



Swansea University
Prifysgol Abertawe



Cronfa - Swansea University Open Access Repository

This is an author produced version of a paper published in:
IEEE Transactions on Nanotechnology

Cronfa URL for this paper:
<http://cronfa.swan.ac.uk/Record/cronfa38744>

Paper:

Deng, S., Zhang, Y. & Li, L. (2018). Strain magnitude and direction effect on the energy band structure of hexagonal and orthorhombic monolayer MoS₂. *IEEE Transactions on Nanotechnology*, 1-1.
<http://dx.doi.org/10.1109/TNANO.2018.2805770>

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

<http://www.swansea.ac.uk/library/researchsupport/ris-support/>

Strain magnitude and direction effect on the energy band structure of hexagonal and orthorhombic monolayer MoS₂

Shuo Deng, Yan Zhang, Lijie Li, *Senior Member, IEEE*

Abstract—We report changes of the band structure of hexagonal and orthorhombic cells of the monolayer molybdenum disulfide (MoS₂) subject to various magnitude and direction of the mechanical strains based on the first principle method. The conduction band minimum (CBM) of this two-dimensional (2D) material has been calculated to establish the relation with both the magnitude and direction of the strains. It is found that the CBM at Γ point of the hexagonal cell decreases in a slight concave shape for the tensile strain, and a convex shape for the compressive strain. For the orthorhombic cell, we demonstrate that the effect is almost independent on the direction of the applied tensile strain. However, there is a strong directional dependence for compressive strain.

Index Terms—Band structure, MoS₂, Mechanical strain

I. INTRODUCTION

THE transition-metal dichalcogenide semiconductor molybdenum disulfide (MoS₂) has attracted much attention owing to its superior electronic, optical, and catalytic properties [1] [2] [3] [4]. It has been found that the monolayer has several distinctive electronic and optical properties including a direct bandgap with a band gap of about 1.8eV [2], strong excitonic effects [5] [6] [7] [8] and the possibility of full optical control of the valley and spin occupation [9] [10] [11] [12]. These properties will significantly enhance the potential in applications such as lithium ion battery [13] and nanoelectromechanical systems (NEMS) devices [14]. A vast number of first principle calculations [15] [16] [17] [18] and experiments [19] have been recently reported that under large mechanical strains, the band gap of the monolayer MoS₂ changed from direct to indirect, more specifically the band gap has been narrowed, eventually leading to the CBM plunge to below the Fermi level [16] [18]. This implicates that the material becomes exhibiting metal properties. However, the study on the directional dependence of the mechanical strain has not been conducted so far. It is worth to state that in the real applications it would be hard to have a mechanical strain precisely along a certain direction and magnitude. Hence the critical issue is to study the band structure under strain in

various magnitudes and directions. In this work, we investigate the band structure of hexagonal and orthorhombic monolayer MoS₂ cells under a wide range of strain magnitudes in different directions with various amplitudes using first principle method. This theoretical method has been used in many previous studies on 2D materials [15], [16], [20]–[22]. Our aim is to theoretically explore the impact on the band structure of hexagonal monolayer MoS₂ i.e. CBM and band gap when the material undergoes mechanical strains. Furthermore, the directional properties of strains acting on the orthorhombic monolayer MoS₂ transition will be explored. The effect of various directions and magnitudes of strains on the monolayer MoS₂ will be detailed in the following sections of this paper.

II. COMPUTATIONAL METHOD

We start modelling the monolayer MoS₂ by creating two types of crystal cells using the Atomistix ToolKit (ATK) [23] simulation tools. Based on a lattice constant of MoS₂ bulk ($a=b=3.16\text{\AA}$) [24] [25] [26], and the arrangements with the bond length between S and Mo being 2.40\AA , the initial model of monolayer MoS₂ is established. Shown in the Figure 1a and 1b, the hexagonal cell of monolayer MoS₂ can be viewed as cleaved from the (0001) surface of bulk MoS₂, where one Mo atom binds to six S atoms covalently. For the hexagonal cell, in order to maintain the crystal symmetry, the strain has to be applied in both the $a-$ and $b-$ directions. Figure 1c and 1d show that the orthorhombic cell of monolayer MoS₂. We define the $a'-$ and $b'-$ direction along the armchair and zigzag edge, respectively. We can apply a strain in any direction within the x/y plane.

The energy band of the monolayer MoS₂ is calculated by the density functional theory (DFT) using ATK. We use the generalized gradient approximation (GGA) with the parametrization of Perdew-BurkeErnzerhof (PBE) [27], mush cut-off energy of 75 Hartree and $9\times 9\times 1$ k -point grid are used for the relaxation calculations. A large vacuum spacing of at least 20\AA is added along the z -direction to avoid the interactions that arises while calculating the periodic boundary conditions. In order to optimize the geometries, we have utilized the Limited-memory Broyden Fletcher Goldfarb Shanno (LBFGS) algorithm [24] with the maximum stress tolerance value of 0.05 eV/\AA^3 . The structure is fully relaxed until the force on each atom becomes smaller than 0.01 eV/\AA . The strain is simulated by setting the lattice parameter to a fixed larger value

S. Deng is with School of Logistic, Wuhan University of Technology. Y. Zhang is with School of Physics, School of Physical Electronics, University of Electronic Science and Technology of China. L. Li is with the college of engineering, Swansea University, Swansea, UK, SA1 8EN. Email: l.li@swansea.ac.uk

The authors would like to thank Swansea University for support.
Manuscript accepted February 2018

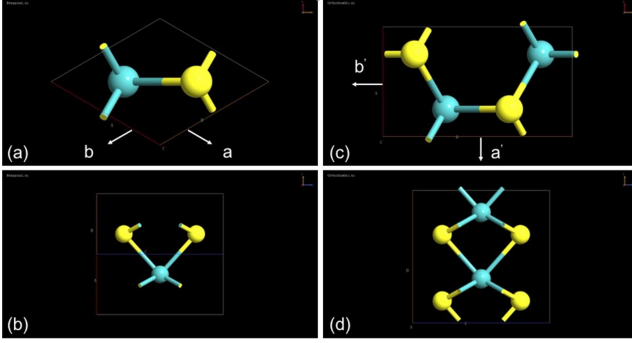


Fig. 1. Schematic graphs of the MoS₂ cells: (a) Top views of hexagonal MoS₂ cell, where a - and b - directions are defined; (b) Side views of hexagonal MoS₂ cell; (c) Top views of orthorhombic MoS₂ cells, where a' - and b' - directions are defined; (d) Side views of orthorhombic MoS₂ cell.

and relaxing the atomic positions. The magnitude of strain is defined as: $\epsilon = (a - a_0)/a_0$, where a_0 and a are the lattice parameters of the unstrained and strained cells, respectively. Using the DFT-GGA calculations, we show that the band gap of monolayer MoS₂ is 1.76 eV which is very close to recent DFT calculations [28] [29] [30] [31] [32], but slightly smaller than that measured using complementary techniques of optical absorption, photoluminescence and photoconductivity (1.80 eV) of monolayer thick MoS₂ [2]. The band gap problem can be addressed more accurately by the different exchange correlation approximations which have not been carried out in this paper. However, this trend is not generalized, which depends on the material considered. Therefore, we believe that our choice of using the DFT-GGA for the MoS₂ structure is appropriate.

III. RESULTS AND ANALYSIS

Firstly, the hexagonal cell has been simulated subjecting to $\epsilon > 0$ and $\epsilon < 0$. The strains are evaluated as the lattice stretching percentage. A wide range of strain along (up to 13%) both directions has been employed in the study. The band structure was calculated for the path through $\Gamma - M - K - \Gamma$ points. It is seen in the Figure 2 that the CBM was observed to move toward 0 eV. At very large strains the CBM plunges to below 0 eV. The $\epsilon > 0$ (tensile strains) leads to a slight concave shape, whilst $\epsilon < 0$ (compressive strains) causes a convex shape. The threshold strain for the tensile strain is at around 11%, and 12% for the compressive strain. Figure 2 also shows that the total energy of monolayer MoS₂ under compressive strain is higher than the tensile strain. When the compressive strain is applied, the semiconducting MoS₂ monolayer turns out to be less stable than under the tensile strain.

The bold black lines in Figures 3 and 4 are the energy bands when there is no strain is applied. It is also found that the tensile strain causes the energy band in K point decreasing as the value of strain increases (Figure 3). The band structure has also changed from a direct bandgap to an indirect bandgap when $3\% < \epsilon < 11\%$ and the metal-semiconductor transition occurs in $\epsilon > 11\%$. It is also shown that the valence band maximum (VBM) of the energy band at Γ increases with the increasing strain. For a compressive strain (Figure 4) the trend

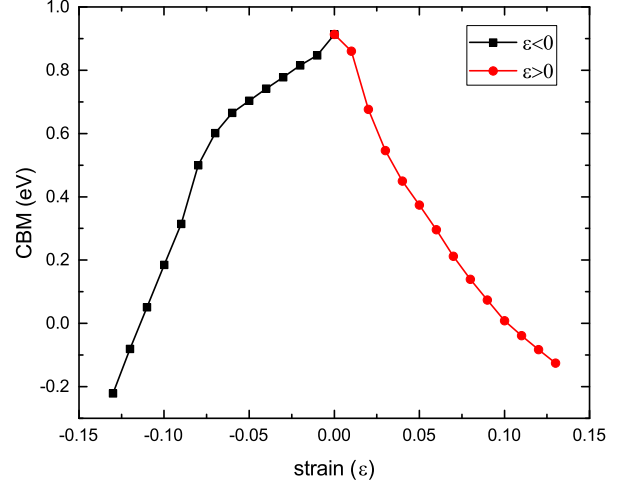


Fig. 2. CBM vs. strains ($\epsilon > 0$ and $\epsilon < 0$) for the hexagonal MoS₂ cell.

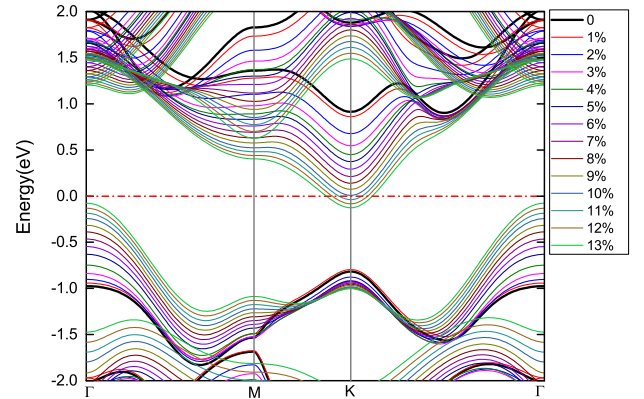


Fig. 3. Energy band structures of the hexagonal MoS₂ cell under tensile strain in a - and b - directions. The ratio of a/b remains unchanged.

is similar as shown in Figure 3, it transits into indirect semiconductor within region $1\% < \epsilon < 12\%$, when $\epsilon > 12\%$, the monolayer MoS₂ experiences semiconductor-metal transition. However, the CBM of an energy band decreases more rapidly at the middle of points K and Γ , which is different with Figure 3. Analysis of the partial density of states indicates that the CBM is mainly contributed to by Mo-4d orbitals, while the VBM is contributed to by Mo-4d and S-3p orbitals [15] [16] [17]. Mo-4d and S-3p orbitals are together hybridized at the VBM. It means that a strong bonding exists between Mo and S atoms. The mirror symmetrical bonding configuration in the tri-layer S-Mo-S system results in a weak π bond-like interaction, which is very sensitive to the variation of the distances between the atoms. Application of compressive strains on MoS₂ decreases the Mo-Mo and Mo-S bond length. The effect is an increase in the Mo- d orbital and S- p orbital

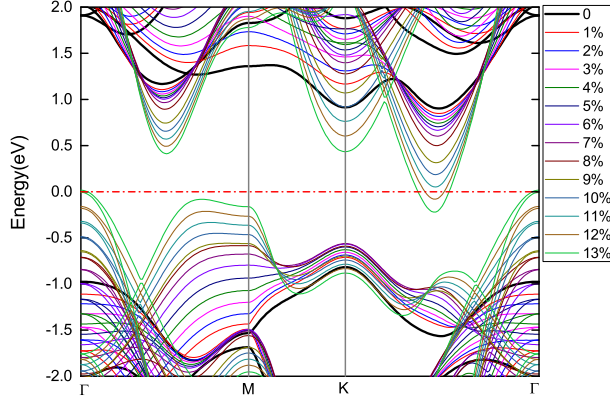


Fig. 4. Energy band structures of the hexagonal MoS₂ cell under compressive strain in a - and b - directions. The ratio of a/b remains unchanged.

coupling. However, for the tensile strains, the Mo-Mo and Mo-S bond length increases. The net effect is a reduction in the Mo- d orbital and S- p orbital coupling. As a result, the CBM change under compressive strain decreases more rapidly than under tensile strain. Although the decline of the CBM is difficult to elucidate analytically, simple atomic chain model can be used to qualitatively interpret the DFT results. From the model, the changing of the energy band is mostly due to the change of the interaction energy between an atom and its nearest two atoms assuming the overlap of the atomic orbitals to be negligible. So the total energy of the system E_t is the sum of the energy of an electron in one atomic orbital E_s and the interaction energy E_i multiplying N (where N is total number of electrons), which is $E_t = N(E_s + E_i)$. E_t can be derived from the Bloch equation that describes electron wavefunction in a chain of atoms, $E_t = \int \psi_k^* H \psi_k$, where $\psi_k(x) = \sum e^{iknd} \phi_n(x)$. Here n is the atom number, d is the lattice spacing. Then the E_i can be expanded to $E_i = N(e^{-ikd} + e^{ikd}) \int \phi_k^* H \phi_k$. This model qualitatively explains that a stronger orbital interaction causes the bands to become more disperse (higher energy values). For the tensile strains on the hexagonal cell, the atoms are brought further apart, leading to reduced interaction energy, subsequently reducing the total energy. Eventually the CBM declines to the Fermi level at very large tensile strain. For the compressive strain on the hexagonal cell, it is more complicated, the point in between K and Γ is affected by the compressive strain, where the energy reduces significantly. The energy at K point actually increases at small strains (Figure 4), which aligns with the simplified model prediction.

For the orthorhombic cell, the strain can actually have a random direction. Hence we are able to investigate the CBM of the energy band due to strain in directions between a' - and b' -. Firstly, the simulation was conducted by setting the a -direction tensile strain increasing from $\epsilon = 0$ to around $\epsilon = 17\%$, and then repeating the calculation when b' -direction tensile strain increases by a small step. In this

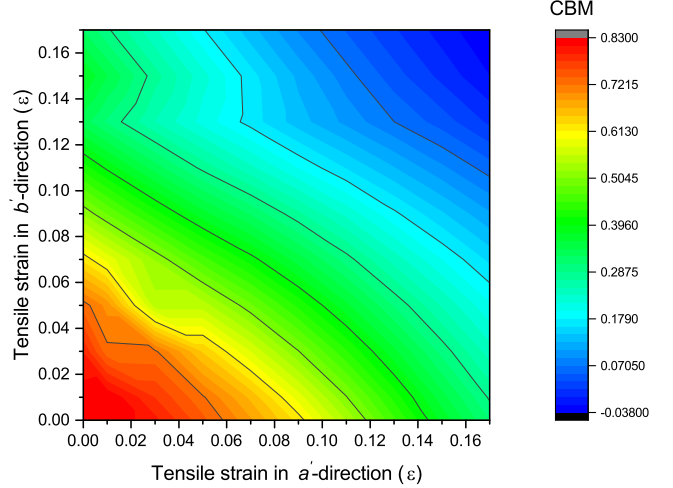


Fig. 5. 3D plot of the orthorhombic MoS₂ cell under tensile strains in both a' - and b' - directions.

way, the strain direction between a' - and b' - that leads to the most notable change of the CBM can be obtained. It is seen from the simulation results in the Figure 5 that applying tensile strains in only a' - or b' - does not cause semiconductor-to-metal transition up to the maximum strain of 17%. When the combined tensile strains are at around middle of the a' - and b' - (45) direction, it causes the CBM to plunge towards zero at $\epsilon_a = \epsilon_b = 16\%$, corresponding a total strain of $\sqrt{\epsilon_a^2 + \epsilon_b^2} = 22.6\%$. From the Figure 5, it can be concluded that for the tensile strain, the effect on the band structure is almost independent on the direction of the strain, as indicated by the black contour lines (nearly straight lines at the angle of 135° to the horizontal axis). Similar approaches have been used to calculate the CBM of energy band under the compressive strain. Calculation results in Figure 6 display a strong directional dependence effect. More specifically, contour lines are approximately parallel to the vertical and horizontal axes forming a right angle facing to the origin. This implicates that the CBM declines more quickly under a pure a' - or b' - axis strain than the strains along the 45° angle between a' - and b' -. Numerically the CBM plunges towards 0 eV at the strain magnitude of 13% in pure a' - or b' - direction, 17% in the 45° direction.

The direction independent absolute strain with the relation to the CBM has been plotted in Figures 7 and 8. The absolute strain is defined as: $|\epsilon| = (\epsilon_a^2 + \epsilon_b^2)^{1/2}$, where $|\epsilon|$, ϵ_a and ϵ_b are the absolute strain, a - and b - directional strain. Figures 7 and 8 show the semiconductor-to-metal transition at the absolute tensile strain of 22%, while this percentage for absolute compressive strain is 17%. These results agree closely with the one obtained in Figures 5 and 6.

In Figures 5 and 6, the CBM is independent on the direction of strains, as the ratio of the lattice dimensions are unchanged. With regards to the orthorhombic cell, strain in pure a -/ b - direction induces a quicker effect on the reduction of the CBM, which is envisaged as the consequence of the combined effect

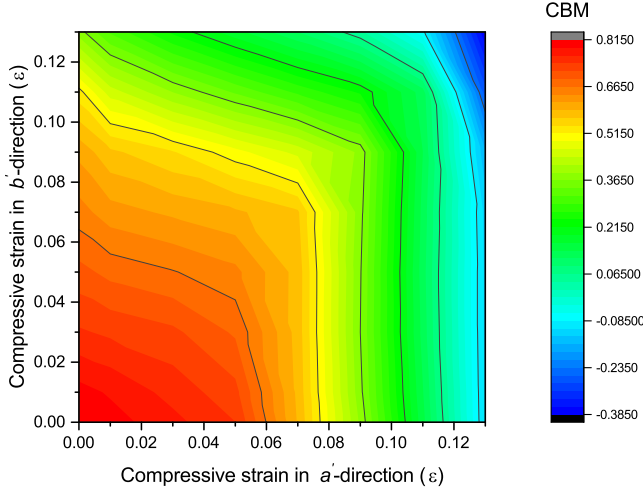


Fig. 6. 3D plot of the orthorhombic MoS₂ cell under compressive strains in both a' - and b' - directions.

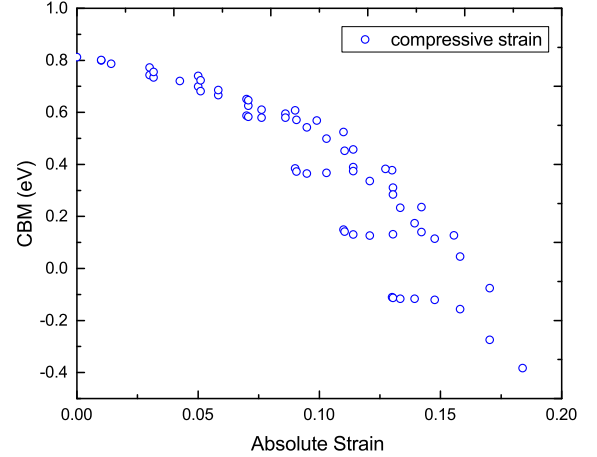


Fig. 8. Absolute compressive strain (angle independence) vs. CBM.

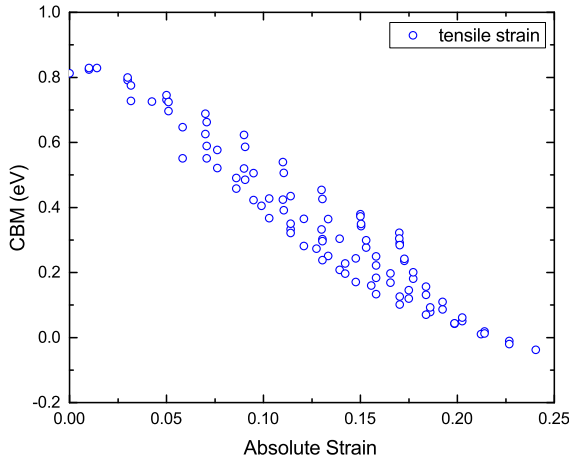


Fig. 7. Absolute tensile strain (angle independence) vs. CBM.

from both the broken crystal symmetry and the reduced interaction energy. However for the strain with the direction in 45° between a' - and b' -, it is only the effect from the interaction energy, the crystal structure still remains symmetric. The study will have potential applications in engineering nanometer sized strain sensors or mechanically adjustable resistive switching devices. In our work, we intended to unveil the threshold strain points at which the CBMs reach to 0 eV. Although the monolayer MoS₂ may have a breaking strain at a lower strain than the maximum value used in the analysis, it will be interesting to theoretically widen the strain range to find out this threshold point in terms of the magnitude and direction of the strains.

IV. CONCLUSION

It can be concluded from our analysis that, for the 2D monolayer MoS₂, the band structure changes significantly

subjecting to a large mechanical strain. For the orthorhombic cell, applying tensile strains in only a' - and b' - does not cause semiconductor-to-metal transition up to the maximum strain of 17%. When the combined strains are at around middle of the a' - and b' - (45°) direction, it causes the CBM plunge towards 0 at $\epsilon_a = \epsilon_b = 16\%$. For the compressive strains, the CBM declines more quickly under a pure a' - and b' - axis strain than the strains along the 45° angle between a' - and b' -. Numerically the CBM plunges towards 0 eV at the strain magnitude of about -13% in pure a' - and b' - direction, -17% in the 45° direction. The study reported here reveals that CBM at Γ of hexagonal cell decrease in a slight concave shape for the tensile strain, and convex shape for the compressive strain. For the orthorhombic cell, strain at middle of the a' - and b' - (45°) has less effect on the CBM than strain in pure a' - / b' - directions. Our calculation shows that the absolute strain leading to the threshold of the semiconductor-to-metal transition is 22% and 17% for tensile strain and compressive strain respectively. This study paves the way for further exploitation of 2D MoS₂ in tunable electronic device.

ACKNOWLEDGEMENTS

This work is supported by the SPARC II project. We would like to thank Wuhan University of Technology, China and Swansea University, UK for support. China Scholarship Council is also appreciated for support.

REFERENCES

- [1] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer mos2 transistors," *Nature Nanotechnology*, vol. 6, no. 3, pp. 147–150, 2011.
- [2] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically thin mos2: A new direct-gap semiconductor," *Physical Review Letters*, vol. 105, no. 13, p. 136805, 2010.
- [3] L. Li and Y. Zhang, "Controlling the luminescence of monolayer mos2 based on the piezoelectric effect," *Nano Research*, pp. 1–8, 2017.
- [4] X. Huang, W. Liu, A. Zhang, Y. Zhang, and Z. Wang, "Ballistic transport in single-layer mos2 piezotronic transistors," *Nano Research*, vol. 9, no. 2, pp. 282–290, 2016.

- [5] K. F. Mak, K. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, and J. Shan, "Tightly bound trions in monolayer mos₂," *Nature Materials*, vol. 12, no. 3, pp. 207–211, 2013.
- [6] J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, and X. Xu, "Electrical control of neutral and charged excitons in a monolayer semiconductor," *Nature Communications*, vol. 4, p. 1474, 2013.
- [7] T. Cheiwchanchamnangij and W. R. L. Lambrecht, "Quasiparticle band structure calculation of monolayer, bilayer, and bulk mos₂," *Physical Review B*, vol. 85, no. 20, p. 205302, 2012.
- [8] A. Ramasubramaniam, "Large excitonic effects in monolayers of molybdenum and tungsten dichalcogenides," *Physical Review B*, vol. 86, no. 11, p. 115409, 2012.
- [9] H. Zeng, J. Dai, W. Yao, D. Xiao, and X. Cui, "Valley polarization in mos₂ monolayers by optical pumping," *Nature Nanotechnology*, vol. 7, no. 8, pp. 490–493, 2012.
- [10] T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, Q. Niu, P. Tan, E. Wang, B. Liu, and J. Feng, "Valley-selective circular dichroism of monolayer molybdenum disulfide," *Nature Communications*, vol. 3, p. 887, 2012.
- [11] G. Sallen, L. Bouet, X. Marie, G. Wang, C. R. Zhu, W. P. Han, Y. Lu, P. H. Tan, T. Amand, B. L. Liu, and B. Urbaszek, "Robust optical emission polarization in mos₂ monolayers through selective valley excitation," *Physical Review B*, vol. 86, no. 8, p. 081301, 2012.
- [12] S. Wu, J. S. Ross, G.-B. Liu, G. Aivazian, A. Jones, Z. Fei, W. Zhu, D. Xiao, W. Yao, D. Cobden, and X. Xu, "Electrical tuning of valley magnetic moment through symmetry control in bilayer mos₂," *Nature Physics*, vol. 9, no. 3, pp. 149–153, 2013.
- [13] M. Shanmugam, C. A. Durcan, and B. Yu, "Layered semiconductor molybdenum disulfide nanomembrane based schottky-barrier solar cells," *Nanoscale*, vol. 4, no. 23, pp. 7399–7405, 2012.
- [14] K. F. Mak, K. L. McGill, J. Park, and P. L. McEuen, "The valley hall effect in mos₂ transistors," *Science*, vol. 344, no. 6191, pp. 1489–1492, 2014.
- [15] E. Scalise, M. Houssa, G. Pourtois, V. Afanasev, and A. Stesmans, "Strain-induced semiconductor to metal transition in the two-dimensional honeycomb structure of mos₂," *Nano Research*, vol. 5, no. 1, pp. 43–48, 2012.
- [16] C. V. Nguyen, V. V. Ilyasov, H. V. Nguyen, and H. N. Nguyen, "Band gap and electronic properties of molybdenum disulfide under strain engineering: density functional theory calculations," *Molecular Simulation*, vol. 43, no. 2, pp. 86–91, 2017.
- [17] Q. Yue, J. Kang, Z. Shao, X. Zhang, S. Chang, G. Wang, S. Qin, and J. Li, "Mechanical and electronic properties of monolayer mos₂ under elastic strain," *Physics Letters A*, vol. 376, no. 1213, pp. 1166–1170, 2012.
- [18] P. Johari and V. B. Shenoy, "Tuning the electronic properties of semiconducting transition metal dichalcogenides by applying mechanical strains," *ACS Nano*, vol. 6, no. 6, pp. 5449–5456, 2012.
- [19] K. He, C. Poole, K. F. Mak, and J. Shan, "Experimental demonstration of continuous electronic structure tuning via strain in atomically thin mos₂," *Nano Letters*, vol. 13, no. 6, pp. 2931–2936, 2013.
- [20] M. Ghorbani-Asl, S. Borini, A. Kuc, and T. Heine, "Strain-dependent modulation of conductivity in single-layer transition-metal dichalcogenides," *Physical Review B*, vol. 87, no. 23, p. 235434, 2013, pRB.
- [21] M. G. Senosy, D. Vinichenko, W. Chen, C. M. Friend, and E. Kaxiras, "Strain effects on the behavior of isolated and paired sulfur vacancy defects in monolayer mos₂," *Physical Review B*, vol. 95, no. 1, p. 014106, 2017, pRB.
- [22] P. Lu, X. Wu, W. Guo, and X. C. Zeng, "Strain-dependent electronic and magnetic properties of mos₂ monolayer, bilayer, nanoribbons and nanotubes," *Physical Chemistry Chemical Physics*, vol. 14, no. 37, pp. 13 035–13 040, 2012.
- [23] "http://quantumwise.com/, quantumwise atomistic toolkit (atk)."
- [24] K. K. Kam and B. A. Parkinson, "Detailed photocurrent spectroscopy of the semiconducting group vib transition metal dichalcogenides," *The Journal of Physical Chemistry*, vol. 86, no. 4, pp. 463–467, 1982.
- [25] P. A. Young, "Lattice parameter measurements on molybdenum disulfide," *Journal of Physics D: Applied Physics*, vol. 1, no. 7, p. 936, 1968.
- [26] T. Bker, R. Severin, A. Miller, C. Janowitz, R. Manzke, D. Vo, P. Krger, A. Mazur, and J. Pollmann, "Band structure of mos₂, mose₂, and alpha-mote₂: Angle-resolved photoelectron spectroscopy and ab initio calculations," *Physical Review B*, vol. 64, no. 23, p. 235305, 2001.
- [27] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters*, vol. 77, no. 18, pp. 3865–3868, 1996.
- [28] S. Lebgue and O. Eriksson, "Electronic structure of two-dimensional crystals from ab initio theory," *Physical Review B*, vol. 79, no. 11, p. 115409, 2009.
- [29] H. S. S. RamakrishnaMatte, A. Gomathi, A. Manna, D. Late, R. Datta, S. Pati, and C. N. R. Rao, "Mos₂ and ws₂ analogues of graphene," *Angewandte Chemie International Edition*, vol. 49, no. 24, pp. 4059–4062, 2010.
- [30] A. Kuc, N. Zibouche, and T. Heine, "Influence of quantum confinement on the electronic structure of the transition metal sulfide ts₂," *Physical Review B*, vol. 83, no. 24, p. 245213, 2011.
- [31] A. H. Reshak and S. Auluck, "Calculated optical properties of 2h-mos₂ intercalated with lithium," *Physical Review B*, vol. 68, no. 12, p. 125101, 2003.
- [32] —, "Band structure and optical response of 2h-mox₂ compounds (x=s, se, and te)," *Physical Review B*, vol. 71, no. 15, p. 155114, 2005.

Shuo Deng is currently a visiting student at college of engineering, Swansea University, UK. His research interests is in first principles study.

Yan Zhang is a professor at School of Physics, School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu. His research interests are in NEMS, piezotronics, piezo-phototronics, semiconductor, nanotechnology.

Lijie Li (SM'10) is an associate professor at college of engineering, Swansea University, UK. His research interests are in MEMS, NEMS, sensors and actuators, piezotronics.