Electric Field-Tunable Structural Phase Transitions in Monolayer Tellurium

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ABSTRACT: Electronic properties of monolayer tellurium (Te) with three proposed atomic configurations under external electric field were investigated through first-principles calculations. The calculated results demonstrate that α-Te and γ-Te have indirect band gaps, whereas β-Te, when no electric field is applied, can be considered as a direct semiconductor. An interesting structural change occurs in α- and γ-phase Te under a specific electric field strength, as does a change in structural chirality. In the presence of a perpendicular electric field, the band gaps can be modified and drawn close to 0 eV at a certain critical electric field strength. Before that, the band gaps of α-Te and γ-Te are nearly constant, while that of β-Te shows a quadratic relationship to electric field strength. These findings not only enrich our understanding of the electronic properties of monolayer tellurium but also show that monolayer tellurium has tremendous potential in nanoscale electronic devices owing to its tunable band gaps.

1. INTRODUCTION

Recently, the two-dimensional (2D) material tellurium has been widely researched through both theoretical and experimental methods.1−11 Tellurium has been found to possess some intriguing physical properties and can be a promising material for electronic and optoelectronic devices. Four monolayer Te phases were theoretically predicted, of which one was proven to be unstable at room temperature.1,3 Among the remaining ones, two of them were experimentally synthesized by molecular beam epitaxy.2,4 According to previous reports, α-Te can be obtained on a graphene/6H−SiC(0001) substrate,2 while β-Te was grown on highly oriented pyrolytic graphite.4 Interesting results have arisen when few-layer Te is under external force or charge modulation.5−14 These factors can effectively tune the electronic properties and, noticeably, induce phase transitions.12,13

Electronic property modulation on low-dimensional materials like 2D materials is a hot issue and has been widely investigated.15−20 For instance, application of an electric field has been found to modulate the band gap of the GeC bilayer.15 As reported, an external electric field can also tune the band gap of the SnC/BAs heterostructure linearly and induce a semiconductor-to-metal transition in the presence of a strong electric field.16 Moreover, type-I to type-II or indirect-to-nearly direct transition has been found with an external electric field applied to a 2D type-I α-tellurene/MoS2 heterostructure.17 In addition to theoretical investigations, electric field modulation of the band gap has also been studied experimentally, such as bilayer graphene.18 In this study, although certain manipulated high electric field strength is hardly to be achieved under existing experimental conditions, the behavioral tendencies can be exhibited. Accordingly, the effects of an external electric field applied to monolayer Te are of great interest. To the best of our knowledge, however, related studies are still lacking.

In this paper, the response of the electronic properties of monolayer Te to a perpendicular electric field was systematically studied using first-principles calculations. This paper is organized as follows: first, results including structural and electronic properties of three monolayer Te phases are discussed in Section 2, as is the evolution of electronic properties when subjected to an external electric field; then, conclusions are given in Section 3; finally, detailed computational methods are given in Section 4.

2. RESULTS AND DISCUSSION

2.1. Geometric Structure and Electronic Property of Monolayer Te. With previous reports on the structural properties of 2D Te, four Te phases are proposed and we have chosen three of them to calculate their structural and electronic properties because the remaining one has been proven unstable at temperatures above ~200 °K.1,3 Thus, to investigate their
behavior of structural and electronic properties modulated by the electric field, we adopted such three Te phases which have the same structural features and naming style as reported by Qiao et al.13 Figure 1 presents the top and side views of three different monolayer Te phases and corresponding band structures calculated through PBE + SOC and HSE06 + SOC methods. As is shown in Figure 1, three atoms indicated as orange, gray and blue spheres exist in each optimized unit cell of α-, β-, and γ-Te. Clearly, α- and β-Te both have orthorhombic structures, while γ-Te is hexagonal. The optimized lattice parameters are \( a = 5.99 \, \text{Å}, \, b = 4.48 \, \text{Å} \) for α-Te and \( a = 5.54 \, \text{Å}, \, b = 4.14 \, \text{Å} \) for β-Te, which are in good agreement with present measurements and previous theoretical ones.1,3,4,25 As for γ-Te, it shares the same structure with 1T-MoS\(_2\), with lattice constants \( a = b = 4.15 \, \text{Å} \). Therefore, γ-Te shows isotropic characteristics along X and Y axes based on its isotropic structure, which is different from α- and β-Te. Also, note that α- and β-Te can both be considered as parallel-aligned Te chains from certain angles, as shown in Figure 1a,c. Clearly, α- and β-Te share most structural features and α-Te will turn into β-Te as long as an atom in the helical chain moves toward the adjacent chain. Therefore, we can deduce that α- and β-Te may transform into each other under certain conditions, which is consistent with previous studies.12,13,27 For instance, Xiang et al. found that compression along the in-plane directions facilitates the α to β phase transition.12 Charge doping can also transform the β-bilayer into α-bilayer, according to work by Wang et al.13

Calculated band structures with spin–orbit-coupling (SOC) taken into account are shown in Figure 1 as well. The high symmetry directions are chosen as X−Γ−Y−M−X for α- and β-Te and Γ−M−K−Γ for γ-Te. In α-Te, the conduction band minimum (CBM) is located between the M and X point, while the valance band maximum (VBM) is around the Γ point, which makes α-Te an indirect band gap semiconductor. Similarly, the γ-phase has an indirect band gap, whereas β-Te is regarded as a direct band gap semiconductor with both CBM and VBM located at the Γ point. The obtained band gap from PBE results are 1.08, 1.01, and 0.44 eV for α-, β-, and γ-Te, respectively. Further calculations with the HSE06 approximation give more accurate band gaps of 1.69, 1.41, and 0.65 eV, respectively. Interestingly, a sharp band dispersion of the CBM can be found in γ-Te, which may lead to a small effective mass of electrons and further high electron mobility, consistent with previous findings.1

2.2. Structural Properties under External Electric Field.

The variation of structural properties tuned by external modulations such as strain and charge doping has been investigated.12,13,27 It has been shown that structural transitions can be induced through external modulation. Thus, we have examined the structures under perpendicular electric field carefully. According to our calculations, no phase transition occurs under external electric field as we expected. However, an interesting structural change occurs in α- and γ-Te under a certain electric field strength, \( \varepsilon \), as does a change in structural chirality, whereas no such finding appears in the case of β-Te. Figure 2 presents the top and side views of corresponding atomic configurations in α- and γ-Te. As shown in Figure 2a,b, the chirality changes from a right-handed to a left-handed helical chain under \( \varepsilon = 0.7 \, \text{V/Å} \) in α-Te. As we can see from the bonding situation in an optimized unit cell, it is clear that Te2 atom moves toward the adjacent chain, leading to the realignment of Te bonds. This causes α-Te to change from right-handed into
left-handed configuration, which supports the results in previous work. This investigation found the structural transition of tellurium from right-handed α-type to β-type structure such that a phase transition between the left-handed and right-handed chiral structures in the α-phase could proceed through β-Te with application of external electric field. Similar rearrangement of atoms and then bonding status occurs to γ-Te as well. At ε = 0.3 V/Å, the Te1 atom and Te2 atom exchange their longitudinal position, leading to the change of bonding status. At ε = 0.7 V/Å, things are similar except that the longitudinal positions are exchanged between all three Te atoms.

**Tunable Electronic Properties under External Electric Field.** The dependence of the band gap on the strength of applied perpendicular electric field, ε, for all three monolayer Te configurations are given below in Figure 3. Electric fields are applied from the bottom to top along the z-direction. From Figure 3, it can be seen that the band gaps reduce to 0 eV sharply under a certain electric field, ε, which is 1.0, 0.8, and 0.9 V/Å for α-, β-, and γ-Te, respectively. Before that, they exhibit different patterns between band gap energy and electric field values, with ε ranging from 0 V/Å to εo. For α-Te, its band gap decreases almost linearly with ε increasing from 0 to 0.9 V/Å, while that of β-Te shows a quadratic relation with electric field strength changing from 0 to 0.7 V/Å. When it comes to γ-Te, the relationship between the band gap and electric field value is irregular and the band gap value varies about ~0.5 eV in the range of 0 to 0.8 V/Å. To better understand the electronic properties of monolayer Te under electric field, the variation of valence and conduction bands as a function of electric field strengths are displayed in Figure 4.

From Figure 4a–c, no change is found in the top of the valence bands under external electric field, while the conduction band gradually moves toward the Fermi level in α-Te and β-Te. As for γ-Te, its conduction band varies with the electric field changing from 0 to 0.8 V/Å. Here, it can be seen that the sharp decrease of the band gap under ε, happens because of the fall of the conduction bands under a large electric field strength. What is worth noting is that the band gap of β-Te is more effectively modulated by applied perpendicular electric field when compared to α-Te and γ-Te. In β-Te, its CBM changes from the Γ point to the X point and then to the Γ point with the increase of electric field strength, while the VBM remains at the Γ point, which induces a direct-to-indirect (with ε around 0.1 V/Å) and then an indirect-to-direct (with ε around 0.7 V/Å) band gap transition in β-Te.

Charge density can be helpful to visually understand the respective response of monolayer Te to external electric field. Figure 5 displays the charge density difference (δρ) for (a) α-Te, (b) β-Te, and (c) γ-Te. The given charge density difference is defined as δρ = ρ(ε) − ρ(0), where ρ(ε) is the charge density of the system under ε, and ρ(0) is the charge density without the presence of an electric field. Therefore, the positive δρ value indicates that more electrons are localized with external electric field applied, while the negative value represents the loss of electrons. In Figure 5, the increase of the charge density, that is, the positive δρ value, appears in green and the decrease is shown in purple. Here, the color bars are also given. The values of ε have been chosen to be 1.0, 0.8, and 0.9 V/Å for α-, β-, and γ-Te, respectively. One can deduce from Figure 5 that application of a perpendicular electric field causes charge redistribution, with the electrons being moving outward and the bonds between Te atoms are enhanced in the presence of an electric field. This results in stronger atomic interaction and thus a smaller band gap.

3. CONCLUSIONS

In summary, the structural and electronic properties of three monolayer Te configurations in the presence of external electric field have been investigated through first-principles calculations. According to our calculations, α- and γ-phases show indirect band gaps, whereas β-Te can be regarded as a direct band gap semiconductor. In addition, it was found that application of the external electric field can not only modulate the band gap but also induce a chirality change between left-handed and right-handed chirality in α- and γ-Te under certain electric field strengths. As for the relationship between the band gap and electric field strength, the band gaps decrease to 0 eV eventually under certain electric fields, εo, but different phenomena appear in different structures. The values of εo are 1.0, 0.8, and 0.9 V/Å for α-, β-, and γ-Te, respectively. For α-Te, its relationship can be regarded as linear with ε increasing from 0 to 0.9 V/Å, while that of β-Te shows a quadratic relationship with ε changing from 0 to 0.7 V/Å. As for γ-Te, the relationship between band gap and electric field value is irregular. Moreover, it seems that the electric field has more effective influence on the band gap of β-Te. We believe that our calculations will help advance the understanding of the electronic properties of monolayer Te, so that its application in electronics can be extended.
Figure 4. Valence and conduction bands under different electric field strengths for (a) \( \alpha \)-Te, (b) \( \beta \)-Te, and (c) \( \gamma \)-Te.

Figure 5. Charge density difference \( \delta \rho \) of (a) \( \alpha \)-Te, (b) \( \beta \)-Te, and (c) \( \gamma \)-Te between 0 V/Å and applied electric field \( \varepsilon \) in different structural conformations. The manipulated electric fields are chosen to be 1.0, 0.8, and 0.9 V/Å, respectively, when band gaps vanish. The color bars (unit: e/Å\(^3\)) are also given. Green indicates an increase in the charge density, and purple represents a decrease.

4. COMPUTATIONAL METHODS

All calculations, including structural relaxation and electronic calculations, were carried out using the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).\(^{28-30}\) We employed the generalized gradient approximation using the Perdew–Burke–Ernzerhof (PBE) functional including SOC to evaluate the exchange–correlation potential.\(^{31}\) The electron–ion interactions were treated using the projected augmented wave potentials.\(^{32}\) The valence orbitals and electrons for pseudoatoms were 5s\(^2\) and 5p\(^4\) for Te. In addition, a vacuum layer with a thickness of \(~16\) Å is applied to the z-direction to avoid spurious interactions between layers caused by the periodic boundary condition. The kinetic energy cutoff for the plane-wave basis set was chosen as 500 eV. For structural relaxation, the reciprocal space was meshed at 15 \( \times \) 15 \( \times \) 1 for \( \gamma \)-Te and \( \alpha \)-Te (or \( \beta \)-Te), respectively, using the Monkhorst–Pack method.\(^{33}\) The screened hybrid functional method in the HSE06 level with SOC included is also applied to obtain a more accurate band gap.\(^{34,35}\) The van der Waal interaction was considered with the DFT-D2 method from Grimme.\(^{36}\) All atoms were allowed to relax with the total energy less than 10\(^{-6}\) eV/atom and calculated forces less than 0.01 eV Å\(^{-1}\), and the external electric field is applied along the z-direction.\(^{37-40}\) Here, we impose an \( E \)-field by applying a classical dipole sheet at the middle of the vacuum region in the z-direction. Dipole correction is included in the calculations.

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Notes

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REFERENCES

(1) Zhu, Z.; Cai, X.; Yi, S.; Chen, J.; Dai, Y.; Niu, C.; Guo, Z.; Xie, M.; Liu, F.; Cho, J. H.; Jia, Y.; Zhang, Z. Multivalency-driven formation of Te-based monolayer materials: a combined first-principles and experimental study. Phys. Rev. Lett. 2017, 119, 106101.

(2) Huang, X.; Gao, Z.; Liu, B.; Xie, M.; Li, J.; Xie, M.; Tu, B.; Xing, S.; Zhang, W.; Guo, J. Epitaxial growth and band structure of Te film on graphene. Nano Lett. 2017, 17, 4619–4623.

(3) Qiao, J.; Pan, Y.; Yang, F.; Wang, C.; Chai, Y.; Ji, W. Few-layer tellurium: one-dimensional-like layered elementary semiconductor with striking physical properties. Sci. Bull. 2018, 63, 159–168.

(4) Chen, J.; Dai, Y.; Ma, Y.; Dai, X.; Ho, W.; Xie, M. Ultrathin beta-tellurium layers grown on highly oriented pyrolytic graphite by molecular-beam epitaxy. Nanoscale 2017, 9, 15945–15948.

(5) Wu, L.; Huang, W.; Wang, Y.; Zhao, J.; Ma, D.; Xiang, Y.; Li, J.; Ponny, J. S.; Dhanabal, S. C.; Zhang, H. 2D Tellurium Based High-Performance All-Optical Nonlinear Photonic Devices. Adv. Funct. Mater. 2019, 29, 1806346.

(6) Rikken, G. L. J. A.; Avarvari, N. Strong electrical magnetochiral anisotropy in tellurium. Phys. Rev. B 2019, 99, 245153.

(7) Liu, G.; Gao, Z.; Ren, J. Anisotropic thermal expansion and thermodynamic properties of monolayer β-Te. Phys. Rev. B 2019, 99, 195436.

(8) Han, J. C.; Wu, C. Y.; Sun, L.; Gong, H. R.; Gong, X. Influence of trigonal deformation on band structure and Seebeck coefficient of tellurium. J. Phys. Chem. Solids 2019, 135, 109114.

(9) Guo, Y.; Wang, S.; Jia, Y.; Su, W.-S. Structural, electronic, and optical properties of α-Te tubular nanostructures: A first-principles study. APL Mater. 2019, 7, 031105.

(10) Yan, J.; Zhang, X.; Pan, Y.; Li, J.; Shi, B.; Liu, S.; Yang, J.; Song, Z.; Zhang, H.; Ye, M.; Quehe, R.; Wang, Y.; Yang, J.; Pan, F.; Lu, J. Monolayer tellurene—metal contacts. J. Mater. Chem. C 2018, 18217–18219.

(11) Wang, Y.; Xiao, C.; Chen, M.; Hua, C.; Zou, J.; Wu, C.; Jiang, J.; Yang, S. A.; Lu, Y.; Ji, W. Two-dimensional ferroelectricity and switchable spin-textures in ultra-thin elemental Te multilayers. Mater. Horiz. 2018, 5, 521–528.

(12) Xiang, Y.; Gao, S.; Xu, R.; G.; Wu, W.; Leng, Y. Phase transition in two-dimensional tellurene under mechanical strain modulation. Nano Energy 2019, 58, 202–210.

(13) Wang, C.; Zhou, X.; Qiao, J.; Zhou, L.; Kong, X.; Pan, Y.; Cheng, Z.; Chai, Y.; Ji, W. Charge-governed phase manipulation of few-layer tellurium. Nanoscale 2018, 10, 22263–22269.

(14) Zhang, W.; Wu, Q.; Yazeyev, O. V.; Weng, H.; Guo, Z.; Cheng, W.-D.; Chai, G.-L. Topological phase transitions driven by strain in monolayer tellurium. Phys. Rev. B 2018, 99, 151407.

(15) Liu, M.-Y.; Huang, Y.; Chen, Q.-Y.; Li, Z.-Y.; Cao, C.; He, Y. Strain and electric field tunable electronic structure of buckled bismuthene. RSC Adv. 2017, 7, 39546–39553.

(16) Nigam, S.; Gupta, S. K.; Majumder, C.; Pandey, R. Modulation of band gap by an applied electric field in silicone-based hetero-bilayers. Phys. Chem. Chem. Phys. 2015, 17, 11324–11328.

(17) Ou, Y. C.; Chiu, Y. H.; Lu, J. M.; Su, W. P.; Lin, M. F. Electric modulation effect on magneto-optical spectrum of monolayer graphene. Comput. Phys. Commun. 2013, 184, 1821–1826.

(18) Tsai, S.-J.; Ho, J.-H.; Chiu, Y.-H.; Lin, M.-F. Band structures of Bernal graphene modulated by electric fields. Physica E 2010, 42, 2796–2798.

(19) Xue, X.-X.; Feng, Y.-X.; Liao, L.; Chen, Q.-J.; Wang, D.; Tang, L.-M.; Chen, K. Strain tuning of electronic properties of various dimension tellurium with broken screw symmetry. J. Phys.: Condens. Matter 2018, 30, 125001.

(20) Mak, K. F.; Liu, C. H.; Shan, J.; Heinz, T. F. Observation of an Electric-Field-Induced Band Gap in Bilayer Graphene by Infrared Spectroscopy. Phys. Rev. Lett. 2009, 102, 256405.

(21) Wang, J.; Guo, Y.; Qiao, C.; Shen, H.; Zhang, R.; Zheng, Y.; Chen, L.; Wang, S.; Jia, Y.; Su, W.-S. Investigation of electronic property modulation driven by strain in monolayer tellurium. Chin. J. Phys. 2019, 62, 172–178.

(22) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169–11186.

(23) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50.

(24) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758–1775.

(25) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865–3868.

(26) Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953–17979.

(27) Monkhorst, H. J.; Pack, D. Special points for Brillouin-zone integrations. Phys. Rev. B: Solid State 1976, 13, 5188–5192.

(28) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. J. Chem. Phys. 2003, 118, 8207–8215.

(29) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. J. Chem. Phys. 2006, 125, 224106.

(30) Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 2006, 27, 1787–1799.

(31) Neugebauer, J.; Scheffler, M. Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111). Phys. Rev. B: Condens. Matter Mater. Phys. 1992, 46, 16067–16080.

(32) Feibelman, P. J. Surface-diffusion mechanism versus electric field. Phys. Rev. Lett. 2001, 86, 224106.