Electronic Properties of Phosphorene/$MoSe_2$ Vertical Hetero-structures

Sumandeep Kaur[1], Ashok Kumar[2], Sunita Srivastava[1], K. Tankeshwar[3]

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

Abstract. We report three structurally different and stable phases of $MoSe_2$ namely h-$MoSe_2$ (trigonal prismatic phase), t-$MoSe_2$ (distorted octahedral coordinated phase) and o-$MoSe_2$ (consisting of repeated octagon pairs) and their hetero-structures with black phosphorene. The $MoSe_2$-octa phase possesses graphene-like character i.e. Dirac cone feature at the Fermi level. All the considered hetero-structures are energetically equally favorable. The h-$MoSe_2$/black-P is found to be a semiconductor in nature while on the other hand t-$MoSe_2$/black-P and o-$MoSe_2$black-P are metallic. These novel hetero-structures may be useful in the fabrication of nano-electronic devices based on phosphorene hetero-structures.

Keywords: Hetero-structure, Phosphorene, $MoSe_2$, Dirac cone.
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INTRODUCTION

Since the discovery of graphene using mechanical exfoliation in 2004 [1], 2D atomic layers have been emerged as promising materials for various applications [2]. Layered transition metal dichalchogenides (LTMDs) [3], silicene, germanene and phosphorene [4] are such materials which are interesting to study from both fundamental and application point of view.

LTMDs have attracted intensive research interests because of their unique chemical and physical properties and find application in the areas of optoelectronic, spintronic and nano-electronic devices [5]. Unlike graphene, monolayers of TMDs are triatomic, in which the metal atoms are sandwiched between two atomic planes of chalcogen atoms.

Recently, the monolayer of black phosphorene (BP) [6] which exhibit a puckered hexagonal structure has gained enormous amount of attention because of the high on–off ratio of up to 10^6 and high hole mobility of up to 1000 $cm^2V^{-1}s^{-1}$. The bandgap of BP is found to vary with number of layers, strain and transverse electric field [7, 8]. All these novel properties render BP as an ideal contender for nano and optoelctronic applications.

In this paper, we propose the vertical hetero-structures of black-P with various stable structural phases of $MoSe_2$ within the framework of density functional theory (DFT).

COMPUTATIONAL DETAILS

DFT calculations are performed by means of numerical atomic orbitals (NAOs) basis sets and pseudopotential, as implemented in SIESTA simulation package [9]. Conjugate gradient method is used to perform structural optimizations until the residual forces on each atom is less than 0.01 eV/Å. The electron-electron interactions are treated using GGA (generalized gradient approximation) as exchange correlation functional in the form of Perdew-Burke-Ernzerhof (PBE). The Kohn-Sham orbitals are expanded using double zeta polarization (DZP) basis sets with mesh cutoff energy of 200 Ry and Monkhorst-pack scheme with a 30×30×1 mesh to sample the Brillouin zone for all the calculations.

RESULTS AND DISCUSSION

Figures 1 show the various structural phases of $MoSe_2$ along with monolayer black-P. In case of $MoSe_2$, we have found that in addition to the stable trigonal prismatic phase (h-phase), it can also exhibit a distorted octahedral coordinated phase (t-phase) as well as a structural phase constructed by repeating the

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square octagon ring structure in a square lattice (octa-phase). We have used rectangular unitcells for h- and t- phases in order to construct commensurable van der Waals hetero-structure with black-P that incorporates the features of its monolayer counterparts.

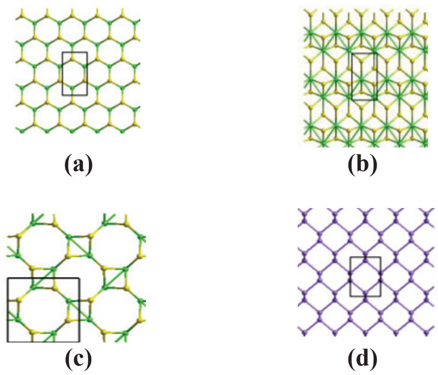

FIGURE 1. The top view of (a) h-$MoSe_2$ (h-phase), (b) t-$MoSe_2$ (t-phase), (c) o-$MoSe_2$ (octa-phase) and (d) black phosphorene (black-P). The green and yellow balls represent molybdenum and selenide atoms respectively, while violet balls represent phosphorous atoms. The rectangular box in each figure indicates 1×1 unitcell.

The structural differences in all the three phases of $MoSe_2$ also lead to a difference in their band-structures

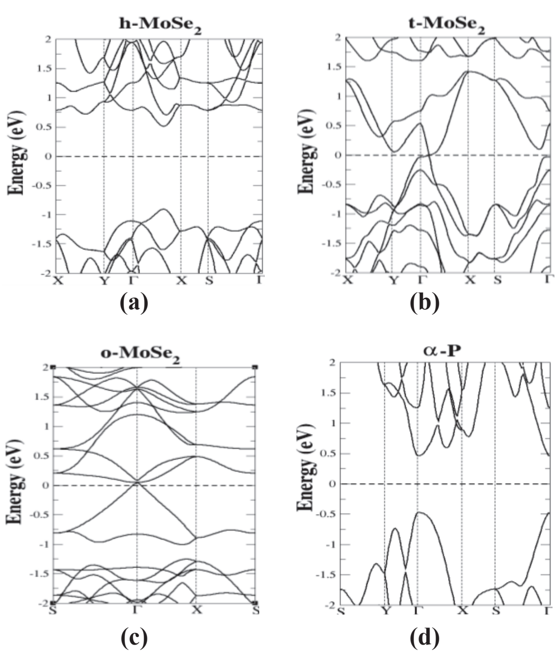

FIGURE 2. The band-structure of (a) h-$MoSe_2$ (h-phase), (b) t-$MoSe_2$ (t-phase), (c) o-$MoSe_2$ (octa-phase) and (d) black phosphorene (black-P).

(Figure 2). h-$MoSe_2$ is a direct bandgap semiconductor as the valence band maximum (VBM) and conduction band minimum (CBM) lies at same high symmetry point which is in between Γ and X points. The bandgap is calculated as 1.7 eV (Table 1) at GGA-PBE level of theory. t-$MoSe_2$ is metallic with zero bandgap while o-$MoSe_2$-octa is a semimetal possessing Dirac cone at the Γ point. On the other hand, monolayer black-P is a direct bandgap semiconductor with a bandgap of 0.92 eV at the Γ-point.

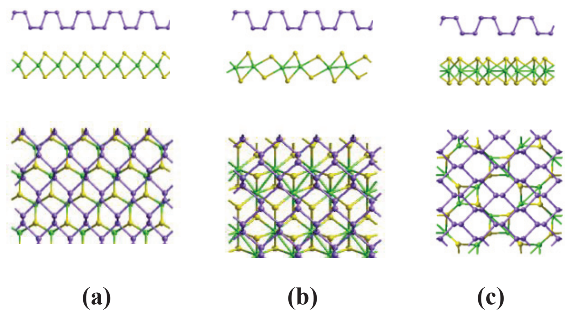

FIGURE 3. The side and top view of hetero-structures of (a) h-MoSe2black-P, (b) t-MoSe2/black-P and (c) o-MoSe2/black-P.

Figure 3 depicts the equilibrium hetero-structures constructed using all the three possible structural phases of $MoSe_2$. The hetero-structure of h-$MoSe_2$/black-P is composed of 1×4 units of h-$MoSe_2$ and 1×5 units of black-P while the t-$MoSe_2$/black-P hetero-structure consists of 1×3 units of t-$MoSe_2$ and 1×4 units of black-P. On the other hand, the supercell of o-$MoSe_2$/black-P hetero-structure consists of 1×2 units of o-$MoSe_2$ and 2×3 units of Black-P. These choices of supercells ensure the minimization of interfacial strain due to lattice mismatch.

TABLE 1: Lattice constants (a, b), Number of atoms (N), equilibrium separation between layers (d), binding energy (B.E.) of bilayer structure and the bandgap of the considered heterobilayers.

	Black-P/h-$MoSe_2$	**Black-P/ t-$MoSe_2$**	**Black-P/ o-$MoSe_2$**
Lattice constant (a, b)	3.34 22.55	3.34 18.04	6.67 13.53
Number of atoms (N)	44	34	48
d (Å)	3.55	3.37	3.55
B.E. (meV/atom)	19.78	20.63	20.96
E_g (eV)	0.99	0.00	0.00

The strain induced in h-MoSe2/black-P, t-MoSe2/black-P and o-MoSe2/black-P hetero-structures is approximately 2.8%, 1.5% and 1.6%, respectively.

The stable configuration for each hetero-structure was found after energy optimization. For equilibrium configuration of each hetero-structure, we calculate the binding energy as $(E_P + E_{MoSe2} - E_{MoSe2/black\text{-}P})/N$ where E_P (E_{MoSe2}) is the total energy of Black-P ($MoSe_2$), $E_{MoSe2/black\text{-}P}$ is the total energy of the hetero-structures and N is the number of atoms in the hetero-structures. Also, the binding energy/atom of all the considered hetero-bilayers is of the order of a few meV (Table 1) indicating van der Waals forces of interaction between the layers.

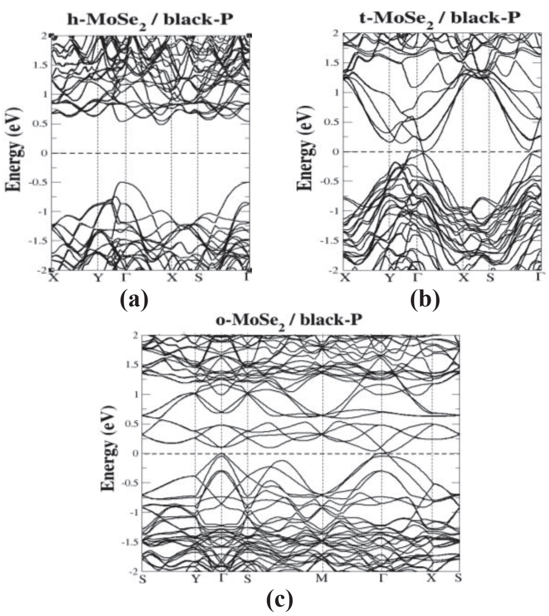

FIGURE 4. The band-structure of (a) h-MoSe2/black-P, (b) t-MoSe2/black-P and (c) o-MoSe2/black-P hetero-structures.

The three proposed hetero-structures also differ in their electronic properties. The $h\text{-}MoSe_2$/black-P is an indirect bandgap semiconductor with VBM at Γ and CBM at a point between Γ and X while $t\text{-}MoSe_2$/black-P and $o\text{-}MoSe_2$/black-P are found to be metallic (Figure 4). A closer look at the band structure of o-MoSe2/black-P shows that the Dirac cone of $o\text{-}MoSe_2$ remains intact in the hetero-structure but with a tiny splitting of about 0.1 eV, however, a crossover of the band lines is observed at the Fermi level between points Γ and X which gives it a metallic character. All these three hetero-structures with their unique electronic properties may be useful for future fabrication of nano-electronic devices.

CONCLUSIONS

In the present work, DFT calculations have been performed to investigate the electronic properties of van der Waals hetero-structure of black phosphorene with various structurally different phases of $MoSe_2$ i.e., trigonal prismatic phase (h-phase), distorted octahedral coordinated phase (t-phase) and a phase formed by repetition of square octagon pairs in a square lattice (octa-phase). The h-, t- and o-phase are found to be semiconductor, metal and semimetal (possessing a Dirac cone at the Fermi level) respectively. The hetero-structures of $h\text{-}MoSe_2$/black-P possess semiconducting character while the hetero-structures of t-MoSe2/black-P as well as o-MoSe2/black-P are metallic in nature. These proposed hetero-structures may find applications in the nano-electronic device fabrication industry for the production of heterojunctions based on Van der Waal multilayers.

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