

Electronic scale properties of pristine stanene and tin forms using *ab-initio* methods

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Abstract

In the current study, elastic properties of stanene, a hexagonal honeycomb allotrope of tin is investigated using tools in computational material science. The simulations are performed using Quantum Espresso, an open-source package suit used for conducting *ab-initio* density functional theory simulations. The lattice structure of stanene analogous to the other group-IV elements 2D structures like graphene, silicene, and germanene. The relaxed structure of stanene in hexagonal honeycomb structure is found to have a lattice parameter $a_0 = 4.62 \text{ \AA}$. Unlike pristine graphene which has no buckling, stanene structure shows a buckling $d_0 = 0.87 \text{ \AA}$. All the calculations are carried out using generalized gradient approximation (GGA), and the exchange-correlation is treated using Perdew-Burke-Ernzerhof (PBE) functional. The cohesive energy of the structure is found to be $3.85 \text{ eV/\AA}^0$. The calculations are conducted at groundstate without the inclusion of spin orbit coupling. The band structure, total and partial density of states at the ground state reveal the conducting nature of stanene. In addition, the second order elastic constants evaluated are reported and compared with the α -tin and β -tin counterparts. Copyright © 2019 VBRI Press.

Keywords: Stanene, 2D Materials, Density Functional Theory (DFT), Second Order Elastic Constants (SOEC), Quantum Espresso (QE).

Introduction

Research on 2D materials has been an important aspect of material science since the discovery of graphene [1]. Graphene proved to show exceptional physical, chemical and mechanical properties, which delivered significant research values and broad applicability in electronic devices, high strength materials, biomedical applications, and many. However, one crucial aspect featuring zero band gap has limited its applicability to semi-conducting device applications. Then came the interest in exploring other 2D material analogs of group IV elements of the periodic table like silicene, germanene, stanene. Recently added are the 2D transition metal dichalcogenides (TMDC) [2] which gained a hot spot in the research of 2D materials. Stacking separate layers of the atomic planes forming heterostructures [3] also helped numerous in advancing through robust materials and their applications.

The distinct band gap in specific 2D materials arises due to a remarkable phenomenon, spin-orbit coupling (SOC). The 2D materials exhibiting high SOC are used as spin filters and topological insulators (TI) [4]. In the case of TI, the electrons travel faster through the surface than bulk.

Stanene is a 2D hexagonal honeycomb structure analogous to graphene, except that there is an out of plane buckling as shown in Fig. 1. In honeycomb lattice, the SOC increases with increase in atomic mass. Hence

stanene is considered to have very high SOC capability [5] making room for distinct band gap and room temperature TI applications.

Stanene has the highest hexagonal lattice void compared to other group IV 2D structures like graphene, silicene or germanene.

While graphene has the potential applicability in hydrogen separation, permeability is weak, and it requires the inclusion of defects. Selectivity and permeability are the two most essential characteristics looked at, to be an excellent membrane. However, even without the inclusion of any defects, stanene based layer has enough void size to act as a sieve for selectivity, with potentially promising applicability for hydrogen separation. Based on the work by Gao *et al.* [6] the addition of fluorine to stanene resulting in Sn-F structure had a larger sized hexagonal void compared to pure stanene.

Stanene is extracted experimentally using Molecular beam epitaxy [7, 8]. Feng-Feng *et al.* [9] have successfully grown stanene with Bi_2Te_3 as the substrate. The process results in a substrate covered by about 90% by stanene, while 10-15 % Sn atoms remain as islands on the top. Synthesis of few-layer stanene analogous to few-layer graphene is presented by Sumit Saxena *et al.* [10]. The method utilizes Ultra-fast laser-material interactions. Altogether, stanene is an exciting material to be studied using electronic scale DFT calculations basing on its potential applications.

The article is organized as follows: The first section defines the methods used in the current ab-initio simulations; the second section involves building the stable structure of stanene followed by the third section, which describes bulk forms of tin and a comparison of their stability. The results section presents the cohesive energies, band structure, the density of states, charge density, second-order elastic constants (SOEC) obtained for different tin forms along with stanene.

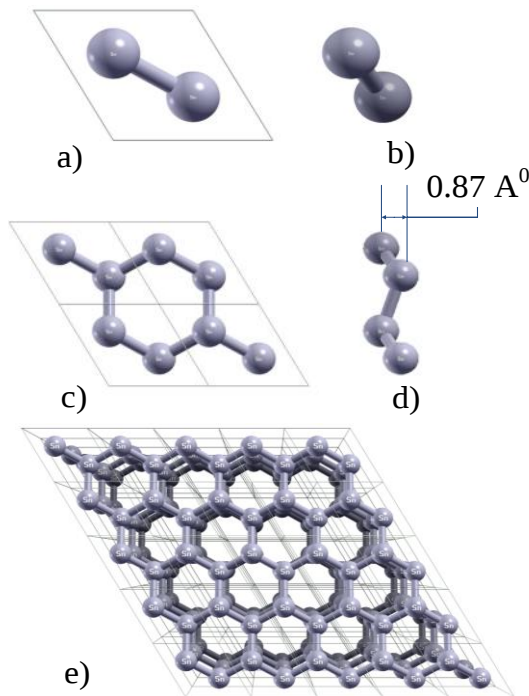


Fig. 1. Stanene structure. Front and side views (a-b) of primitive cell containing two tin atoms, (c-d) Front and side views of conventional cell containing 2X2 repetitions of primitive cell. (e) Perspective view of conventional cell containing 3X3X2 unit repetitions of primitive cell. Visualized using Xcrysden [11].

Methods

Determining the structure of stanene and its properties at the ground state using ab-initio computational electronic scale DFT is the prime objective of the current study. The band structure and SOEC are determined using Quantum Espresso [12-13]. All the calculations are performed by implementing generalized gradient approximation (GGA) method. GGA is an ultrasoft method in which the exchange-correlation is treated using Perdew-Burke-Ernzerhof (PBE) [14] functional. Local density approximation (LDA) [15] based calculations are also performed to verify the GGA estimates.

In the current investigations, all the calculations are performed without the inclusion of spin-orbit coupling. Total energy as a function of Lagrangian strain is numerically obtained using fitting procedure [16]. Later, the SOEC is determined by taking the second derivative of total energy with respect to the Lagrangian strain. The ElastiC package [17] is employed for estimating the SOEC.

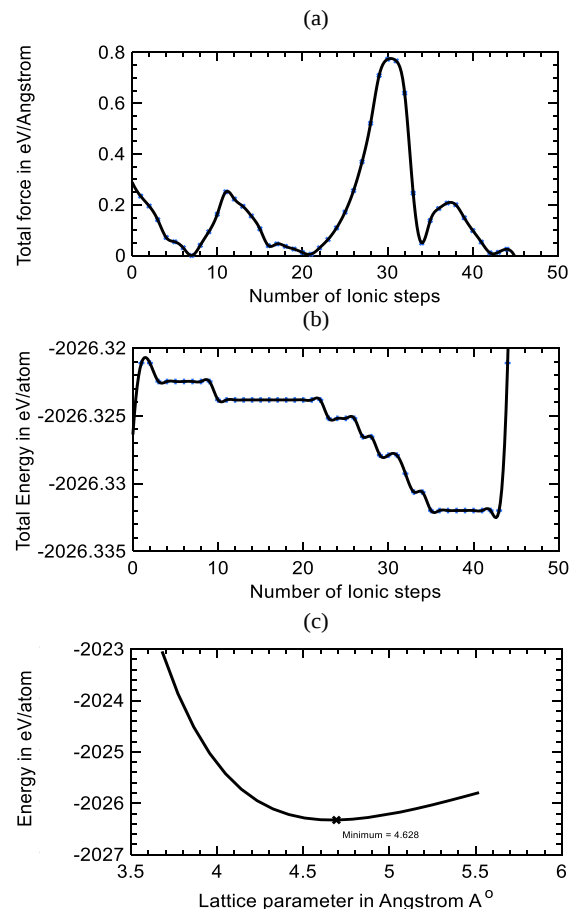


Fig. 2. Variable cell relaxation performed on stanene structure (a) force convergence vs. number of ionic steps (b) Energy convergence versus the number of ionic steps (c) Energy versus Lattice parameter curve for stanene.

Structure of stanene

The structure of Stanene is built with two atoms in the primitive cell as shown in **Fig. 1 (a)**. A 11X11X1 K-grid is chosen after carrying out an energy convergence calculation. Relaxation performed on the structure is to a force convergence of 1.3×10^{-5} eV per atom as shown in **Fig. 2(a-b)** with 42 ionic steps. The lattice parameter after structural relaxation is found to be 4.71 Å° from the energy versus lattice parameter curve in the **Fig. 2(c)**. The inter-planar distance for sStanene is chosen in such a way that the two layers are noninteracting. Periodic boundary conditions are imposed in the calculations mimicking the full structure of Stanene. Stanene exhibits buckling of 0.87 Å° in the c direction as shown in **Fig. 1(d)**.

Bulk forms of tin (Sn)

Tin exists in two stable phases α -tin and β -tin. α -tin has diamond cubic structure whereas the β -tin has a tetragonal structure. The transformation from α -tin to β -tin takes place at a temperature $\sim 13^\circ\text{C}$. **Fig. 3** shows the various phases or configurations of tin and their corresponding cohesive energies depicting their stability. The α -tin is the most stable among all while β -tin also called white tin is stable at room temperature.

However, the comparison made here is based on the ground state DFT calculation. Stanene has cohesive energy lower than both α -tin and β -tin. Defective configuration with a single stone-wales (5-7 pair) [18] defect in stanene is also added to the comparison list, and it has the least cohesiveness among all.

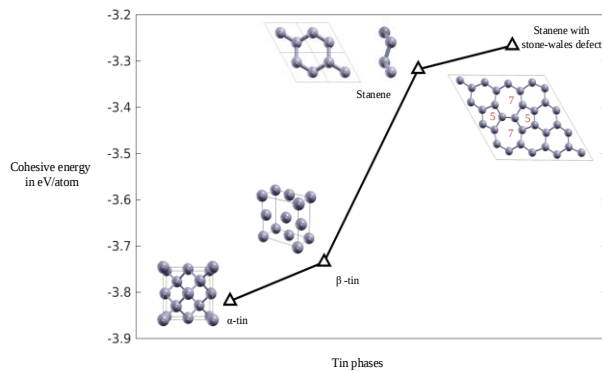


Fig. 3. Comparison of cohesive energies of α -tin, β -tin, stanene and a single stone-wale (5-7 pair) defected stanene.

Results and discussion

Electronic band structure

Electronic band structure characterizes the quantum mechanical states of electrons in the crystal. The wavevector of the first Brillouin zone in the reciprocal space of the crystal is of particular interest in the calculations. The K-path corresponding to the crystal structure is chosen to be Γ -M-K- Γ [19] as shown in the **Fig. 4(a)**. Another important parameter is the Fermi level which corresponds to the uppermost energy state filled at absolute zero which characterizes the conductivity of a material. If this Fermi level falls in between the bandgap, the material is insulating. If there is an overlap with the valance and conduction bands, they are electrically conducting. In the current case, the bandstructure in **Fig. 4(b)** shows overlapping at the point K corresponding to the K-path near the Fermi level which depicts the material to be conductive. The same can be supported using the Density of States plot as shown in the **Fig. 4(c)** [20].

The charge density distribution can provide information about the nature of bonding between various atoms. For example, if the valance charges are localized at the atomic locations, and no charges are present in between the atoms, or in the interstitial spaces, then the material has ionic bonding. On the other hand, if there is a pile-up of valance charges in between the line joining pairs of atoms, then they are covalently bonded. A significant amount of delocalized valance charge density is indicative of metallic bonding. The charge density of the system can be efficiently computed and visualized using the post-processing tools available in QE.

In **Fig. 5** the charge density of stanene is plotted along the atomic plane. The charge density shows a significant delocalization of electrons depicting finite charge transport capabilities.

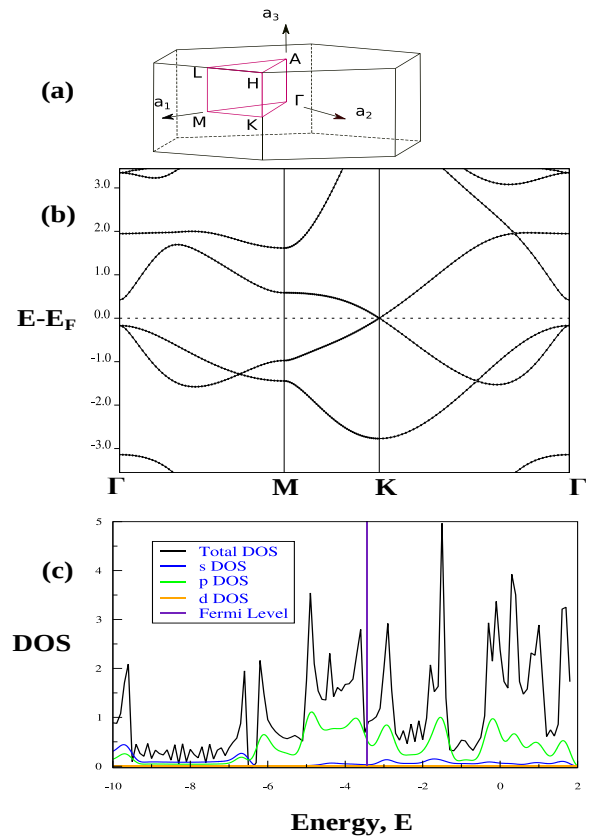


Fig. 4. (a) K-path in the I Brillouin zone for stanene. Band structure of stanene, 4(c) Density of states for the corresponding band structure, calculated using QE.

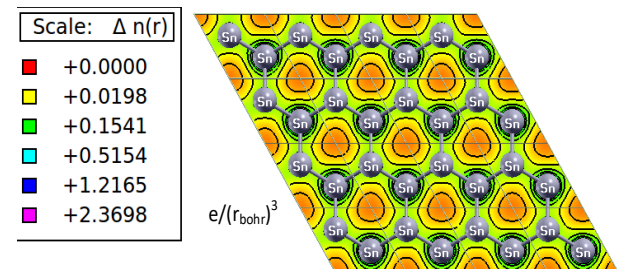


Fig. 5. The charge density of stanene, contour plot generated using Xcrysden.

Cohesive energy

Cohesive energy is the energy with which the atoms are bound together.

$$E_{\text{cohesive}} = E_{\text{structure}} - n * E_{\text{free structure}} \quad (1)$$

The cohesive energy of stanene is found to be -3.85 eV/atom in the current calculations as shown in **Table 1**, evaluated based on Eq. (1).

Table 1. Cohesive energies of stanene calculated in QE using DFT.

Material	Simulation technique	Cohesive Energy in (eV/atom)	
Stanene	DFT	-3.85	Current study
Graphene	DFT	-7.60	Huang <i>et al.</i> [21]

Second order elastic constants

The approach used in determining the SOEC of stanene is described below. The description of SOEC or elastic properties can be linked to the Lagrangian theory of elasticity of material coordinates. The stress is represented as τ and the strain is represented as η . Using Hookes' law the Lagrangian stress and strains are related using the expression in Einstein's summation notation.

$$\tau_{ij} = C_{ijkl}\eta_{kl} \quad (2)$$

where the values of $ijkl$ in Eq. (2) vary from 1 to 3. Here C_{ijkl} is called the elastic stiffness tensor of second order or SOEC tensor. The compliance matrix tensor S_{ijkl} is obtained by inverting the above equation

$$\eta_{ij} = S_{ijkl}\tau_{kl} \quad (3)$$

The total energy of the crystal can also be expressed in terms of the Taylor series expansion of strain with the following expression.

$$E(\eta) = E(0) + V_0\tau_{ij}^0\eta_{ij} + \frac{V_0}{2!}C_{ijkl}\eta_{ij}\eta_{kl} + \dots, \quad (4)$$

In the above expression $E(0)$ represents the reference structure energy and V_0 represents the reference structure volume. By using Voigt notation, the i, j values varying to 1 to 3 can be replaced by α, β varying from 1 to 6. The Eq. (2) can now be expressed as

$$\tau_\alpha = C_{\alpha\beta}\eta_\beta \quad (5)$$

The $C_{\alpha\beta}$ can be derived from Eq. (5) as

$$C_{\alpha\beta} = \frac{\partial \tau_\alpha}{\partial \eta_\beta} \Big|_{\eta=0} \quad (6)$$

The method of determining the C_{ijkl} from Eq. (6) is termed *stress approach*. Eq. (4) can be written in Voigt notation as,

$$E(\eta) = E(0) + V_0\tau_\alpha^0\eta_\alpha + \frac{V_0}{2!}C_{\alpha\beta}\eta_\alpha\eta_\beta + \dots \quad (7)$$

The $C_{\alpha\beta}$ corresponding to Eq. (7) is written as,

$$C_{\alpha\beta} = \frac{1}{V_0} \frac{\partial^2 E}{\partial \eta_\alpha \partial \eta_\beta} \quad (8)$$

C_{ijkl} obtained using Eq. (8) is called *Energy approach*.

In the current calculation on stanene, energy approach is followed in determining the stiffness parameters. The detailed description of the approach used in determining the stiffness values can be found in the article by Golesorkhtabar *et al.* [17]

The structure of stanene is of hexagonal crystal family. The generated structure falls into the category of trigonal crystal system. The corresponding Laue group is *R-II*, and the space group number is 164. The number of

independent elastic constants are six. However, owing to the 2D nature of the stanene structure, the number of non-zero elastic constants are limited to two. The β -tin has a tetragonal structure with Laue group *T-I* has a space group number 141. α -tin has a cubic crystal structure with Laue group *C-I* and space group number 227. All three structures are simulated for SOEC with 83 equally spaced deformations and the maximum Lagrangian strain applied is 0.03. The order of the fitting is chosen to be 6. The resulting stiffness components are presented in **Table 2** using parameters fitted in the **Fig. 6 (a-f)**. The SOEC tensor of α -tin and stanene satisfied positive definiteness, which can be attributed to the stability at the ground state. Owing to the unstable nature at the ground state (stable at $\sim 13^\circ$), the SOEC tensor for β -tin did not satisfy positive definiteness.

Table 2. Independent SOEC values of α tin, β tin and stanene calculated using DFT.

Stiffness component In GPa	α tin	β tin	Stanene
C_{11}	183.1	106	19.0
C_{33}	-	-188	-
C_{44}	62.3	98	-
C_{12}	59	270.2	7.4
C_{13}	-	77.3	-
C_{14}	-	-	-
C_{66}	-	30.4	-

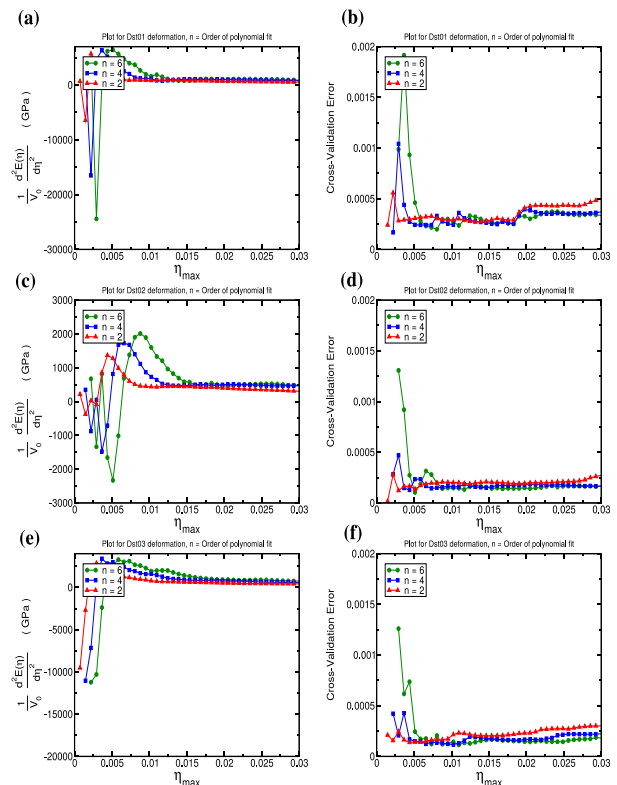


Fig. 6. Independent stiffness components obtained using deformations produced in the crystal for α -tin. (a-c-e) the three stiffness components for α -tin. (b-d-f) the cross validation error evaluated for the three independent stiffness components to determine the fitting order for the polynomial. The fitting orders are 2, 4 and 6 in all the cases.

Conclusion

In summary, the 2D hexagonal honeycomb structure of tin called stanene is successfully simulated using electronic scale DFT methods. All the calculations are performed at ground state. The cohesive energy of stanene is found to be close to 3.54 eV/atom which is ~0.5 times that of graphene. The charge density also shows a considerable variation in the hexagonal void and cohesiveness, and this can be attributed to the increasing nature of sp^2 - sp^3 hybridization as we go down the group IVA of the periodic table. Also, the partial density of states plot depicts that the p-contribution is high compared to the s-contribution. The independent second order stiffness values are determined for stanene in addition to the bulk forms of tin, and the resulting values are reported. The hexagonal void size is found to be around 4.6217 Å⁰ which is about 1.88 times that of graphene cell void, opening the opportunity for selectivity applications in the coming days.

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