bandgap only in the monolayer,$^{4,5}$ with well-pronounced spin-splitting$^{6,7}$ and valley degrees of freedom.$^{8,9}$ Other structural phases stemming from different stacking orders between transitional metal and chalcogen layers deliver distinct physical properties even with the same constituent atoms.

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1T'-'MX₂ (M = Mo, W; X = S, Se, Te) has gained particular interest regarding its topological properties. While its three-dimensional bulk form has been explored in terms of type-II Weyl semimetal,10–13 the monolayer is predicted to host a quantum spin Hall (QSH) insulator.3 A QSH insulator, or a two-dimensional (2D) topological insulator, is a topologically nontrivial quantum state, which is hallmark by the helical edge state protected by time reversal symmetry and the bulk (as opposed to the edge) bandgap opening due to strong spin-orbit coupling (SOC).14–16 The resulting transport properties exhibit quantized Hall conductance even in the absence of magnetic field, and spin-polarized edge current is expected to be useful for the spintronic applications. The QSH phase in 1T' TMDC has been recently realized only in 1T'-'WTe₂.17,18 It is of great interest whether it is possible to realize a QSH state in other 1T' TMDCs and whether fundamental parameters such as bulk bandgap would be different from those of 1T'-'WTe₂.

Many efforts have been devoted to achieve a QSH state in monolayer 1T'-'MoTe₂.3,19–21 From the electronic structure point of view, two critical elements of achieving a QSH state in group VI TMDCs are the band inversion caused by the structural distortion from the 1T phase to 1T' phase and the 2D bulk bandgap induced by strong SOC.18 The former has been well established by the previous theoretical calculations.3,19,20 However, as shown in Table I, the calculated bandgap size varies significantly depending on calculation methods, even to a degree that it is not clear whether 1T'-'MoTe₂ is a semiconductor or a semimetal. Optical absorption and transport measurements report a 60 meV bulk gap in few-layer mechanically exfoliated (ME) 1T'-'MoTe₂,20 while CVD-grown monolayer 1T'-'MoTe₂ shows a metallic transport behavior.21 Whether the SOC is strong enough to open a bulk gap is still not very clear. A characterization tool that can directly visualize the band structure and the size of the bandgap, such as angle-resolved photoemission spectroscopy (ARPES),22,23 would provide a clearer insight on this aspect.

In this letter, we report a successful growth of monolayer 1T'-'MoTe₂ on a bilayer graphene (BLG) substrate using molecular beam epitaxy (MBE). The electronic structure of epitaxial 1T'-'MoTe₂ has been investigated by in situ ARPES. We found that the SOC indeed breaks the band degeneracy points and separates the valence and conduction bands. However, the strength of SOC is not enough to open a 2D bulk bandgap, which makes monolayer 1T'-'MoTe₂ on BLG a semimetal.

Both thin film growth and ARPES characterization of 1T'-'MoTe₂ were performed at the Beamline 10.0.1, Advanced Light Source, Lawrence Berkeley National Laboratory. 1T'-'MoTe₂ was grown by MBE with a base pressure of ∼2 × 10⁻¹⁰ Torr. Mo (99.99% purity) and Te (99.999% purity) were evaporated by an e-beam evaporator and a Knudsen cell, respectively, with the flux ratio of ∼1:20. The substrate was BLG prepared by vacuum graphitization of 6H–SiC(0001).24 The substrate temperature was set at 280°C for growth. The growth rate was 15 min per layer. Following the growth, a 20-min post-annealing process at the same temperature was performed. Additional ARPES measurements were performed at the Beamline 5-4, Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory. The band structure calculation is performed by using the generalized gradient approximation method with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional as implemented in the VASP.25 The lattice constants used are a = 6.38 Å and b = 3.45 Å for 1T'-'MoTe₂.

### Table I. Gap sizes derived from different calculation methods and experimental measurements.

<table>
<thead>
<tr>
<th>Calculation or experiment method</th>
<th>Sample fabrication method and thickness</th>
<th>Gap size (eV)</th>
<th>Bulk conductivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>...</td>
<td>−0.262</td>
<td>Metallic</td>
<td>3</td>
</tr>
<tr>
<td>G0W0</td>
<td>...</td>
<td>−0.300</td>
<td>Metallic</td>
<td>3</td>
</tr>
<tr>
<td>PBE + HSE06</td>
<td>...</td>
<td>0.03</td>
<td>Semiconductor</td>
<td>20</td>
</tr>
<tr>
<td>Transport</td>
<td>CVD monolayer</td>
<td>...</td>
<td>Metallic</td>
<td>21</td>
</tr>
<tr>
<td>Optical absorption</td>
<td>ME few layer</td>
<td>0.06</td>
<td>Semiconductor</td>
<td>20</td>
</tr>
<tr>
<td>ARPES</td>
<td>MBE monolayer</td>
<td>...</td>
<td>Metallic</td>
<td>This work</td>
</tr>
</tbody>
</table>
The crystal structure of 1T'\textsuperscript{′}-MoTe\textsubscript{2} is illustrated in Fig. 1(a). It can be seen as distorted 1T-MoTe\textsubscript{2}, for which Mo atoms are in octahedral coordination with Te atoms. With the distortion, Mo atoms shift off the center of Te octahedra along X direction forming zigzag metal chains along the Y direction. The Te atoms also shift accordingly, making two types of Te with inequivalent coordinations. Figure 1(b) shows the Brillouin zone of 1T'\textsuperscript{′}-MoTe\textsubscript{2}. The reflection high-energy electron diffraction (RHEED) patterns before and after the thin film growth are shown in Fig. 1(c). The sharp diffraction stripes after growth indicate the high crystalline quality of the 1T'\textsuperscript{′}-MoTe\textsubscript{2} thin film. The thermal stability of the sample was checked by annealing the sample at 350 °C under Te atmosphere. No obvious change in the RHEED pattern was observed, indicating that growth temperature 280 °C is far below the decomposing temperature, thus retaining high crystallinity of the sample.\textsuperscript{26} Using the lattice constant of BLG ~\textasciitilde2.46 Å as a reference, one can get the lattice parameter of 1T'\textsuperscript{′}-MoTe\textsubscript{2} on BLG ~\textasciitilde6.3 Å, which is consistent with reported values.\textsuperscript{3} Figure 1(d) is the angle-integrated core level spectrum, clearly showing the characteristic Mo 4\textit{p} peak and Te 4\textit{d} peaks. Figure 2 is the low-energy electron
diffraction (LEED) pattern taken with an electron kinetic energy of 94 eV to reveal the surface symmetry and lattice structure. The blue solid circles indicate the first-order diffraction from a BLG substrate. The six spots surrounding each of them come from $6\sqrt{3}R30^\circ$ superlattice diffractions between graphene and SiC. Due to the symmetry mismatch between three-fold rotational symmetric BLG and two-fold symmetric $1T'\text{-MoTe}_2$, there are three energetically equivalent rotational alignments between BLG and $1T'\text{-MoTe}_2$. This results in three sets of reciprocal lattices superposed in both LEED and ARPES data. The LEED pattern from different domains of $1T'\text{-MoTe}_2$ is indicated by the dotted lines with different colors in Fig. 2(a). Using the in-plane lattice constant of graphene $a = 2.46 \ \AA$, one can get the lattice constants of $1T'\text{-MoTe}_2$, $a = 6.3 \ \AA$ and $b = 3.4 \ \AA$, consistent with the previously reported values as well as with that from our RHEED measurement. Figure 2(b) shows the superposition of the Brillouin zones from three equivalent $1T'\text{-MoTe}_2$ and graphene lattices.

Figure 3 show the overall electronic structure and Fermi surface (FS) topology from ARPES measurements on monolayer $1T'\text{-MoTe}_2$/BLG. Figure 3(a) is the FS intensity map, which shows six-fold symmetry due to the superposition of three $1T'\text{-MoTe}_2$ domains with $120^\circ$ rotation with respect to each other. One may extract a single-domain FS from the ARPES data as shown in Fig. 3(b). There are one hole pocket located at the zone center, two electron pockets along the $\Gamma Y$ direction, and two more electron pockets located at the zone boundaries. The topology of the FS plays a key role in understanding the transport properties of the semimetal in which the hole and electron carriers coexist. Perfect electron-hole compensation is proposed to be responsible for the non-saturating magnetoresistance in three-dimensional bulk $1T'\text{-WTe}_2$. However, too many bands crossing the Fermi energy ($E_F$) in a confined momentum space have challenged ARPES measurements and interpretations. The simplified FS in monolayer $1T'\text{-MoTe}_2$ makes the evaluation easier and reliable. We have obtained the concentration ratio between the $n$ and $p$ type carriers $\sim 6:10$. Considering that the volume of the electron (hole) pocket increase (decrease) very quickly above $E_F$, one may easily achieve the balance of $n$ and $p$ carries with slightly doping on the film to realize the electron-hole compensation condition in the monolayer.

Figure 3(c) is the overall band structure along the $\Gamma Y$ direction measured by in situ ARPES, superimposed with the theoretical calculation made with the PBE method. Due to the superimposed rotational domains, the signal from the $\Gamma P$ direction [Fig. 1(b)] overlaps with that from the $\Gamma Y$ direction within a single detection plane. However, the low-energy bands from $\Gamma P$ are contained within the envelop of $\Gamma Y$ bands in both theory and experiment. The domain size of the film is estimated to be tens of nanometers, which call for further studies with characterization tools with high spatial resolution such as STM and nano-ARPES to disentangle the superposition of signals from domains with different orientations. Overall, the experimental band structure and FS topology from ARPES agree well with the theoretical calculation.

**FIG. 3.** Electronic structure of monolayer $1T'\text{-MoTe}_2$. (a) Fermi surface intensity map from ARPES measurement of monolayer $1T'\text{-MoTe}_2$. The intensity is integrated within a ±10 meV window around the Fermi energy. The red, blue, and green rectangles indicate three Brillouin zones from three rotational domains, $120^\circ$ with respect to each other. (b) Fermi surface topology extracted from ARPES data for a single domain. The red and blue pockets represent the hole and electron pockets, respectively. (c) The second derivative of the ARPES spectrum along $\Gamma Y$ superposed with PBE calculation. The red and blue lines are calculated bands along the $\Gamma Y$ and $\Gamma P$ directions, respectively.
Now we focus on the low-energy electronic structure right near $E_F$. According to theoretical calculations, the transition from 1T to 1T’ inverts the band order leading to a band degeneracy point between the valence and conduction bands at $\Delta$ point [Fig. 4(a), left]. The SOC then lifts the degeneracy at the cross point [Fig. 4(a), right] to make the system to be an insulator with a bulk bandgap or a semimetal, depending on the strength of the coupling. The low-energy band dispersion along both $\Gamma X$ and $\Gamma Y$ directions [Figs. 4(b) and 4(c)] and corresponding momentum distribution curves (MDCs) and energy distribution curves (EDCs) along the $\Gamma Y$ direction [Figs. 4(d) and 4(e)] clearly indicate well-separated valence and conduction bands confirming the scenario mentioned above. However, the band structure measured by ARPES clearly exhibits that the hole band at $\Gamma$ crosses $E_F$, while the conduction band minimum locates well below $E_F$, leading to a FS with both electron and hole pockets. This shows that monolayer 1T’-MoTe$_2$ on BLG is a semimetal with a moderate strength of SOC.

Considering the weaker SOC in Mo compared to W, in general, one would expect that the SOC-induced energy bandgap in 1T’-MoTe$_2$ is smaller than that in 1T’-WTe$_2$. In addition, strain and electron-electron interaction are believed to play important roles in the low-energy electronic structure of 1T’-MoTe$_2$. As shown in the calculations, the size of the gap is very sensitive to the lattice constant. However, a large strain, ~4%–6% of the lattice constant, is needed to lift the crossover of the conduction and valence bands and to open a bulk gap. It has been known that van der Waals epitaxy adopted in our growth of 1T’-MoTe$_2$ on graphene minimizes the strain effect caused by lattice mismatch. A strong electron-electron correlation, which is largely screened in the bulk 1T’-MoTe$_2$, could also enlarge the separation between the conduction band and the valence band. As calculated in Ref. 32, even with a very strong on-site Coulomb repulsion ~5 eV, the bandgap remains closed for 1T’-MoTe$_2$. In our 1T’-MoTe$_2$/BLG thin films, the screening from conducting graphene substrate lowers the strength of on-site Coulomb interactions, which would act against the bulk gap opening due to the electron-electron interaction.

In summary, high-quality monolayer 1T’-MoTe$_2$ has been grown on the BLG substrate by MBE. In situ LEED and ARPES measurements are performed to characterize the crystal and electronic structure. It has been shown that three equivalent rotational domains of 1T’-MoTe$_2$ coexist and contribute to our spectra. The overall electronic structure obtained from ARPES exhibits excellent agreement with theoretical calculations, including the predicted degeneracy lifting induced by SOC. However, the splitting due to the SOC is not large enough to open a 2D bulk gap. The valence band maximum locates above the conduction band minimum resulting in a FS with both electron and hole pockets.

FIG. 4. Detailed view of the low-energy electronic structure of monolayer 1T’-MoTe$_2$. (a) The band evolution of 1T’-TMDCs under strong and weak SOC. (b) and (c) are detailed ARPES spectra along the $\Gamma X$ and $\Gamma Y$ directions, respectively. (d) and (e) are MDCs and EDCs along the $\Gamma Y$ direction corresponding to the boxed area in (c).
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