Electronic and structural investigation of buckled antimonene using density functional theory calculation

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Abstract. Electronic and structural analysis of buckled antimonene has been performed using density functional theory-based *ab-initio* approach. Geometrical parameters such as bond length and bond angle are very close to the single ruffle layer of rhombohedral antimony. Phonon dispersion along the high symmetry point of the Brillouin zone does not signify any soft mode. Electronic indirect band gap of 1.61 eV is observed for the single-layer antimonene. However, the occurrence of bilayered quasi-2D sheet consequent to metallic behaviour is due to significant electronic charge dispersion between interlayer region.

Keywords. Hexagonal nanowire (h-NW); Optical properties; Stability; Density functional theory.

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1. Introduction

Graphene as 2D materials has attracted a lot of attention [1–3]. Ultrafast electron mobility makes graphene highly conductive; however its limitation is that it is a zero-band gap material which makes it useless for optoelectronic and device applications [4]. Other cousins of graphene have been introduced by scientific community for overcoming the limitations exhibited by this 2D material. Some of these are: BN-sheet [5], silicene [6], phosphorene [7,8] and arsenene [9,10]. Recently, single atomic layer of arsenene with an indirect band gap is theoretically proposed as a semiconducting material [6,7]. Comparative analyses of the buckled, puckered and flat arsenene reveal that puckered configuration is comparatively more stable. However, discrepancy in computational parameter opted for phononic calculation might have results to significant soft mode near the high symmetry point of Brillioun zone is expected by Zhang *et al* [9]. Motivated by the on-going race for finding novel 2D nanomaterials, in the present article we have investigated the structural and electronic properties of single atomic thin layer antimonene sheet in buckled phase.

2. Computational method

A 4×4 supercell from repetitive growth of hexagonal unit cell having a lattice parameter of 4.12 Å and large vacuum of 20 Å along the *c* direction is taken as the model system. This monolayer consists of 32 Sb atoms and the hexagonal supercell has a lattice constant of 16.48 Å as shown in figure 1a. It consists of two layers of Sb atoms with an interplanar separation of 1.61 Å and the Sb–Sb bond length is kept at 2.89 Å similar to the bond length in the bulk phase of rhombohedral antimonene [11]. The system is further relaxed in the self-consistent field of DFT to obtain ground-state geometry. Core and valence electrons are respectively defined in terms of Troullier–Martins [12] pseudopotential and double-ζ-polarized (DZP) orbital. Brillouin zone integrations are carried out using Monkhorst–Pack [13] scheme. k-point sampling of $5 \times 5 \times 1$ and $10 \times 10 \times 1$ are opted for geometry optimization and electronic properties, respectively. Double-layer graphene model with an interlayer distance of 3.95 Å is another interesting part of the present calculations.

3. Results and discussion

If the ruffled layer of Sb from its rhombohedral crystal structure along the [1 1 1] direction is exfoliated, one can obtain a monatomic thin layer of buckled antimonene. The optimized Sb–Sb bond and Sb–Sb–Sb bond angle are on an average 2.9 Å and 90.5°, respectively, which
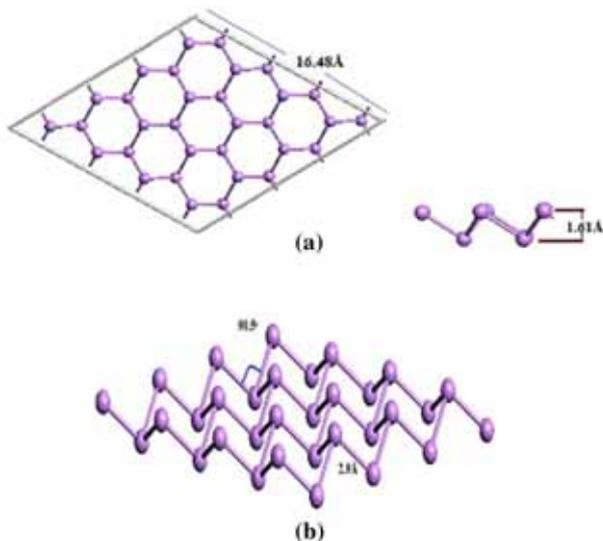
Figure 1. (**a**) Supercell consisting of 32 Sb atoms and (**b**) respective optimized geometry with a geometrical parameter.
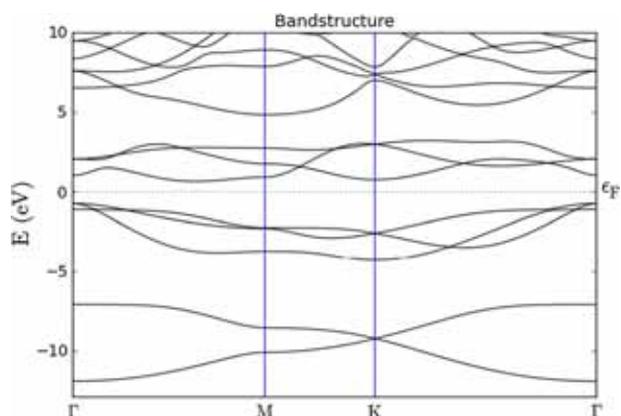

Figure 2. Band structure along high symmetry point in Brillouin zone of buckled antimonene.

Figure 3. Interfrontier orbital diagram for optimized antimonene sheet.
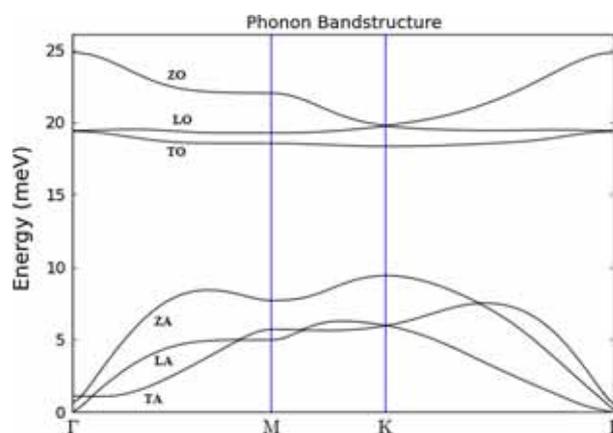
Figure 4. Phonon dispersion curve along high symmetric point.

is very similar to the ruffled antimonene layer of the bulk Sb phase [11]. Bonding analysis suggests that lone pair electrons are mainly located at the atomic centre. Electronic bonds between two atomic layers are σ type, mainly consisting of the oblique component of p-orbitals. Band-structure diagram (figure 2) exhibits an indirect band gap of 1.6 eV representing the semiconducting behaviour for buckled antimonene sheet. Valance band maxima (VBM) and conduction band minima (CBM) at Γ and K points, respectively, have similar curvature for energy band diagram. This symmetric behaviour result to almost equal effective mass of hole ($0.40 m_e$) and electron ($0.41 m_e$). Some of the interfrontier orbital diagrams presented in figure 3 suggesting highest occupied molecular orbital (HOMO) or VBM, consist of mainly localized σ-bonding orbitals.
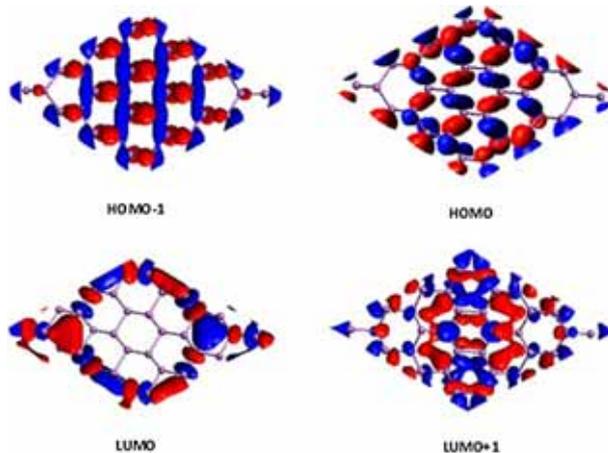
The next lower occupied orbital (HOMO-1) has primarily the contribution of lone pair electrons. The lowest unoccupied molecular orbital (LUMO) or lower conduction band and its nearest unoccupied orbital have σ^* bonding character. Phonon calculations did not conclude any soft mode in phonon dispersion spectra suggesting that the sheet configuration is structurally stable. The three acoustic modes dominate the low-temperature scattering where two modes (LA, ZA) have a linear q-dependence and the third (TA) mode is invariant near the Brillioun zone centre (see figure 4). LA, TA and ZA are respectively, longitudinal, transverse and out-of-plane acoustic modes.

Three optical branches are observed at high-energy range where the highest one is out-of-plane and lowest is transverse in plane nature at Γ point. The bilayer antimonene is further investigated, in this case no electronic band gap across the Fermi level is observed. VBM cross symmetrically across Fermi level in the middle of
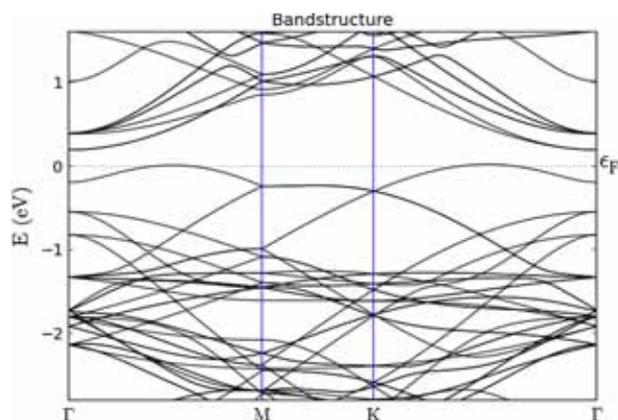
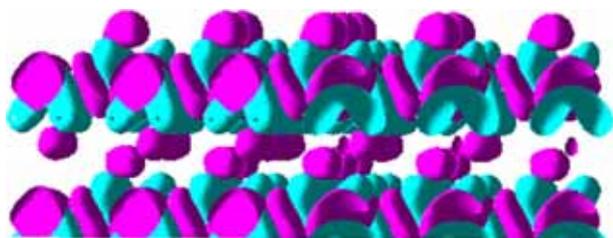**Figure 5.** Band structure diagram of bilayer antimonene.

Figure 6. Electron difference density plot of bilayer antimonene at an isovalue of 0.02 e/Å^3.

the Γ–M and Γ–K directions of the Brillouin zone's high symmetric path. Lowering of conduction band can be observed from the band-structure diagram (figure 5) suggesting strong coupling between molecular orbital from the surface of the quasi-2D nanosheets. Charge difference density at a contour value of 0.02 e/Å^3 is shown for bilayer antimonene in figure 6. A significant amount of electronic charge seems to disperse between the interlayer of the sheets and serve for weak interlayer binding.

4. Conclusion

Ab-initio study suggests that the isolated buckled antimonene has stable geometric configuration. The bond length and bond angle are relatively unchanged compared to their contemporary single ruffled layer of rhombohedral antimony in bulk phase. Phonon calculation confirms the stability of the proposed quasi-2D nanosheets with no soft mode observed at all in the phonon dispersion curve. Indirect band-gap nature of this quasi-2D material might have appealing prospects for optoelectronic devices. Molecular orbital diagram reveals that HOMO consisting of localized σ-bonding and lone pair are comparatively shifted in occupied orbital state. Bilayer antimonene is found to have metallic behaviour with significant amount of charge dispersed between the quasi-2D layer.

References

[1] S Reich, J Maultzsch, C Thomsen and P Ordejon, *Phys. Rev. B* **66**, 035412 (2002)
[2] K S A Novoselov, A K Geim, S V Morozov, D Jiang, Y Zhang, I V Grigorieva and A A Firsov, *Science* **306**, 666 (2004)
[3] K S A Novoselov, A K Geim, S V Morozov, D Jiang, M Katsnelson, I Grigorieva, S Dubonos and A Firsov, *Nature* **438**, 197 (2005)
[4] S L Chuang, *Physics of optoelectronic devices* (Wiley, 1995)
[5] W Q Han, L Wu, Y Zhu, K Watanabe and T Taniguchi, *Appl. Phys. Lett.* **93**, 223103 (2008)
[6] B Lalmi, H Oughaddou, H Enriquez, A Kara, S B Vizzini, B N Ealet and B Aufray, *Appl. Phys. Lett.* **97**, 223109 (2010)
[7] A H Woomer, T W Farnsworth, J Hu, R A Wells, C L Donley and S C Warren, *ACS Nano* **9**, 8869 (2015)
[8] H Liu, A T Neal, Z Zhu, D Tomanek, *ACS Nano* **8**, 4033 (2014)
[9] C Kamal and M Ezawa, *Phys. Rev. B* **91**, 085423 (2015)
[10] Z Zhang, J Xie, D Yang, Y Wang, M Si and D Xue, *Appl. Phys. Express* **8**, 055201 (2015)
[11] E Wiberg, N Wiberg and A F Holleman, *Inorganic chemistry* (Academic Press, 2001), ISBN 0-12-352651-5
[12] N Troullier and J L Martins, *Phys. Rev. B* **43**, 1993 (1991)
[13] H J Monkhorst and J D Pack, *Phys. Rev. B* **13**, 5188 (1976)