PAPER

Moiré modulation of lattice strains in PdTe_{2} quantum Films

To cite this article: Jacob Cook et al 2023 2D Mater. 10 035005

View the article online for updates and enhancements.

You may also like

- <u>Protonation enhanced superconductivity in</u> <u>PdTe</u> Zhen Liu, Tao Han, Mengqin Liu et al.
- Electronic transport properties of intermediately coupled superconductors: PdTe, and Cu_{0.04}PdTe, M. K. Hooda and C. S. Yadav
- Layer-dependent band engineering of Pd dichalcogenides: a first-principles study Liang-Ying Feng, Rovi Angelo B. Villaos, Zhi-Quan Huang et al.

2D Materials

PAPER

RECEIVED 25 January 2023

CrossMark

REVISED 27 March 2023

ACCEPTED FOR PUBLICATION 13 April 2023

PUBLISHED 26 April 2023

Moiré modulation of lattice strains in PdTe₂ quantum Films

Jacob Cook^{1,4}, Dorri Halbertal^{2,4}, Qiangsheng Lu¹, Xiaoqian Zhang¹, Clayton Conner¹, Geoff Watson¹, Matthew Snyder¹, Mathew Pollard³, Yew San Hor³, Dmitri N Basov² and Guang Bian^{1,*}

¹ Department of Physics and Astronomy, University of Missouri, Columbia, MO 65211, United States of America

Department of Physics, Columbia University, New York City, NY 10027, United States of America

³ Department of Physics and Astronomy, Missouri University of Science and Technology, Rolla, MO 65409, United States of America

These authors contributed equally to this work.

⁶ Author to whom any correspondence should be addressed.

E-mail: biang@missouri.edu

Keywords: moiré pattern, transition metal dichalcogenide, topological insulator, heterostructure

Abstract

We report the epitaxial growth of PdTe₂ ultrathin films on a topological insulator Bi₂Se₃. A prominent moiré pattern was observed in scanning tunneling microscope measurements. The moiré periodicity increases as film thickness decreases, indicating a lattice expansion of epitaxial PdTe₂ thin films at lower thicknesses. In addition, our simulations based on a multilayer relaxation technique reveal uniaxial lattice strains at the edge of PdTe₂ domains, and anisotropic strain distributions throughout the moiré supercell with a net change in lattice strain up to ~2.9%. Our density functional theory calculations show that this strain effect leads to a narrowing of the band gap at Γ point near the Fermi level. Under a strain of ~2.8%, the band gap at Γ closes completely. Further increasing the lattice strain makes the band gap reopen and the order of conduction band and valence bands inverted in energy. The experimental and theoretical results shed light on a method for constructing quantum grids of topological band structure under the modulation of moiré potentials.

1. Introduction

Van der Waals (vdW) materials have aroused great interest for their exceptional mechanical, electrical, thermal, and optical properties [1, 2]. In vdW materials, strong covalent bonds provide in-plane stability while weak interlayer couplings enable atomic-scale construction of a huge variety of layered heterostructures with diverse functionalities [3-5]. It is desirable to use two vdW materials as components of the heterostructure for an atomically sharp interface that can reduce the interfacial disorders and enhance proximity effects. Among a myriad of vdW materials, Bi₂Se₃ and PdTe₂ are of particular interest for their nontrivial electronic band structure. Bi2Se3 is an archetypal topological insulator with topologically protected Dirac surface states [6-10]. PdTe₂ is known to host rich electronic properties such as intrinsic type-I superconductivity [11–15] with anomalous type-II surface behavior [16, 17], a type-II Dirac cone [18–21], topologically non-trivial surface states [18, 22, 23]. More interestingly, it has

been shown that $PdTe_2$ maintains its superconducting state even with thickness down to two monolayers (MLs), and $T_c = 1.42$ K at 2 ML [24]. $PdTe_2$ also holds in-plane crystal lattice parameters close to those of Bi₂Se₃. Therefore, building a heterostructure of Bi₂Se₃ and PdTe₂ offers a promising platform for exploring the interaction of superconductivity with topological Dirac states and other unusual properties related to the topological electronic states.

In this work, we perform the epitaxial growth of PdTe₂ films on topological insulator Bi₂Se₃. The electronic structure of a heterostructure is probed by angle-resolved photoemission spectroscopy (ARPES). Our scanning tunneling microscope (STM) measurements reveal a very strong and dynamic moiré pattern. Moiré patterns, in general, can arise from twisting rotations between adjacent crystal layers [25] or the lattice mismatch at the interface between two films [26, 27]. Moiré patterns and related long-range potentials have profound effects on the electronic and magnetic properties of heterostructures, such as superconductivity of twisted bilayer graphene [25], modulation of edge modes [27], tunable electronic properties [27–31], and periodic modulation of the local topological order in vdW heterobilayers [32]. The moiré pattern in the $PdTe_2/Bi_2Se_3$ heterostructures arises from the lattice mismatch between the epitaxial $PdTe_2$ and Bi_2Se_3 substrate. A thickness dependency of the moiré pattern is observed, suggesting increases in moiré periodicity with decreasing thickness. Theoretical analysis of the moiré system reveals inhomogeneous lattice strains in $PdTe_2$ films, and a band inversion induced by lattice strains.

1.1. Experimental and computational methods

The PdTe₂ thin films were grown on the (001) surface of Bi₂Se₃ substrates in an integrated molecular beam epitaxy (MBE) -STM ultrahigh vacuum system with base pressure below 2×10^{-10} mbar. The Bi₂Se₃ was prepared by *in-situ* cleaving the surface and subsequent annealing to 250 °C for 1 h. Then, high-purity Pd (99.95%) and Te (99.9999%) were evaporated from an electron-beam evaporator and a standard Knudsen cell, respectively, with a flux ratio of 1:10. The deposition rate of Pd and Te atoms was monitored by a quartz oscillator. The temperature of substrate was kept at 210 °C during the growth.

The surface topography mapping was performed *in-situ* by using the SPECS Aarhus-150 STM with a tungsten tip at room temperature. After STM, the film was transferred *in-situ* to the ARPES stage. ARPES measurements were performed at 100 K using a SPECS PHOIBOS-150 hemisphere analyzer with a SPECS UVS 300 helium discharge lamp (He $I\alpha = 21.2$ eV and He II $\alpha = 40.8$ eV). The energy resolution is 40 meV at 100 K.

Thickness dependent lattice expansion and relaxation was calculated using a multilayer relaxation technique [33], a newer methodology for stacked thin film crystals utilizing material parameters, sheer moduli, and generalized stacking fault energy to calculate interactions and relaxations of layered materials.

We also performed first-principles calculations with density functional theory (DFT) as implemented in the Vienna *ab initio* Simulation Package. We used the Perdew–Burke–Ernzerhof form for the exchange-correlation functional with a plane-wave cut-off energy of 300 eV. The super cell includes PdTe₂ layers and a vacuum layer of about 20 Å. The PdTe₂ layers were allowed to relax during the geometry optimization.

2. Results

 $PdTe_2$ has a layered trigonal crystal structure, belongs to the 1T-CdI₂ structure type, and the *P*3*m*1 space group with AA stacking, meaning there is no rotation between layers (figure 1(a)). The bulk in-plane lattice parameters are a = 4.028 Å for PdTe₂ [24] and a = 4.14 Å for Bi₂Se₃ [34]. The STM topography (figure 1(b)) shows single-crystalline 1T-PdTe₂ films grown on the Bi₂Se₃ (001) surface. The apparent height profile demonstrates a PdTe₂ island with domains of different thicknesses, namely, 3 ML, 4 ML, and 5 ML. A hexagonal moiré pattern is visible in PdTe₂ films with different thicknesses. Atomicresolution STM images (figures 1(c) and (d)) of the Bi₂Se₃ substrate and 10 ML PdTe₂ show the hexagonal lattice structure with the average lattice constants of $a = 4.15 \pm 0.1$ Å and $a = 3.98 \pm 0.1$ Å for Bi₂Se₃ and PdTe₂, respectively, consistent with literature.

2.1. ARPES analysis

ARPES measurements further confirm the high crystallinity of both the substrate and epitaxial films (See figure 2). The ARPES spectrum of Bi_2Se_3 (figure 2(a)) shows the band gap between the conduction and valence bands and the topologically protected surface states (TSS). The ARPES result of a 10 ML PdTe₂ film grown on Bi_2Se_3 (figure 2(b)) are consistent with that of pristine $PdTe_2$ films (figure 2(c)) and the DFT calculation (figure 2(d)), indicating the high structural quality of the epitaxial films. The ARPES result from a 3-4 ML PdTe2 film grown on Bi2Se3 (figure 2(e)) shows a mixture of the ultra-thin film PdTe₂ and the Bi₂Se₃ substrate. This is due to the island growth behavior in the early stage of MBE growth, which is consistent with the STM characterizations (figure 1(b)). The ARPES spectrum from a pristine 4 ML PdTe₂ grown on graphene is plotted in figure 2(f) for a comparison. The results indicate the nonuniform structural property of PdTe₂ films on Bi₂Se₃ at low coverage.

2.2. Moiré analysis

To understand the moiré pattern observed in the PdTe₂/Bi₂Se₃ heterostructure, we need to determine the relation between the lattice parameters of the two surfaces, which play an important role in the growth mode of epitaxial layers. Lattices with close to commensurate conditions likely align with minimal rotations, while a slight difference in the magnitude of lattice parameters can cause a long-range modulation in the interfacial atomic alignment, leading to a measurable, periodic pattern on the crystal surface. In general, the atomic layers in vdW materials are not rigid, but instead behave as deformable membranes. When two layers with an interfacial defect (i.e. lattice mismatch or twist angle) come in contact, the atomic positions relax to minimize the total energy. Naturally, the relaxation itself is strongest at the defect interface [33, 35–37]. Therefore, thinner



Figure 1. Crystal structure and scanning tunneling microscopy (STM) characterizations. (a) Crystal structure of PdTe₂ on Bi₂Se₃. (b) STM topography of PdTe₂ growths on Bi₂Se₃. Inset shows the height profile designated by the blue arrow. (c) Atomic-resolution STM images of the Bi₂Se₃ substrate and (d) 10 monolayer (ML) PdTe₂ crystal surface, both with surface atom overlays. Periodicity was determined by a cut along the blue arrow.



Ines. (b) ARPES spectrum for 10 monolayer (ML) $PdTe_2$ on the Bi_2Se_3 substrate along the M- Γ -M direction. (c) ARPES spectrum for 10 ML $PdTe_2$ on a graphene substrate along the M- Γ -M direction. (d) Density functional theory (DFT) calculated band structure of 10 ML $PdTe_2$ along the M- Γ -K direction. (e) ARPES spectrum for 3–4 ML $PdTe_2$ on the Bi_2Se_3 substrate along the M- Γ -M direction. (f) ARPES spectrum for 4 ML $PdTe_2$ on a graphene substrate along the M- Γ -M direction. (g) DFT calculated band structure of 4 ML $PdTe_2$ along the M- Γ -K direction.

epitaxial films experience a stronger substrate effect, tend to adopt a lattice constant closer to that of the substrate, and create a thickness-dependent moiré pattern.

By taking the interfacial atoms of the $PdTe_2/Bi_2Se_3$ heterostructure and overlaying them (figure 3(a)), we can see this long-range moiré pattern form from the alignment of the top Bi and Se atoms of the substrate and the bottom Pd and Te of the PdTe₂. This reveals three primary stacking configuration regions at the interface (figures 3 (b)–(d)).



We can calculate the maximum moiré periodicity by aligning the lattices with a 0° twisting angle and finding the distance between the regions with the same stacking order. Using this method with the literature lattice parameter, the moiré periodicity is found to be 14.49 nm. The proximity of the interfacial atoms in the different alignment regions will affect the stacking energy and the local density of states (LDOS) and can lead to variations in the transport properties along the surface.

Using the multilayer relaxation technique [33], the stacking energy density (SED) was calculated across films with thickness ranging from 3 ML to 12 ML. The calculated SED of 3 ML and 10 ML PdTe₂ on Bi₂Se₃ is shown in figures 3(e) and (f). The map of the SED exhibits a hexagonal moiré pattern with narrow domain walls for 3 ML and a hexagonal moiré pattern (more prominent in large-scale STM image in figure 4) for 10 ML. The moiré periodicity is reduced gradually as the films thickness increases.

The moiré pattern can be resolved via STM since the moiré potential causes a change in the LDOS at the interface. For the 10 ML sample (figure 4(a)), the moiré pattern has the hexagonal morphology with a periodicity of 14.255 nm, smaller than the theoretical value of 14.49 nm based on the bulk lattice parameters. The result indicates that the in-plane lattice parameter of the 10 ML PdTe₂ film is slightly smaller than the bulk value, which can be attributed to the 2D nature of thin films and substrate effects [35– 37]. In contrast, the 3–5 ML sample (figure 4(b)) demonstrates a hexagonal pattern with apparently larger periodicity. The observed periodicity of the moiré pattern in the 3 ML region is 20.114 nm, significantly larger than the literature value, indicating a pronounced tensile lattice strain in 3 ML. The moiré pattern is continuous across the edges of 4 ML and 5 ML patches, confirming that the pattern arises from the interfacial coupling between the Bi_2Se_3 and the PdTe₂ film.

By examining the moiré pattern along different directions and on multiple samples, the averaged moiré periodicity for the varying thicknesses of PdTe₂ films was obtained. The thickness dependence of the averaged moiré periodicity (figure 4(a)) shows that periodicity increases monotonically as film thickness decreases. For theoretical calculations, the lattice constants of Bi2Se3 are fixed since it is a bulk crystal with a much more rigid structure. The calculated lattice constants of PdTe₂ films are plotted in figure 4(d) which shows a thickness-dependent lattice expansion as the film thickness decreases, consistent with theory. The average lattice expansion of the 3 ML PdTe₂ film is about 0.7%. We note that the calculated lattice parameter is a global value averaged over many samples and thus it shows no information about the local variations in the lattice expansion.

2.3. Strain analysis

Interestingly, the moiré pattern can be distorted by the local lattice irregularities such as edges and defects (figure 5). Near the edge of the 3 ML sample, we observed a region with uniaxial distortion of the moiré pattern (figure 5(a)). To calculate the SED and relaxation for non-periodic structures, a modified version of the multilayer relaxation code was designed for the non-trivial strain cases. Under this methodology, the film was treated as a single membrane.







compressive/tensile strain values ranging from -0.7% to 3.4%. (m) Calculated upper and lower band binding energies versus

The uniaxial distortion is in good agreement with the SED calculated by using this theory (figure 5(b)) [38]. The SED map is obtained by minimizing the surface energy near the edge.

strain. The band inversion occurs at 2.81% strain.

The in-plane strain map for the 3 ML edge data (figure 5(c)) reveals that the uniaxial expansion of the PdTe₂ lattice increases as one moves closer to the edge of the crystal. This can be quantified by plotting the moiré periodicity as a function of the distance in both perpendicular (α) and parallel (γ) directions relative to the edge (figure 5(d)). The uniaxial distortion of moiré pattern towards the edge is due to the interplay of the interfacial effect and the breaking of the translational symmetry at the edge. The moiré periodicity has little changes parallel to the edge because the translational symmetry is intact in the γ direction.

We also observed an irregular distortion of moiré pattern in the central region of the 3 ML sample (figure 5(e)). This anisotropy in the distorted moiré pattern can be reproduced by plotting the SED over the distorted region (figure 5(f)). From the theoretical model, we extracted the compressive/tensile and sheer strain in PdTe₂ lattice at both the uniform and distorted regions, as shown in figure 6. Near the distorted region, the strain in PdTe₂ lattice ranges from a compression of -0.7% at the high LDOS regions to a massive 2.2% expansion at the centers of the hexagonal moiré supercell (figure 5(g)). This corresponds to a net change of 2.9% in the lattice parameter of PdTe₂ at different locations of moiré supercells. A zoom-in image shows the local variations of lattice strains within a single, undistorted moiré supercell (figure 5(h)).





change in the band structure of 3 ML PdTe₂ near the Γ point at the Fermi level (E_f) (figures 5(i)–(l)). With a strain of -0.7%, which corresponds to a slight lattice compression, there is an inverted band gap between the p_z and $p_{x,y}$ bands with a gap size of 0.125 eV (figure 5(i)).

At the observed maximum lattice expansion of 2.2%, the band gap shrinks to 0.055 eV (figure 5(j)). Beyond the observed strain values, DFT calculations show the band gap closes completely at the expansion of 2.8% (figure 5(k)). This theoretical strain accidentally matches with the maximum possible lattice strain of PdTe₂ on Bi₂Se₃, at which the two in-plane lattice constants of PdTe₂ on Bi₂Se₃ are identical. Further increasing the lattice expansion leads to reopening of the band gap and restoring the normal order of the p_z and $p_{x,y}$ bands in energy (figure 5(l)).

This shows that under sufficient strains with a moiré supercell, 3 ML PdTe₂ can undergo a topological transition from topological semimetal (with an inverted band order) to trivial semimetal. Interestingly, this topological phase transition is localized and confined to each moiré supercell. In other words, within each moiré supercell there exists a mesh region with TSS, while the core region is isolated and becomes topologically trivial. This is literally equivalent to a grid of topological insulator quantum domains with size of tens of nanometers. The separation between these quantum domains is controlled by the moiré periodicity of heterostructure.

3. Conclusion

We grew PdTe₂ thin films with thickness down to 3 ML on topological insulator Bi₂Se₃ by using MBE. A very prominent moiré pattern was observed in the STM mapping. The moiré periodicity increases as film thickness decreases, indicating a lattice expansion of PdTe₂ epitaxial thin films. This moiré pattern arises from the interface lattice mismatch between the PdTe₂ and Bi₂Se₃ crystals. The observed moiré pattern shows the in-plane lattice parameter PdTe₂ epitaxial films approaches that of Bi₂Se₃ in the 2D limit. The SED and in-plane strain maps for this heterostructure reveal uniaxial strain at the edge and anisotropic strain distributions throughout the moiré supercell with a net change in lattice strain of PdTe₂ up to $\sim 2.9\%$.

Our DFT calculations show that this strain effect leads to a narrowing of the band gap at Γ point near the Fermi level. Under a strain of ~2.8%, the maximum possible lattice strain at which PdTe₂ becomes commensurate with Bi2Se3, the band gap closes completely. Further increasing the lattice strain (for example, by using a substrate with a larger lattice constant compared to Bi₂Se₃) will make the band gap reopen and the order of conduction band and valence bands inverted in energy. This means that under enhanced strain, the band topology of PdTe₂ could undergo a phase transition. Enhanced strain can be produced by changing the substrate to one with slightly larger lattice constants.

Furthermore, since the maximum lattice strain is observed at the center of the moiré supercell, the topological phase with nontrivial band order is localized and confined in each moiré supercell in real space, as schematically shown in figure 7. Though the observed lattice strain in the

6





PdTe₂/Bi₂Se₃ heterostructure is insufficient to induce the band inversion, our results shed light on a new avenue of producing topological phase transitions in real space and creating a nanometer-sized grid of topological insulators for device applications [32].

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgments

G B was supported by the Research Council Award from the University of Missouri. Research on atomic relaxation at Columbia is supported by W911NF2120147. D N B is Moore Investigator in Quantum Materials EPIQS GBMF9455. D H was supported by a Grant from the Simons Foundation (579913). Y S H would like to acknowledge the support of NSF under Project Number DMR 1255607. X Z acknowledges the support of the fellowship of China Postdoctoral Science Foundation (2021M701590).

ORCID iD

Guang Bian
https://orcid.org/0000-0001-7055-2319

References

- [1] Ajayan P, Kim P and Banerjee K 2016 Phys. Today 69 38
- [2] Duong D L, Yun S J and Lee Y H 2017 ACS Nano 11 11803
- [3] Liu Y, Weiss N O, Duan X, Cheng H-C, Huang Y and Duan X 2016 Nat. Rev. Mater. 1 16042
- [4] Novoselov K S, Mishchenko A, Carvalho A and Castro Neto A H 2016 Science 353 aac9439
- [5] Wang Q H et al 2022 ACS Nano 16 6960
- [6] Hasan M Z, Xu S-Y and Bian G 2015 Phys. Scr. T164 014001
- [7] Hosur P, Ghaemi P, Mong R S K and Vishwanath A 2011 *Phys. Rev. Lett.* **107** 097001
- [8] Hasan M Z and Kane C L 2010 Rev. Mod. Phys. 82 3045
- [9] Sun H et al 2016 Phys. Rev. Lett. 116 257003
- [10] Yang F et al 2012 Phys. Rev. B 86 134504

- [11] Das S, Sirohi A, Yadav L, Gayen S, Singh Y and Sheet G 2018 Phys. Rev. B 97 014523
- [12] Leng H, Paulsen C, Huang Y K and de Visser A 2017 *Phys. Rev.* B **96** 220506
- [13] Leng H, Orain J C, Amato A, Huang Y K and de Visser A 2019 Phys. Rev. B 100 224501
- [14] Singh A and Singh Y 2018 Phys. Rev. B 97 054515
- [15] Garcia-Campos P, Huang Y K, de Visser A and Hasselbach K 2021 Phys. Rev. B 103 104510
- [16] Sirohi A, Das S, Adhikary P, Chowdhury R R, Vashist A, Singh Y, Gayen S, Das T and Sheet G 2019 J. Phys. Condens. Matter 31 085701
- [17] Le T, Yin L, Feng Z, Huang Q, Che L, Li J, Shi Y and Lu X 2019 Phys. Rev. B 99 180504
- [18] Fei F et al 2017 Phys. Rev. B 96 041201
- [19] Zheng W et al 2018 Phys. Rev. B 97 235154
- [20] Noh H-J, Jeong J, Cho E-J, Kim K, Min B I and Park B-G 2017 Phys. Rev. Lett. 119 016401
- [21] Teknowijoyo S, Jo N H, Scheurer M S, Tanatar M A, Cho K, Bud'ko S L, Orth P P, Canfield P C and Prozorov R 2018 *Phys. Rev.* B 98 024508
- [22] Clark O J et al 2018 Phys. Rev. Lett. 120 156401
- [23] Lui Y et al 2015 Chin. Rev. Lett. 32 067303
- [24] Liu C et al 2018 Phys. Rev. Mater. 2 094001
- [25] Tarnopolsky G, Kruchkov A J and Vishwanath A 2019 Phys. Rev. Lett. 122 106405
- [26] Parkinson B A, Ohuchi F S, Ueno K and Koma A 1991 Appl. Phys. Lett. 58 472
- [27] Kezilebieke S, Vaňo V, Huda M N, Aapro M, Ganguli S C, Liljeroth P and Lado J L 2022 Nano Lett. 22 328
- [28] Andrei E Y, Efetov D K, Jarillo-Herrero P, MacDonald A H, Mak K F, Senthil T, Tutuc E, Yazdani A and Young A F 2021 *Nat. Rev. Mater.* 6 201
- [29] Cao Y, Rodan-Legrain D, Rubies-Bigorda O, Park J M, Watanabe K and Taniguchi T 2020 Nature 583 215
- [30] Kennes D M, Claassen M, Xian L, Georges A, Millis A J, Hone J, Dean C R, Basov D N, Pasupathy A N and Rubio A 2021 Nat. Phys 17 155
- [31] Zheng Z et al 2020 Nature 588 71
- [32] Tong Q, Yu H, Zhu Q, Wang Y, Xu X and Yao W 2017 Nat. Phys. 13 356
- [33] Halbertal D, Klebl L, Hsieh V, Cook J, Carr S, Bian G, Dean C R, Kennes D M and Basov D N 2023 Phys. Rev. X 13 011026
- [34] Cava R J, Ji H, Fuccillo M K, Gibson Q D and Hor Y S 2013 J. Mater. Chem. C 1 3176
- [35] Lewis B F, Lee T C, Grunthaner F J, Madhukar A, Fernandez R and Maserjian J 1984 J. Vac. Sci. Technol. B 2 419
- [36] Badano G, Gergaud P, Robin I C, Baudry X, Amstatt B and Gemain F 2010 J. Electron. Mater. 39 908
- [37] Tourbot G, Bougerol C, Grenier A, Den Hertog M, Sam-Giao D, Cooper D, Gilet P, Gayral B and Daudin B 2011 Nanotechnology 22 075601
- [38] Halbertal D, Shabani S, Passupathy A N and Basov D N 2022 ACS Nano 16 1471–1476