Stability and electronic properties of two dimensional pentagonal layers of palladium chalcogenides

Cite as: AIP Conference Proceedings **2115**, 030387 (2019); https://doi.org/10.1063/1.5113226
Published Online: 12 July 2019

Ashok Kumar, Mukesh Jakhar, Sunita Srivastava, and K. Tankeshwar

Stability and Electronic Properties of Two Dimensional Pentagonal Layers of Palladium Chalcogenides

Ashok Kumar[1,a)], Mukesh Jakhar[1], Sunita Srivastava[2,3] and K. Tankeshwar[2,3]

[1]*Department of Physical Sciences, School of Basic and Applied Sciences, Central University of Punjab, Bathinda, 151001, India*
[2]*Department of Physics, Panjab University, Chandigarh-160014, India*
[3] *Department of Physics, Guru Jambheshwar University of Science and Technology, Hisar, Haryana-125001, India 151001*

[a)]Corresponding Author: ashokphy@cup.edu.in

Abstract. We report structural and electronic properties of pristine and hybrid monolayers/bilayers of Pd chlcogenides within state-of-the-art density functional theory (DFT) calculations. The calculated cohesive energy suggests hybrid systems to be more stable than pristine monolayer/bilayer system. The considered structures show indirect band gap which get reduced on going from monolayer to bilayers. Spin-orbit coupling (SOC) further reduce the bandgap by shifting the band edges towards Fermi level. The reduction in band gap of hybrid bilayers is more pronounced which is attributed to the electronegativity difference between chalcogen S/Se atoms and greater charge redistribution between the layers. We believe that our theoretical study will add more 2D materials in the fascinating class of new 2D family and may guide the experimentalists to realize them for various future nano-electronic applications.

INTRODUCTION

Since the discovery of graphene, the investigations of two dimensional (2D) crystals have gained great deal of attention [1-4]. Graphene, being a first 2D crystal, possess superior electronic properties due to the presence Dirac-cone features at the Fermi level that leads to the very high electronic conductivity. However, graphene is zero gap 2D material that limits its applications in nanoscale devices such as transistor technology. Among the other 2D materials, layered transition metal dichalcogenides (TMDs) are more versatile due to the presence of inherent band gap [5]. Notably, most of the stable 2D materials are found to exists in hexagonal structure. However, 2D $PdSe_2$ has been found to possess stable pentagonal rings structure [6]. Transistor based on 2D $PdSe_2$ has been successfully fabricated that shows tunable ambipolar characteristics [7]. Also, very recently, $PdSe_2$ bilayers are experimentally synthesized on graphene substrate [8] which are expected to play important role in the future nanoelectronic device fabrications.

Motivated by these studies, we have investigated the structural and electronic properties of pristine and hybrid mono as well as bilayers of $PdSe_2$. The effect of spin orbit coupling (SOC) on the electronic structure of pristine $PdSe_2$ and hybrid (PdSSe) monolayer has been investigated. Electronic structure of pristine and hybrid bilayers has also been quantified in terms of charge density distribution profiles.

COMPUTATIONAL DETAILS

Electronic structure calculations were performed using density functional theory (DFT) as implemented in Vienna ab initio simulation package (VASP) [9]. Generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) parameterization is used to describe exchange correlation functional. We have included the spin-orbit coupling (SOC) effects in our calculations. A cutoff energy of 450 eV for the plane wave basis set and a Monkhorst–Pack mesh of (12 x 12 x 1) for Brillouin zone integration were employed. A 15 Å vacuum region along

DAE Solid State Physics Symposium 2018
AIP Conf. Proc. 2115, 030387-1–030387-4; https://doi.org/10.1063/1.5113226
Published by AIP Publishing. 978-0-7354-1851-6/$30.00

z-direction ensures the modelling of a 2D crystal. All the structures are fully relaxed, with residual forces smaller than 0.01 eV/Å on each atom.

RESULTS AND DISCUSSION

The monolayers of $PdSe_2$ has six atoms in nearly square unit cell with lattice parameters : a= 5.75 Å and b=5.92 Å. The thickness of monolayer is calculated to be 1.53 Å [Table 1]. The lattice parameters and thickness of hybrid

Table 1: Lattice parameters (a,b), thickness (T), cohesive energy (E_c) and band gap (E_g) of mono and bilayer of Pd diselenide. Interlayer distance and binding energy of bilayers are also given.

	Monolayer		**Bilayer**	
	$PdSe_2$	**PdSSe**	**$PdSe_2/PdSe_2$**	**$PdSe_2/PdS_2$**
Lattice Parameters (a,b) [in Å]	5.75, 5.92	5.62, 5.76	5.77, 5.91	5.60, 5.73
T [in Å]	1.53	1.39	6.07 (3.05)[#]	6.04 (3.00)[#]
E_c [in eV/atom]	2.69	2.71	2.70 (0.011)[$]	2.72 (0.103)[$]
E_g [in eV]	1.31	1.23	0.97	0.55
[#] interlayer separation, [$] binding energy				

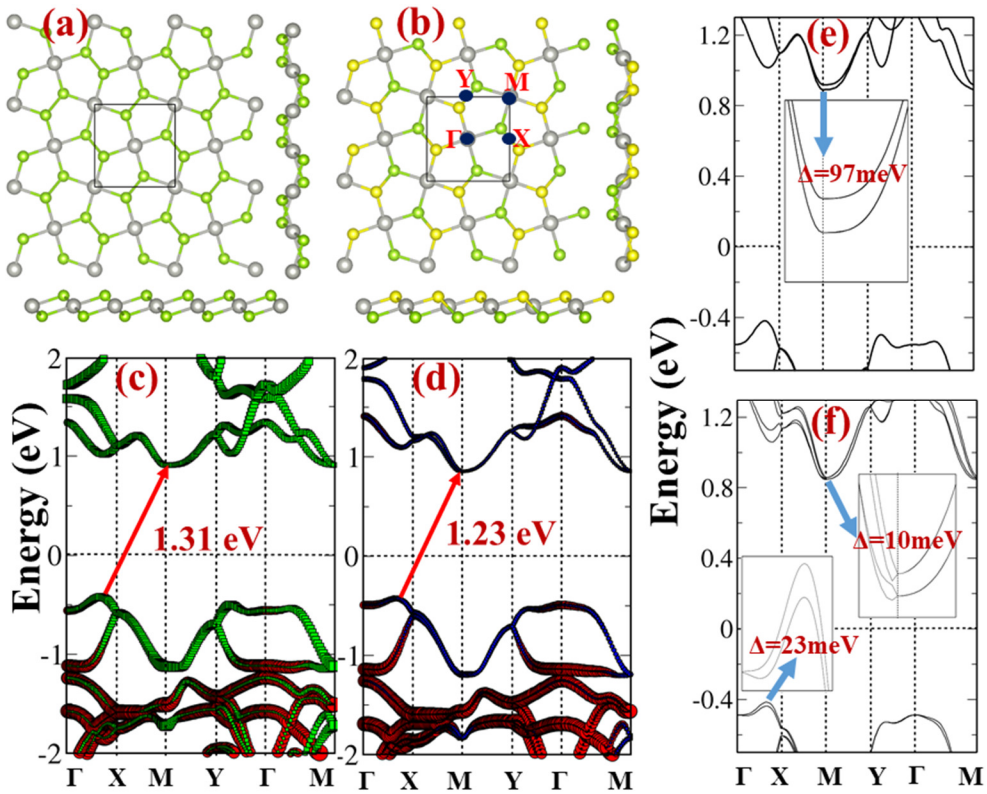

FIGURE 1. (a) Top and side vies of monolayer $PdSe_2$. The grey and green balls represent Pd and Se atoms, respectively. (b) Top and side views of monolayer PdSSe. The grey, yellow and green balls represent Pd, S and Se atoms, respectively. The high symmetry points for band structure calculations are also given in the square Brillouin zone. (c) Orbital resolved electronic band structure of monolayer $PdSe_2$. Red and green color indicate Pd-d and Se-P states, respectively. Indirect band gap of 1.31 eV is also shown. (d) Orbital resolved electronic band structure of monolayer PdSSe. Red and blue color indicate Pd-d and Se-P states, respectively. S and Se bands are hybridized. Indirect band gap of 1.23 eV is also shown. (e) SOC induced electronic band structure of monolayer $PdSe_2$. Inset shows CBM splitting due to SOC effect. (f) SOC induced electronic band structure of monolayer $PdSSe_2$. Inset shows VBM and CBM splitting due to SOC effect.

monolayer (PdSSe) reduces due to the shorter Pd-S and S-S bond lengths. Cohesive energy of hybrid monolayer is calculated to be higher than pristine $PdSe_2$ monolayer that indicates higher stability of hybrid monolayer than its

pristine counterpart. Note that cohesive energy has been obtained as the difference between the total energy per atom of mono or bilayer system and free atom(s) energy.

In the electronic structure of monolayer $PdSe_2$, the bands around the Fermi level is mainly derived from the p-orbitals of chalcogens. Electronic band structure has been calculated along Γ-X-M-Y-Γ-M direction [Figure 1(b)]. Valance band maximum (VBM) and conduction band minimum (CBM) lies at Γ-X and M point, respectively, showing indirect band gap nature. The calculated band gap value is 1.31 eV [Figure 1(c)]. In case of hybrid PdSSe monolayer, the bands around Fermi level are contribute by p-states of both S and Se. Hybrid monolayer also show indirect band gap with value 1.23 eV [Figure 1(d)]. It is important to investigate the SOC effect on these monolayers. We found that CBM get splitted (97 meV) by SOC effect, however, SOC effect does not apply on VBM [Figure 1(e)]. On the other both VBM and CMB have been found to get splitted by 23 meV and 10 meV respectively, on the influence of SOC effect.

Next we consider bilayer of $PdSe_2$ and its vertical hybrid with PdS_2. The interlayer distance is calculated to be 3.05Å and 3.0 Å, respectively, for homo and heterobilayers [Figure 2]. Despite the nearly same interlayer distance, the electronic structure show distinctly different features. For example, the band gap of homobilayer is 0.97 eV [Figure 2(a)] while it significantly reduces to 0.55 eV in hybrid bilayers [Figure 2(b)]. This reduction in band gap can be attributed to the interlayer binding energy which is calculated to be 0.011 eV/atom for homobilayer and 0.103 eV/tom for heterobilayer. Therefore, heterobilayer show stronger interlayer interactions that homobilayers. To get deeper insight into this behavior, we calculate charge density difference profiles for both homo and hetero bilayers. Note that charge density difference was calculating by subtracting sum of the charge densities of constituents monolayers from total charge density of bilayer. It is found that, heterobilayer show greater charge redistribution in between layers [Figure 2(b)] which may be attribute to the electronegativity difference between S and Se atoms which resides on the surface of each constituents layers. This greater charge redistribution leads to the shift in CBM energy towards Fermi level and hence reduced the band gap at greater extent as compared to homobilayer.

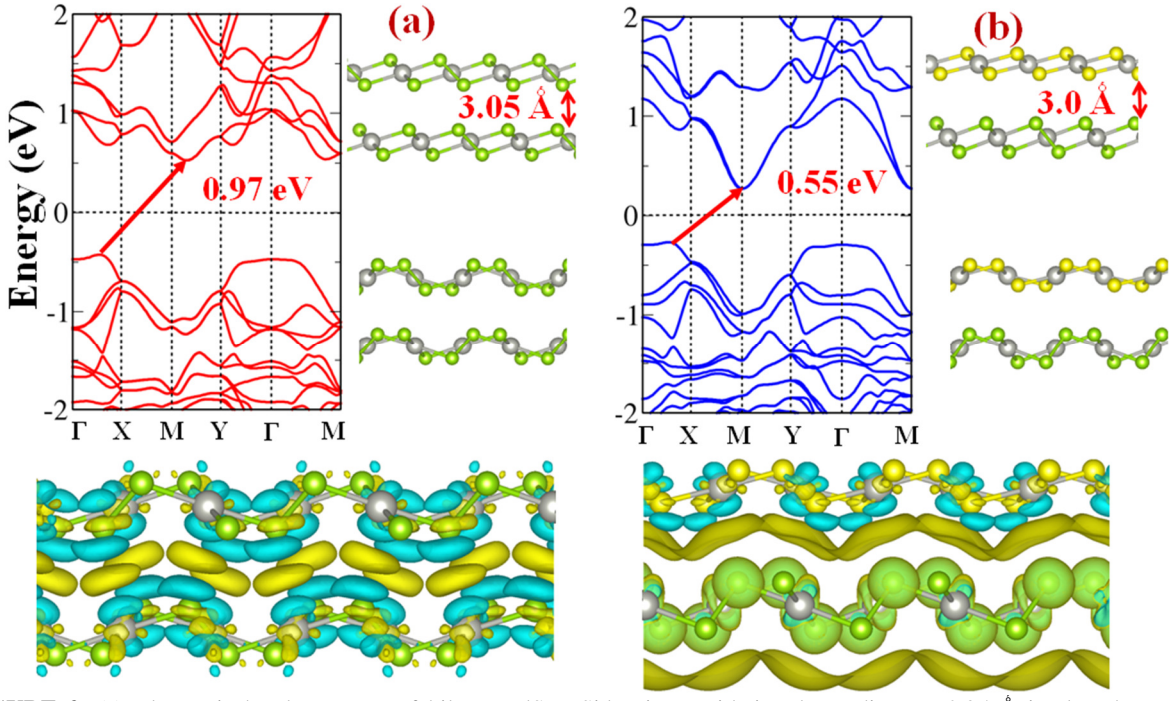

FIGURE 2. (a) Electronic band structure of bilayer $PdSe_2$. Side views with interlayer distance 3.05 Å is also shown. (b) Electronic band structure of bilayer PdSSe. Side views with interlayer distance 3.0 Å is also shown. In the bottom panel charge density difference profile is presented. The isosurface is taken at 10^{-3} e/Å^3.

CONCLUSIONS

In summary, structural and electronic structure of pristine and hybrid mono and bilayers of Pd chalcogenides are investigated. Cohesive energies of bilayer systems are marginally higher than the corresponding monolayers. All are found to be indirect band gap semiconductors. VBM/CBM are found to get splitted by SOC effect which is found more pronounced in hybrid monolayer. Band gap is calculated to be reduced on going from monolayer to bilayer which is attributed to the interlayer interactions and charge redistribution between layers of both homo and hybrid bilayers. These results suggest that 2D $PdSe_2$ may be a potentials candidate for future nanoelectronic device applications.

ACKNOWLEDGEMENTS

AK gratefully acknowledge University Grants Commission for providing start-up grant (Grant No. 30-318/2016 (BSR)) to accomplish the work presented in the paper.

REFERENCES

1. C. Tan, X. Cao, X. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G. Nam, M. Sindoro and H. Zhang, Chem. Revs. **117**, 6225-6331 (2017).
2. P. Jamdagni, A. Kumar, A. Thakur, R. Pandey and P. K. Ahluwalia, Mater. Res. Exp., **2**, 016301 (2015).
3. P. Jamdagni, A. Kumar, M. Sharma, A. Thakur and P. K. Ahluwalia, Physica E, **85**, 65 (2017).
4. P. Jamdagni, A. Kumar, A. Thakur, R. Pandey and P. K. Ahluwalia, J. Phys. Condens. Matter, **29,** 395501 (2017).
5. A. Kumar and P. K. Ahluwalia, Eur. Phys. J. B. **85,** 186 (2012).
6. A. D. Oyedele, S. Yang, L. Liang, A. A. Puretzky, K. Wang, J. Zhang, P. Yu, P. R. Pudasaini, A. W. Ghosh, Z. Liu, C. M. Rouleau, B. G. Sumpter, M. F. Chisholm, W. Zhou, P. D. Rack, D. B. Geohegan and K. Xiao , J. Am. Chem. Soc. **139,** 14090 (2017).
7. W. L. Chow, P. Yu, F. Liu, J. Hong, X. Wang, Q. Zeng, C. Hsu, C. Zhu, J. Zhou, X. Wang, J. Xia, J. Yan, Y. Chen, D. Wu, T. Yu, Z. Shen, H. Lin, C. Jin, B. K. Tay and Z. Liu, Adv Maters. **29**, 1602969 (2017).
8. E. Li, D. Wang, P. Fan, R. Zhang, Y. Y. Zhang, G. Li, J. Mao, Y. Wang, X. Lin, S. Du and H. J. Gao, Nano Res. DOI: 10.1007/s12274-018-2090-0 (2018).
9. G. Kresse and J. Furthmuller, *Phys. Rev.* B, **54** 11169 (1996).