Band Splitting in Bilayer Stanene Electronic Structure scrutinized via first principle DFT Calculations

Mohammed Ghadiyali and Sajeev Chacko
Department of Physics, University of Mumbai, Kalina Campus, Santacruz (E), Mumbai - 400 098, India.

The recent work on stanene as quantum spin Hall insulators made us investigate bilayer stanene using first principle calculations. With an aim of improving and developing new properties, via modulating the stacking order (and angle) of the bilayers. This stacking of layers has been proven technique for modulating the properties of monolayer materials. Here we design multiple bilayer systems, with different stacking angles and AA and AB configurations. Rather observing an improvement in band gap due to spin orbit coupling (SOC), we witness a splitting of band due to SOC, a characteristic behavior of stacked MoS$_2$ sheets. This splitting of the bands gives rise to different, independent and distinct spin-up and spin-down channels, manifesting a valley dependent spin polarization. Also, as a contrast to stacked MoS$_2$ system we notice in our system the stacking angle and order, does effect electronic states.

I. INTRODUCTION

The exfoliation of graphene has generated a huge interest in the field of condensed matter physics. The honeycomb lattice structure of graphene represents the Haldane model. Materials represented by Haldane model generally host quantum Hall effect. The spin-orbital coupling (SOC) in such materials could lead to quantum spin Hall effect (QSH). The first experimental observation of QSH in HgTe quantum well led to the development of Topological Insulators (TI). TIs are the class of material which could assist to bring the dream of creating dissipationless conduction channel for electrons a reality. Two-dimensional versions of these TIs are called as quantum spin Hall insulators (QSHI). However, the 2D QSHI have a weak SOC, a very small band gap ($\sim 10^{-3}$ meV), making it unsuitable for most of the applications. Much of the work in the last decade has been dedicated on identification and synthesis of these materials.

One way around is to investigate other honeycomb lattices such as those formed out of group IV A elements right below Carbon in the periodic table. This has led to buckled honeycomb lattice of Silicon and Germanium, which have been computationally verified and experimentally synthesized. Unfortunately, these also have a very small band gap. A 2D buckled honeycomb lattice of Tin (stanene), which is computationally predicted as a QSHI, is supposed to have a sufficient band gap required for practical use as QSHI. It was fabricated on Bi$_2$Te$_3$ (111) substrate via molecular beam epitaxy. The issue with it is that although it has been synthesized, its electronic states are pinned on the substrates i.e. stanene’s valence bands with conduction bands of substrate, giving stanene a metallic interface and losing its QSHI nature. The band gap of free standing stanene is deemed to be sufficient but still small. To improve the band gap functionalization as well as passivation with different groups like -H (hydrogenation), -F (halogen), -CN (Cyanide) etc. have been proposed. Studies of van der Waal type structures like stanene on graphene, stanene between two Ba layers, have been also done and have reported an improvement in the band gap. Apart from its use as QSHI, stanene also has been predicted to be a very good material to adsorb CO, NO$_X$, SO$_2$, etc. gases. It may be noted that most of the above mentioned work is in silico.

In this paper, we perform the first-principle calculations of bilayer of 2D tin (stanene), stacked similarly to that of the bilayer graphene. A similar approach had been used by Kan et al., for performing Density Functional Theory (DFT) studies on the two lattice of stanene, which are stacked upon each other like AB or Bernal-stacked form. In their study the bilayer structure had lost its buckling. However it has been reported that this structure has a lower energy than free standing stanene making it more stable and having a higher band gap. We use a similar approach to construct the stanene bilayer keeping the structure and mechanical exfoliation of bilayer graphene as our template. The proposed systems were not found to be QSHI, albeit a distinctive attributes of band structure due to band splitting is observed.
II. METHOD

First principle plane waves pseudopotential calculations are performed using the DFT as implemented in Quantum ESPRESSO (QE). We have used Perdew-Burke-Ernzerhof (PBE) exchange correlation function and included the DFT-D2 van der Waals corrections for representing the electron dispersion effect due to the bilayer. The converged kinetic energy cutoff was set at 50 Ry, with a k-point mesh of $18 \times 18 \times 1$ (Monkhorst-Pack mesh). To minimize the interaction between neighboring layers a vacuum $\approx 20$Å was set above and below the bilayer. To include the effect of SOC we used fully relativistic pseudopotentials, obtained from pseudopotentials repository at QE website. The calculations of the band structure and the partial charge densities were performed both with and without SOC. The k-point path for band structure calculations were set according to high symmetry path in Brillouin zone for hexagonal lattices, as $M \rightarrow \Gamma \rightarrow K \rightarrow M$. The required k-points for this path were generated using the XCrystDens package.

For constructing the bilayer structures, we first stacked two layers of stanene on each other with an interlayer angle $\theta$ as illustrated in figure 1(a). We then changed the angle of top layer with respect to the bottom layer from $0^\circ$ to $90^\circ$ in steps of $5^\circ$. However, since these transformations were performed on single unit cell, only $0^\circ$, $5^\circ$, $60^\circ$ and $70^\circ$ angles bilayers could be constructed. For other angles, the resultant structures were found to be discontinuous and/or significantly distorted. Therefore, only the un-distorted structures were selected for further analyses. We label these structures as S$_0$, S$_5$, S$_{60}$ and S$_{70}$, respectively. This process was carried out on two different configurations of the tin bilayer as described in section III. Next, we varied the interlayer spacing ($d$) and computed the total energy as a function of $d$. The structure with lowest energy was selected for the further calculations. Choice of this approach over the conventional geometry optimization method was preferred due to the reason that a bilayer or more layered structure can be mechanically exfoliated from their free standing monolayer counterpart. These mechanically exfoliated bilayers can be redesigned by simply rotating the layers with respect to each other. This process gives an extra degree of freedom for development of new materials with unique properties. The structures for present work were created using the VNL-Builder (version 2016.3).

![FIG. 1: (color online) (a) Structure of bilayer stanene. The gray spheres represent atoms in the top layer and the red spheres represent atoms the bottom layer. The angle, $\theta$, between layers is defined as shown in the image. The top and bottom atoms of the top layer are labeled as A1 and A2, respectively, while those in the lower plane are labeled as B1 and B2, respectively. (b) The AA configuration where the A1 atoms are on top of the B1 atoms. (c) The AB configuration where the A1 atoms are on top of the B2 atoms. These labels of the configurations (AA and AB) are strictly in the context of this paper.](image-url)
III. RESULT AND DISCUSSION

A free standing stanene monolayer has a buckled honeycomb lattice with two atoms per primitive unit cell. Each of the tin atoms is sp\(^3\) hybridized to all its neighboring atoms. It is also known to exhibit two stable configurations based on the extent of buckling\(^{26-28}\). The optimized structure has a lattice constant of 4.67 Å with a Sn-Sn bond length of 2.83 Å and a buckling height of 0.86 Å. The energetically less favored low-buckled structure, has been investigated more extensively due to its exotic electronic properties.

For the bilayer, a unit cell of low-buckled structure having the following parameters was used: \(a = b = 4.7\) Å, \(c = 27\) Å. The intralayer Sn-Sn bond length was same as that of the monolayer. An initial separation between the layers was taken to be 2.4 Å. A value of 2.9 Å is reported by Kan et al. for their geometry optimized planner bilayer stanene configuration. However to trace all the possible states a lower value is chosen. Bilayer stanene inherently has two different geometry as it is not planar but buckled. For explaining the structures, we have labeled the atoms in top sheet as A1 and A2 representing the top and bottom atom and the atoms in the bottom layer as atoms B1 and B2, as shown in the figure 1(b). If the atom A1 is on top of atom B1 than system is labeled as AA configuration and if atom A1 is on top of atom B2 than system is labeled as AB configuration, strictly in the context of this paper.

For obtaining a minimum energy structure the interlayer distance \(d\) was varied in the steps of 0.1 Å and the total energy was computed for each structure. The plot of energy versus interlayer spacing is given in the figure 2 and 2. The distance \(d\) corresponding to the lowest energy is given in table 1. These minimum energy structures were used for further analyses. From the table 1 and the figure 2 only one minimum is observed for the AA configuration for all angles of rotation of the top layer with respect to bottom layer. On the other hand, for the AB configuration, two minima are observed for \(S_0\) and \(S_5\) structures. For reference check figure 2.

| Configuration | \(d\) Å |
|---------------|---------|
| \(S_0\)       | 3.4     |
| \(S_5\)       | 3.4     |
| \(S_{60}\)    | 3.2     |
| \(S_{70}\)    | 3.2     |
| \(S_0\)       | 3.2(4.7)|
| \(S_5\)       | 3.3(4.7)|
| \(S_{60}\)    | 4.6     |
| \(S_{70}\)    | 4.6     |

TABLE I: Interlayer distance \(d\) for different angles corresponding to the minimum energy for different configurations of the stanene bilayer. The values of \(d\) for the second minimum for is given in the bracket.

![Graph](image1.png)

FIG. 2: (color online) The total energy v/s the interlayer distance for the configurations (a) AA and (b) AB for interlayer angles of 0°, 5°, 60° and 70°. The inset (b) is an enlarged graph of plot for angles 0° and 5° showing the second minima at \(d = 4.7\) Å.

The band structures along the high symmetry points (\(M \rightarrow \Gamma \rightarrow K \rightarrow M\)) with and without SOC are shown in figure 3 and 4 for configurations AA and AB respectively. It is clear from the band structures that SOC does not open up a gap (as expected in QSHI) but induces a band splitting. Interestingly, in one of the case this band splitting...
decisively converts the semimetallic nature of the system to a metallic one while in other the semiconducting nature is converted into metallic. Such a behavior for materials having Haldane model has not been reported. As conversation is due to band splitting via SOC, the split in bands could have different up and down states which can be exploited for applications in valleytronics.\textsuperscript{29} Hence only the system, expressing this transition were further investigated i.e. system with AA configuration having an interlayer angle of 5\degree, i.e. AA S\textsubscript{5} and AB configuration having an interlayer angle of 70\degree, i.e. AB S\textsubscript{70}. In order to understand the nature of band splitting a cue from the work of Zheng \textit{et al.}\textsuperscript{30} and Zhu \textit{et al.}\textsuperscript{31} on bilayer MoS\textsubscript{2} is taken as template. The calculated results along with band decomposed charge density at specific k-points were investigated by the same method employed by Zheng \textit{et al.}\textsuperscript{30} and Zhu \textit{et al.}\textsuperscript{31}, due to similarity of their and our system in terms of geometric and electronic structure.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(color online) The band structures of the AA system, for angles (a) 0\degree, (b) 5\degree, (c) 60\degree and (d) 70\degree. The dotted red lines represent the bands without SOC and the blue lines represent the bands with SOC.}
\end{figure}
FIG. 4: (color online) The band structures of the AB system for angles (a) 0° ($d = 3.2 \text{ Å}$), (b) 0° ($d = 4.7 \text{ Å}$), (c) 5° ($d = 3.3 \text{ Å}$), (d) 5° ($d = 4.7 \text{ Å}$), (e) 60° and (f) 70°. The dotted red lines represent the bands without SOC and the blue lines represent the bands with SOC.

The figure [5] is an enlarged version of the band structure of AA S$_5$ having interlayer distance of 3.38 Å. From non-SOC band structure represented in red dotted lines, a semimetallic nature is observed due to the interaction between band at $\Gamma$ point and the band left to $K$ point. Also, an indirect band gap is observed between the band next to $K$ point and the band at $K$ point. When the SOC interaction is taken into consideration, the former set of the bands overlap, while the latter indirect band gap is closed. To understand this behavior we first flag the bands, so that the band at $\Gamma$ point is labeled as "G" before splitting and as "G1", "G2" for the top and bottom bands after splitting due to SOC. Similar the bands at $K$ point is labeled as "K", "K1" and "K2", for bands toward the left side of the $K$ point in named as "LK", "LK1" and "LK2". The energy difference between the band $LK1$ and $LK2$ is $\Delta LK$ 95 meV and that between $K1$ and $K2$ is $\Delta K$ 74 meV. Clearly the above effect is due to SOC. To understand the nature of this band splitting we calculate band decomposed charge density for those k-points as its characteristic is well documented and have been used for the similar analysis [30,31].
FIG. 5: (color online) The enlarged band structure of the AA configuration with the angle of 5 degrees and a distance of 3.4 Å between the two layers. The dotted red lines represent the bands without SOC and the blue lines represent bands with SOC. Bottom plots are the band decomposed charge densities at G1, G2, LK1, LK2, K1 and K2 k-points, respectively. From these charge density contour plots one can observe $|↑⟩$ and $|↓⟩$ states.

By including the magnetization direction (of bands) and observations from band decomposed charge density we note the following: G1 has $|↑⟩$ state, G2 has $|↓⟩$ state, K1 has $|↓⟩$ state, K2 has $|↑⟩$ state, LK1 has $|↓⟩$ state and LK2 has $|↑⟩$ state. The splitting at Γ point can be Rashba type splitting as the system has all the necessary requirements.
such as lack of inversion symmetry, band splitting due to SOC and band splitting at Γ point. A detailed analysis shows that it is not a Rashba splitting. However as characteristics of band structure will be dominated by the bands at and near K point. Thus, we can conclude that there are distinct up and down channels, combining both of the analysis it’s also noticed that system only provides a conducting up(down) channel and an indirect band gap for the up(down) channel of the magnitude of 28.13(49.29) meV, in the direction of K and LK points. While in the direction from LK point to Γ point one can note that the down channels overlap while the up channel do have a indirect band gap of ≈ 65 meV.

The above mentioned methodology can be used to interpret the band structure of the AB S70 having an interlayer spacing d 4.60 Å. From the band structure in figure 6 an indirect band gap between the band left to the K point and band left to M point of magnitude of 31 meV. Due to the SOC, an indirect band gap is reduced to null, while converting the semiconducting nature of the material into semimetallic due to the splitting in both bands. Using the same labeling convention as described earlier, the band left to K point is labeled as "LK" - before splitting, "LK1" and "LK2" - after splitting. With an energy difference between LK1 and LK2 as ΔLK 48 meV. Similarly the band left to the M point is labeled as "LM", "LM1" and "LM2". having an energy difference between LM1 and LM2 band is ΔLM 22 meV. From the band decomposed charge density (figure 6) along with the direction of magnetization of band we get, LK1 as |↓⟩ state, LK2 as |↑⟩ state and LM1 as |↑⟩ state, LM2 as |↑⟩ state. This again leads to the AB S70 having a distinct channel for up state with an indirect gap as 8.41 meV. Hence, by combining both of the observations we can assert that the system above provides us with distinct up channel. This property has been observed in multilayer MoS2 and it has been further exploited for designing next generation of electronic devices leading to the development of valleytronics, where the energy of electron and simultaneously valley of the bands is used. Also, from charge distribution of bands (Figure 5 and 6) a spread between layers is observed. This spread of charge density can be directly related strength of the interlayer coupling. As the charge density of these bilayer system is well distributed in between both layers, the interlayer coupling can be considered strong.
FIG. 6: (color online) The enlarged band structure of the AB configuration with the angle of 70 degrees and an interlayer distance of $d = 4.6$ Å between the two layers. The dotted red lines represent the bands without the SOC and the blue lines represent the bands with SOC. The bottom plots are the band decomposed charge densities at LK1, LK2, LM1 and LM2 k-points, respectively.
IV. CONCLUSION

We have studied the bilayer stanene with two stacking configurations AA and AB, using the first principle density functional theory. By changing the interlayer angles we found the minimum energy structure of the bilayer configurations by varying the interlayer distance. For AB stacking configurations of angle $0^\circ$ and $5^\circ$, we observed two minima, while the other configurations energies were found to be of the same magnitude. Hence these systems do have similar probability of being observed experimentally. Nevertheless we observe that a small change in the interlayer angle can affect the electronic properties of the system significantly. Further by including spin orbital coupling effect we observe band splitting, which converts semimetallic nature fo the material to metallic nature. A detailed analysis of the band structure in conjunction with the band decomposed charge density as well as magnetization directions of bands, for our systems namely AA $S_{5}$ and AB $S_{70}$. Help us to conclude that our system could provide energy dependent up/down conduction channels, with an indirect band gaps. The change in stacking order and interlayer distance does affect the electronic properties of the bilayer stanene. Our work indicates that the mechanically exfoliated bilayer stanene can be used for development of spin and valley physics which can be used for next generation of electronic devices.

V. ACKNOWLEDGMENT

The computational work described here is performed at the High Performance Computational Facility at IUAC, New Delhi, India. We would like to express our gratitude to them. Also, we would like to thank the University Grant Commission of India for providing partial funding for the research work through the UGC-BSR Research Startup Grant (Ref. No.F.30-309/2016(BSR)).

---

* Electronic address: ghadiyali.mohd@physics.mu.ac.in
† Electronic address: sajeev.chacko@physics.mu.ac.in; sajeev.chacko@gmail.com
1 Kostya S Novoselov, Andre K Geim, Sergei V Morozov, D Jiang, Yi Zhang, Sergey V Dubonos, Irina V Grigorieva, and Alexandr A Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, 2004.
2 F Duncan M Haldane. Model for a quantum hall effect without landau levels: Condensed-matter realization of the" parity anomaly". *Phys. Rev. Lett.*, 61(18):2015, 1988.
3MZ Hasan and CL Kane. Topological insulators. *arXiv preprint arXiv:1002.3895*, 2010.
4 Markus König, Steffen Wiedmann, Christoph Brüne, Andreas Roth, Hartmut Buhmann, Laurens W Molenkamp, Xiao-Liang Qi, and Shou-Cheng Zhang. Quantum spin hall insulator state in hgte quantum wells. *Science*, 318(5851):766–770, 2007.
5 Will 2-d tin be the next super material? [http://phys.org/news/2013-11-d-tin-super-material.html], 2014.
6 Charles L Kane and Eugene J Mele. Quantum spin hall effect in graphene. *Phys. Rev. Lett.*, 95(22):226801, 2005.
7 Kyozaburo Takeda and Kenji Shiraiishi. Theoretical possibility of stage corrugation in si and ge analogous of graphite. *Phys. Rev. B*, 50:14916–14922, Nov 1994.
8 Boubekeur Lalmi, Hamid Oughaddou, Hanna Enriquez, Abdelkader Kara, Sébastien Vizzini, Bénidicte Ealet, and Bernard Aufray. Epitaxial growth of a silicene sheet. *Appl. Phys. Lett.*, 97(22):223109, 2010.
9 ME Dávila, Lede Xian, Seymur Cahangirov, Angel Rubio, and Gyu Le Lay. Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene. *N. J. of Phys.*, 16(9):095002, 2014.
10 Yong Xu, Binghai Yan, Hai-Jun Zhang, Jing Wang, Gang Xu, Peizhe Tang, Wenhui Duan, and Shou-Cheng Zhang. Large-gap quantum spin hall insulators in tin films. *Phys. Rev. Lett.*, 111(13):136804, 2013.
11 Feng-feng Zhu, Wei-jiong Chen, Yong Xu, Chun-lei Gao, Dan-dan Guan, Can-hua Liu, Dong Qian, Shou-Cheng Zhang, and Jin-feng Jia. Epitaxial growth of two-dimensional stanene. *Nature materials*, 14(10):1020–1025, 2015.
12 Sumit Saxena, Raghvendra Pratap Choudhary, and Shobha Shukla. Stanene: Atomically thick free-standing layer of 2d hexagonal tin. *arXiv preprint arXiv:1505.05062*, 2015.
13 Sheng-shi Li and Chang-wen Zhang. Tunable electronic structures and magnetic properties in two-dimensional stanene with hydrogenation. *Mat. Chem. Phys.*, 173:246–254, 2016.
14 Wei-xiao Ji, Chang-wen Zhang, Meng Ding, Ping Li, Feng Li, Miac-juan Ren, Pei-ji Wang, Shu-jun Hu, and Shi-shen Yan. Stanene cyanide: a novel candidate of quantum spin hall insulator at high temperature. *Sci. Rep.*, 5:18604, 2015.
15 Xianping Chen, Ruishen Meng, Junke Jiang, Qiuhua Liang, Qun Yang, Chunjian Tan, Xiang Sun, Shengli Zhang, and Tianling Ren. Electronic structure and optical properties of graphene/stanene heterobilayer. *Phys. Chem. Chem. Phys.*, 18(24):16302–16309, 2016.
10

Steve M Young, S Manni, Junping Shao, Paul C Canfield, and Aleksey N Kolmogorov. Basn \(2\): A new, wide-gap, strong topological insulator. *arXiv preprint arXiv:1607.05234*, 2016.

Lauren Takahashi and Keisuke Takahashi. Low temperature pollutant trapping and dissociation over two-dimensional tin. *Phys. Chem. Chem. Phys.*, 17(33):21394–21396, 2015.

Chengxi Huang, Jian Zhou, Haiping Wu, Kaiming Deng, Puru Jena, and Erjun Kan. Quantum phase transition in germanene and stanene bilayer: From normal metal to topological insulator. *J. Phys. Chem. Lett.*, 7(10):1919–1924, 2016.

Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, et al. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *J. of Phys. Cond. Matt.*, 21(39):395502, 2009.

John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 77:3865–3868, Oct 1996.

Vincenzo Barone, Maurizio Casarin, Daniel Forrer, Michele Pavone, Mauro Sambi, and Andrea Vittadini. Role and effective treatment of dispersive forces in materials: Polyethylene and graphite crystals as test cases. *Journal of Computational Chemistry*, 30(6):934–939, 2009.

Stefan Grimme. Semiempirical gga-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry*, 27(15):1787–1799, 2006.

Anton Kokalj. Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale. *Comp. Mat. Sci.*, 28(2):155–168, 2003.

Virtual nanolab version 2016.3, quantumwise a/s. [www.quantumwise.com](http://www.quantumwise.com).

P. Rivero, J. A. Yan, V. M. García-Suárez, J. Ferrer, and S. Barraza-Lopez. *Phys. Rev. B*, 90:241408(R), 2014.

B. van den Broek, M. Houssa, E. Scalise, G. Fourtois, and V. V. Afanasev. *2D Mater.*, 1:21004, 2014.

B. van den Broek, M. Houssa, E. Scalise, G. Fourtois, and V. V. Afanasev. *Phys. Rev. B*, 92:045436, 2015.

John R Schaibley, Hongyi Yu, Genevieve Clark, Pasqual Rivera, Jason S Ross, Kyle L Seyler, Wang Yao, and Xiaodong Xu. Valleytronics in 2d materials. *Nature Reviews Materials*, 1:16055, 2016.

Xiaofeng Fan, David J Singh, and Weitao Zheng. Valence band splitting on multilayer mos2: Mixing of spin–orbit coupling and interlayer coupling. *J. Phys. Chem. Lett.*, 7(12):2175–2181, 2016.

Xiaofeng Fan, QT Zheng, Jer-Lai Kuo, David J Singh, CQ Sun, and W Zhu. Modulation of electronic properties from stacking orders and spin-orbit coupling for 3r-type mos2. *Sci. Rep.*, 6:24140, 2016.

Aurelien Manchon, Hyun Cheol Koo, Junsaku Nitta, SM Frolov, and RA Duine. New perspectives for rashba spin-orbit coupling. *arXiv preprint arXiv:1507.02408*, 2015.