Stability and Electronic Structure of Tricycle-type Allotropes of Pnictogen Monolayers

Pooja Jamdagni[1,a)], Anil Thakur[2], Ashok Kumar[3] and P. K. Ahluwalia[1]

[1]*Department of Physic, Himachal Pradesh University, Shimla, H.P., India,171005*
[2]*Department of Physics, P. G. College Solan, H.P. India, 173212*
[3]*Department of Physical Sciences, School of Basic and Applied Sciences, Central University of Punjab, Bathinda 151001, India*

[a)]Corresponding author: j.poojaa1228@gmail.com

Abstract. We report stability and electronic structure of tricycle-type allotrope of pnictogen monolayers within state-of-the-art density functional theory (DFT) calculations. The considered monolayer structure of two-dimensional (2D) As and Sb are found to be energetically more stable than the previously reported puckered and buckled structures, however, 2D Bi prefer zigzag-type high-buckled structure. Electronic band structure calculations suggest the considered monolayers structure to be narrow direct bandgap semiconductors with bandgap ranging 0.2-0.6 eV along with Dirac-cone features at band edges. Spin-orbit coupling (SOC) further reduce the bandgap by shifting the band edges towards Fermi level. We believe that our theoretical study will add more 2D materials with Dirac-cone features in the fascinating class of family and may guide the experimentalists to realize them for various nanoelectronic applications.

INTRODUCTION

Since 2004, there is continuous extension of two-dimensional (2D) atomic-layer family of materials [1-3]. Recently, interest has turned to 2D mono-elemental structures, such as monolayer black phosphorus [4] and, very recently, to monolayers of arsenic, antimony, and bismuth [5-6]. There is exponentially increasing research in arsenene, antimonene and bismuthene, which belong to the fifth main group of elements, the so-called pnictogens. In the past years, many 2D allotropes composed of P atoms with compacted honeycomb or non-honeycomb structures have been proposed from first-principles calculations [4].

As a results of above investigations on the novel monolayer allotropes of phosphorene, tricycle-type phosphorene or red phosphorene is constructed by restructuring the segments of the most stable black and blue phosphorenes, which is confirmed to possess positive dynamical stability and remarkable themodynamical stability between black and blue phosphorenes [7]. Inspired by these developments, it is obvious to look into the electronic structure of tricyclic-type monolayer allotropes of other elements of group-V. In this paper, we investigate the structural and electronic properties of tricyclic pnitogens (arsenene, antimonene and bismuthene). The effect of spin-orbit coupling (SOC) is important to describe the electronic structure of these monolayers.

COMPUTATIONAL DETAILS

Electronic structure calculations were performed using density functional theory (DFT) as implemented in Vienna ab initio simulation package (VASP) [8]. Generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) parameterization is used to describe exchange correlation functional. The van der Waals (vdW) interactions have been incorporated by adding semi-empirical potential to the conventional Kohn-Sham DFT energy by using DFT-D2 method of Grimme [9]. We have also included the spin-orbit coupling (SOC) effects in our calculations as these were found to be important to describe electronic structure of considered systems. A cutoff

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energy of 400 eV for the plane wave basis set and a Monkhorst–Pack mesh of (10 x 10 x 1) for Brillouin zone integration were employed. A 15 Å vacuum region along z-direction ensures the modelling of a 2D material. All the structures are fully relaxed, with residual forces smaller than 0.01 eV/Å on each atom.

RESULTS AND DISCUSSION

The top and side views of relaxed structure of tricyclic pnictogens is shown in figure 1. Their detailed structural information is summarized in table 1. The tricyclic pnictogens has a rectangular lattice. The bond length between the atoms are 2.50 Å, 2.89Å and 3.05 Å for As-As, Sb-Sb and Bi-Bi, respectively.

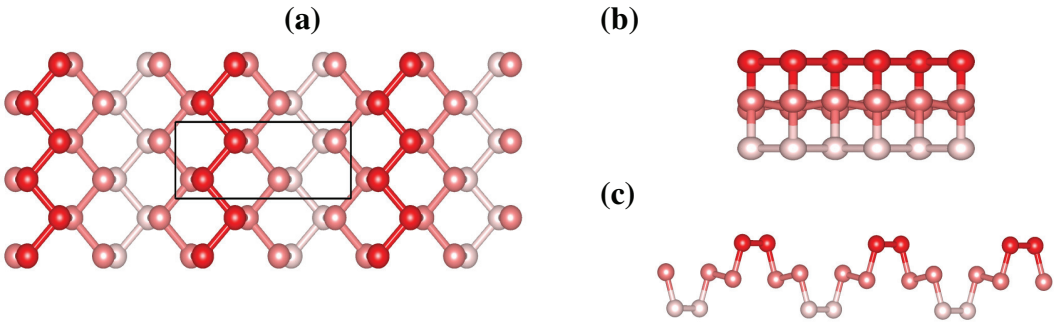

FIGURE 1. Top (a) and side (b,c) views of relaxed structures of tri-cyclic type allotrope of pnictogen monolayers . Unit cell is also shown with solid lines.

Table 1. Calculated Lattice parameters, Bond-lengths, Cohesive Energy and band gaps (with and without SOC) for tricyclic type arsenene, antimonene and bismuthene. Thw cohesive energy of buckled monolayer structures [10] are also given for comparision.

Systems		As	Sb	Bi
Lattice Parameters (Å)		a= 9.36 b=3.65	a=10.00 b= 4.14	a=10.24 b= 4.29
Bond Lengths(Å)		As-As : 2.50	Sb-Sb : 2.89	Bi-Bi : 3.05
E_{coh}(eV)		-4.66 (-4.49)[a]	-4.12 (-3.88)[a]	-3.36 (-3.60)[a]
Band Gap (eV)	Without SOC	0.60	0.22	0.23
	With SOC	0.59	0.16	0.04

[a]Cohesive energy of buckled monolayer structures [10].

Negative value of cohesive energy (E_{coh}) indicates the stability of given monolayers . Note that the cohesive energy was obtained as:

$$\frac{E_T - nE_a}{n} \qquad (1)$$

where E_T is the total energy of a tricyclic structure, E_a is the energy of a free atom and n is the total number of atoms in a monolayer. It is to be noted that group-V monoalyers possess energetically most stable structures in puckered and buckled configurations. Interestingly, the cohesive energy of tricycle-type As and Sb monolayers is found to be 0.17 eV and 0.24 eV per atom higher than that of buckled structures, thereby, suggesting the tricycle-type structure to be energetically more favorable than buckled structures. However, the E_{coh} of tricycle-type Bi is found to be 0.24 eV lower than buckled structure indicating less stability of considered bismuthene in tricycle-type structure.

Electronic Structure

All the considered monolayers are found to be direct band gap semiconductors with a band gap value of 0.60 eV , 0.20 eV and 0.23 eV for As, Sb and Bi monolayers, respectively. Note that our previous calculations [10] report the buckled monolayers of As and Sb to be indirect band gap semiconductor whereas Bi is direct gap semiconductor. The value of band gap in the considered tricycle-type monolayers are very much lower than the calculated values 1.57 eV , 1.17 eV and 0.51 eV, respectively, for buckled monolayers [10], indicating the considerd monolayer structures to be narrow gap semiconductors.

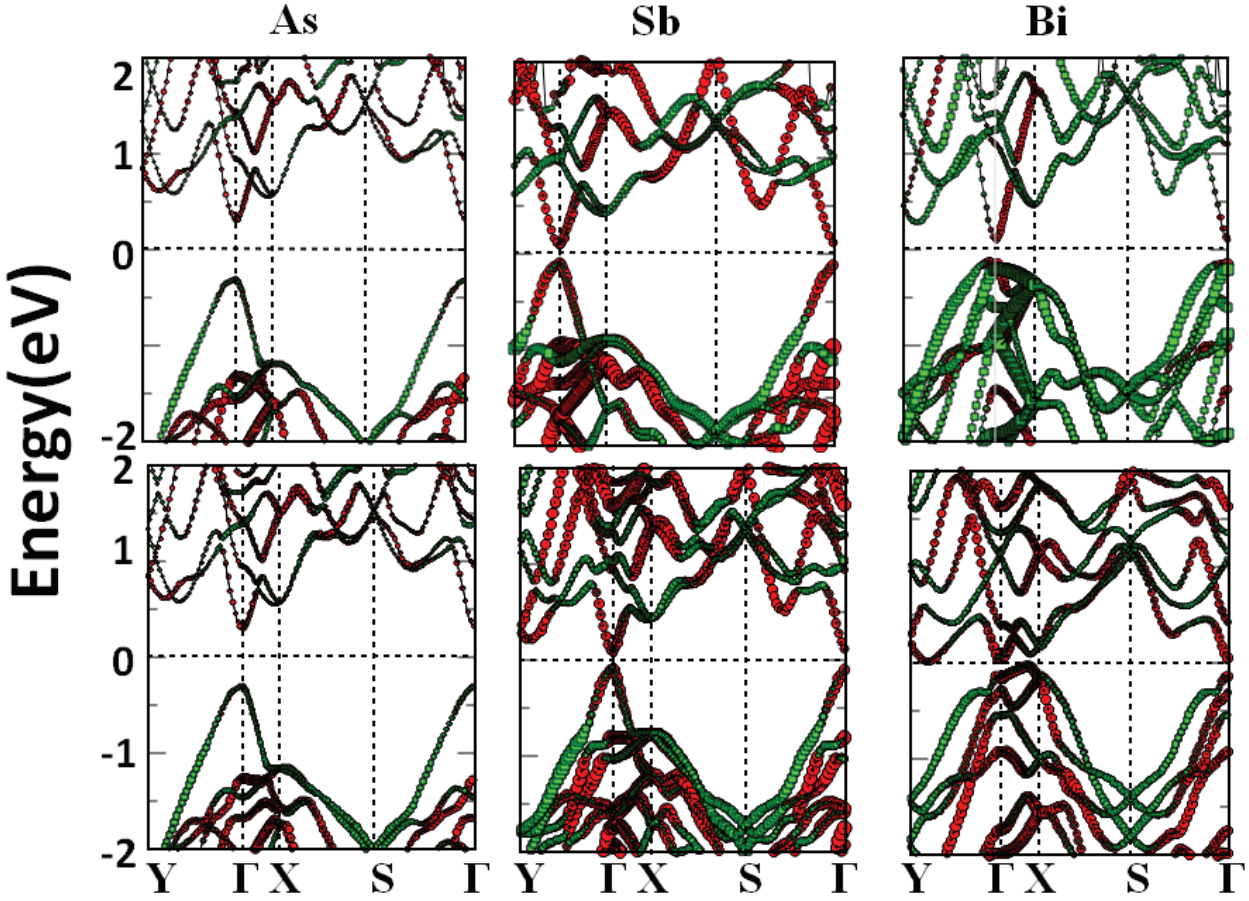

FIGURE 2. Orbital-resolved electronic band structure of tri-cyclic type allotrope without SOC (upper panel) and with SOC (lower panel) effect. Red colour indicated p_x+p_y orbitals and green colour represents p_z orbitals.

In addition, all the considerd monolayer structures show Dirac-cone features at valance band maximum (VBM) and conduction band minimum (CBM). VBM are mainly contributed by the mixture of in-plan and out-of-plan p-orbitals, whereas CBM has most of the contributions from out-of-plan p_z orbitals.On including spin-orbit coupling (SOC), the energy gap get reduced due to shifting of both VBM and CBM towards Fermi level. The effect of SOC is found to be more pronounced for Bi monolayer, where band gap reduces from 0.23 eV to 0.04 eV.

CONCLUSIONS

In summary, energetics and electronic structure of tricycle-type monolayer allotropes of As, Sb and Bi are studied using first principles theory. The cohesive energy of As and Sb monolayers are found to be 0.17 and 0.24 eV per atom higher than the previous reported stable high-buckled structures. Electronic structure calculations show these monolayers to be direct bandgap semiconductors with Dirac fermionic features and strong dependence of band

gap on spin-orbit coupling effect. Our study may be useful for the experimental realization of these monolayers for various applications.

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