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Evidence of a graphene-like Sn-sheet on a Au(111) substrate: electronic structure and transport properties from first principles calculations[†]

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Two dimensional nanostructures of group IV elements have attracted a great deal of attention because of their fundamental and technological applications. A graphene-like single layer of tin atoms, commonly called stanene, has recently been predicted to behave like a quantum spin Hall insulator. Here we report the atomic structure, stability and electron transport properties of stanene stabilized on a gold substrate. The optimization of geometry and electronic structure was carried out using a plane-wave based pseudo-potential approach. This work is divided into three parts: (i) the nature of chemical interaction between tin atoms and the gold support, (ii) the geometrical shape and electronic structure of the tin layer on the gold support and (iii) the electron transport behavior of the gold supported tin layer. The results show that tin atoms bind to the gold support through strong chemical bonds and significant electronic charge transfer occurs from tin to the gold support. Remarkably, for a layer of tin atoms, while a buckled structure is preferred in the free state, a planar graphene-like atomic arrangement is stabilized on the gold support. This structural change corroborates the metal-like band structure of the planar stanene in comparison to the semi-metallic buckled configuration. The tunneling current of the supported tin layer shows Ohmic-like behavior and the calculated STM pattern of the supported tin layer shows distinct images of 'holes', characteristic of the hexagonal lattice.

1. Introduction

Group-IV elements are interesting both for fundamental insights and technological applications.^{1–7} Since the discovery of graphene,^{8–11} a highly promising material with unique physicochemical properties, there has been a surge of interest in synthesizing its analogues. In corroboration of this expectation, experimental studies showed

that two-dimensional hexagonal silicon, the counterpart of graphene, can be stabilized on the Ag(110) or Ag(100) surfaces.¹²⁻²² This has opened a new avenue for material research at the nanoscale. Although a large number of studies reported the stability and other aspects of Si nanotubes and Si-fullerenes, a monolayer of Si was presumed not to exist in the free-standing form. In fact, even before the isolation of graphene, first principles local density functional calculations predicted that in contrast to the planar honeycomb lattice of graphene a buckled honeycomb structure of Si and Ge could exist.²³ The preference of sp³ hybridization over sp² hybridization leads to favor a buckled Si sheet rather than the graphene-like planar sheet. Recently, Feng et al.¹⁹ have reported the evolution of several monolayer nanostructures of silicon on the Ag(111) surface. Subsequent to the discovery of silicene, another graphene analogue, germacene, was synthesized by the exfoliation method.²² As a natural consequence, it is of interest to investigate the graphene-like Sn sheets and, in particular, underscore the electronic properties of the two-dimensional hexagonal lattice of a Sn monolayer, commonly referred to as stanene.

In recent years, the stability and electronic properties of a free standing stanene have been examined. Liu *et al.*⁶ calculated the electronic structure of stanene and concluded that a gap at the Dirac point is observed by incorporating the effective spin–orbit coupling (SOC). Zhang and coworkers²⁴ reported that a two-dimensional Sn sheet shows signatures of a quantum spin Hall insulator. This study has increased excitement and expectations which are evident by the appearance of a large number of every-day news articles, where it is claimed that if the theoretical predictions of Zhang's work can be proved experimentally, which is underway in several laboratories around the world, then two-dimensional Sn sheets can replace silicon devices by increased speed and lower power requirements of the next generation computer chips.

For scalable production of two-dimensional sheets, it is required to stabilize them onto a substrate. In order to fulfill this requirement a large number of studies have been carried out to stabilize two dimensional structures of graphene and silicene.²⁵ It is worth noting here that for C and Si, being lighter

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elements of group IV, it is easier to form sp^2 hybridization than other heavier elements of the group. Sn atoms, with high promotional energy, prefer sp^3 hybridization and form diamond like structures. Consequently, the overlap between two neighboring p_z orbitals of Sn is weak. Therefore, it is envisaged that charge transfer from Sn to a support can enhance sp^2 hybridization leading to the formation of a graphene-like planar sheet with larger overlap between p_z orbitals. In this communication we investigate the stability and electronic structure of a monolayer of tin (both planar and buckled) and underscore the modulation of its properties upon deposition onto a Au(111) substrate. The STM-like conductance of the sheet under the low bias limit is used to image the atomic level structure of the 2D sheet.

2. Computational details

Electronic structure calculations based on density functional theory (DFT) were performed using the plane-wave based pseudo-potential approach as implemented in the Vienna *ab initio* Simulation Package (VASP).^{26,27} The electron–ion interaction term was described by the all-electron projector augmented wave (PAW) method²⁸ and Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) was used to account for the exchange–correlation interactions.²⁹ The cut-off energy for the plane wave basis set was 350 eV. The positions



four layers was used as the model Au(111) substrate. The blue color represents the Sn atoms of a tin cluster. For clarity each atomic layer of gold has been presented in different colors. The relative stability of each structure is presented in eV.



of atoms were optimized until the convergence of the force on each atom was less than 0.01 eV Å⁻¹. The total energy convergence was

tested with respect to the plane-wave basis set and the cell size. The accuracy of the calculation has been verified by increasing the energy

cut-off to 500 eV, which resulted in similar structural and binding

energy. Test calculations were also carried out for different dimers in

order to verify the accuracy of our computational methodology

(Table S1 of ESI⁺). Excellent agreement between the measured

and calculated values suggests the reliability of the computational

method used. In order to test the transferability of pseudo-potentials

at different length scales, test calculations were carried out for bulk

gold. From our calculations the lattice parameters of the Au bulk

were found to be 4.18 Å, which is in good agreement with the corresponding experimental values. The calculated $R_{(Sn-Sn)}$ of a free standing stanene in the flat, planar and buckled configuration is 2.83

and 2.88 Å, respectively, and is in agreement with the previously reported studies based on density functional theory.³⁴ Unlike C and

Si, d-orbital electrons of Sn can influence the chemical bonding. In

order to verify this we repeated the above calculations including d

electrons of Sn. However, no significant change was observed both in

geometry as well as the electronic structure except for an increase in

of four layers in a (5×5) supercell having 100 atoms. A vacuum

The Au(111) surface was simulated with a slab model consisting

the number of energy levels due to d-bands.



and are in agreement with the previously reported values obtained

at the DFT-GGA level of theory.³⁰ All calculations regarding stanene@Au(111) were carried out using a slab model consisting of four layers in a (3×3) supercell having 36 gold atoms, and a further six tin atoms of the sheet reside over six hcp/fcc sites of this slab.

In order to quantify the electron-charge redistribution on atoms, we have calculated the electronic charges on atoms by using the method proposed by Bader.³¹ For this purpose we applied the numerical implementation of the Bader method developed by Henkelman *et al.*³²

3. Results and discussion

3.1. Structure and stability of stanene with and without the support

First we optimized the atomic and electronic structure of the free standing stanene. For this we have used a supercell $(3 \times 3 \text{ unit cells})$ consisting of 18 Sn atoms. The geometry

optimization was carried out by starting with both 'graphenelike' planar and 'silicene-like' buckled atomic structures. On the basis of the total energy of the relaxed structures, it is seen that both planar and non-planar structures are rearranged into buckled conformation, similar to that of silicene with a Sn–Sn interatomic distance of 2.83 Å. Moreover, Sn being heavy metal, we have examined the effect of relativistic corrections in the electronic structure. Remarkably, the results show that the inclusion of the spin–orbit term in the total energy indeed opens up the energy gap slightly between valence and conduction bands. These results are in good agreement with previous reports and thereby give confidence about the present computational approach.^{24,34}

After establishing the atomic and electronic structure of the free-standing stanene we focused our attention on understanding the growth and stability of stanene on the Au substrate. We begin with the investigation of the adsorption behavior of the Sn atom



Fig. 3 A graphene-like Sn sheet deposited on the Au(111) substrate. The color code is the same as that described in Fig. 1. The calculations were carried out with a slab model (3×3) supercell of the Au(111) surface, and six tin atoms of the sheet reside over six hcp/fcc sites of this slab. For clear visualization the large periodic version of a supercell has been presented.



Fig. 4 (top) The iso-density surface and (bottom) charge density difference ($\Delta \rho$) contours of the constituent layers at the interface of the Sn/Au(111) heterostructure. For the 2D plot the charge increased from blue to red in the rainbow. The electron distribution (ρ) has been represented with an iso surface value of 0.04 e bohr⁻³. For charge density differences plot ($\Delta \rho$), the iso-surface value is 0.0015 e bohr⁻³.

on the Au(111) surface. Among the well-defined sites on the Au(111) substrate *viz.* (i) top, (ii) bridge, (iii) the hollow fcc site, and (iv) the hollow hcp site (Fig. S1 of the ESI[†]), we find that the Sn atom prefers to reside on the fcc site with an $R_{(Au-Sn)}$ value of 2.73 Å. The binding energy of the Sn atom on the Au(111) support is expressed as

Binding energy = $E_{(Sn@Au111)} - E_{Au(111)} - E_{Sn}$

The calculated binding energy of the Sn atom at the fcc site is 3.35 eV. The binding of Sn on the hcp site is slightly (0.05 eV) lower in energy than the fcc site. The optimization of Sn on top and bridge sites eventually moves the Sn atom to the fcc site. Fig. 1 displays favorable atomic arrangements of the Sn atom on the Au(111) support. The high binding energy of the Sn atom on Au(111) is a result of large charge transfer from Sn to Au leading to the formation of polar covalent bonds.

Next, we focus on the adsorption behavior of two Sn atoms on the Au(111) substrate. This is important as it gives fundamental information about the adsorbate-adsorbate (Sn-Sn) and adsorbate-substrate (Sn-Au(111)) interaction, which effectively suggests the preference of 'wetting' vis-à-vis 'island' growth models. For optimization of two tin atoms on the Au(111) surface, we have followed two approaches: (i) two Sn atoms are placed far apart on the Au(111) surface and (ii) a Sn-Sn dimer is placed on the surface in parallel and perpendicular orientations. The optimized geometries are presented in Fig. 1. The results show that a Sn dimer placed in parallel configuration, having a Sn-Sn bond, is energetically more favorable (≈ 0.07 eV) on the Au surface in comparison to the case where two Sn atoms are far apart. The perpendicular isomer is found to be 2.1 eV higher in energy. For a Sn dimer, $R_{(Sn-Sn)}$ on Au(111) is found to be 3.15 Å, which is larger than that of the gas phase dimer (2.80 Å). The binding energy of the Sn dimer on the Au(111) substrate is estimated to be 4.40 eV. The charge transfer between Sn and Au atoms has been analyzed by the Bader method and the results are summarized



Fig. 5 Density of states projected on Sn atoms of a buckled and planar sheet of Sn (free standing stanene), and planar Sn/Au(111). For the deposited sheet PDOS for only the Sn sheet has been presented.

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in Table S2 and Fig. S2 of the ESI.† In order to test the growth pattern, calculations were carried out on a ten atom tin cluster deposited on the gold surface. For this, first we have optimized the tetra cap prism configuration, which is the lowest energy isomer of the Sn₁₀ cluster in the gas phase.³³ Further to verify the possibility of a planar configuration of the Sn₁₀ cluster, we have optimized a fused cyclo-hexane structure (similar to that of naphthalene) on the Au(111) surface. Remarkably, we found that the planar naphthalene like structure is 3.33 eV more stable than the tetra cap prism cluster on the surface (viz. Fig. 2). It should be mentioned that when a similar fused cyclo-hexane structure of the Sn₁₀ cluster is optimized in the gas phase, the planar structure is not stable and it turns into a 3D geometry after relaxation. Thus, based on the above results it is believed that the Sn atoms would prefer to form a monolayer rather than an island when atomic vapors of Sn atoms are sprayed over the Au(111) substrate.

After understanding the Sn–Au interactions at the atomic level we investigated the atomic and electronic structure of a layer of tin atoms on the Au(111) surface. Fig. 3 shows a few stable configurations of the graphene-like Sn sheet deposited over the Au(111) substrate. During ionic relaxation, for the stanene over Au(111), it is observed that Sn atoms prefer to occupy either the hcp or fcc surface sites. Sn atoms placed over the top sites of Au slip on the nearby hcp sites. Thus Sn atoms are arranged in a hexagonal graphene-like honeycomb structure over the hollow hcp surface sites of the Au substrate. This clearly suggests that the monolayer of Sn atoms prefers to form a coplanar-sheet over the Au(111) substrate. The placement of the Sn atoms over the hcp hollow site is favored by 0.09 eV in comparison to the fcc hollow site (*viz.* Fig. 3). In this context it is worth mentioning that the Sn–Sn interatomic distance in the free standing stanene with a zigzag configuration is 2.83 Å. The extent of buckling is estimated to be around 0.9 Å. Considering that $R_{(Sn-Sn)}$ is 2.88 Å in the Sn/Au(111) configuration, there appears to be negligible lattice mismatch between the monolayer and the substrate, as $R_{(Au-Au)}$ on the Au(111) surface is 2.89 Å (for details, refer to Fig. S4, ESI[†]). Note that $R_{(Au-Au)}$ is 2.90 Å at the top layer of the Au(111) surface indicating a negligible reconstruction at the top Au layer after the formation of stanene on the substrate.

It is known that the electronic properties of stanene can be modulated depending upon the nature of bonding at the Sn/Au interface. The total binding energy of stanene on the Au(111) surface is 5.82 eV‡ (0.97 eV per Sn atom). Such a higher binding strength is attributed to significant charge transfer at the interface. The Bader charge analysis finds that each Sn atom donates 0.37*e* while each Au atom tends to gain 0.07*e* in the Sn/Au(111) heterostructure. To understand the nature of chemical bonding between stanene and the Au substrate, difference in charge density ($\Delta \rho$) of the Sn/Au(111) heterostructure was calculated. $\Delta \rho$ can be expressed as

$$\Delta \rho = \rho[\text{stanene}(\text{Au}(111))] - \rho[\text{stanene}]_{\text{fix}} - \rho[\text{Au}(111)] \quad (1)$$

' ρ [stanene@Au(111)]' is the charge density of the total system, ρ [stanene]_{fix} is the charge density of the sheet fixed at the



Fig. 6 (a) Band structure of a buckled Sn-monolayer (free standing stanene) with and without SOC (spin orbit coupling). (b) Band structure of a planar sheet of Sn before and after deposition on the Au surface. Few bands have been highlighted to emphasize the effect on the substrate.

deposited geometry, and ρ [Au(111)] is the charge density of the Au(111) substrate.

Fig. 4 shows the contours of the iso-density surface and charge density difference at the stanene/Au(111) heterostructure. The red color represents the maximum electron density and it systematically decreases as the color changes from red to blue in the rainbow. From the variation in the color of the charge density difference plot it is clear that significant charge is transferred from stanene to the Au(111) support. As the atomic arrangement of Sn atoms in stanene becomes planar over the Au(111) support, it is expected that the hybridization of Sn orbitals will change from sp³ to sp²-like character. Fig. 5 and 6 show the calculated density of states and band structure of the Sn/Au(111) heterostructure, respectively. A comparison between the density of states near Fermi energy for the planar (free standing with fixed atomic positions) stanene and Sn/Au(111) hetero-structure clearly shows the suppression of $Sn-p_z$ states. This has been attributed to the Sn-Au(111) interaction through p_7 orbitals. Fig. 6(b) shows the band structure of a planar stanene sheet before and after interaction with the Au(111) substrate. It is important to note here that the inclusion of a spin-orbit coupling term opens the gap between conduction and valence bands, shown in Fig. 6(a), which is consistent with the previous report.²⁴ As a consequence of the charge transfer from Sn to the Au substrate, some of the valence bands shift to the conduction region near the Fermi level.

3.2 Electron transport properties

After establishing the stability and electronic structure of stanene on the Au(111) surface, we have investigated the electron transport behavior of this heterostructure. The Bardeen, Tersoff, and Hamann (BTH) formalism^{35,36} of electron tunneling was used to calculate the current for a setup used in the scanning tunneling microscope (STM), where one electrode is only weakly coupled to the sample.³⁵

The electron tunneling current between two electrodes can be written as I_{total} . In the low-bias limit and at finite temperature, I_{total} is calculated as follows:

$$I_{\text{total}} = \frac{2\pi e}{\hbar} \gamma \int_{-eV/2}^{eV/2} \rho\left(\varepsilon + \frac{eV}{2}\right) \rho\left(\varepsilon - \frac{eV}{2}\right) \times e^{-2d\sqrt{2(m/\hbar^2)(\phi_{\text{av}} - \varepsilon)}} \\ \times \left\{ \left[f\left(\varepsilon - \frac{eV}{2}\right) \right] \left[1 - \left[f\left(\varepsilon + \frac{eV}{2}\right) \right] \right] - \left[f\left(\varepsilon + \frac{eV}{2}\right) \right] \\ \times \left[1 - \left[f\left(\varepsilon - \frac{eV}{2}\right) \right] \right] \right\} d\varepsilon$$

$$(2)$$

where ρ is the projected densities of states (DOSs) of the sample – stanene and the gold cap, respectively, *d* is the distance of the tip from the monolayer, ε is the injection energy of the tunneling electron, *e* is the electronic charge, *m* is the effective mass of the electron, \hbar is the Planck constant, ϕ_{av} is the average work function of stanene and the tip, and *f* is the Fermi distribution function. At the low-bias regime, the effective mass of the electron (*m*) and the average work function are assumed to be

constant. In order to match the respective electrochemical potentials at zero bias, the Fermi energy of the monolayer deposited on a substrate and the probe tip is aligned, and is taken to be the reference energy in eqn (2).

Fig. S5 of the ESI[†] shows the representative setup considered for the electron transport calculations. The setup resembles the conditions of scanning tunneling microscopy (STM) experiments in which a four-layer slab is used to simulate the Au(111) substrate. The cap configuration of the probe tip is modeled with a 43-atom Au cluster. The work function of the monolayer, defined as the energy difference between the vacuum-level potential (calculated from the planar average of the electrostatic potential in the unit cell) and Fermi energy level of its surface, is taken to be 5 eV. The density of states for the tip is broadened using the Gaussian broadening scheme of width 0.1 eV to



Fig. 7 (a) The *I*–*V* characteristics of the Sn monolayer deposited on a Au(111) substrate (b) total density of states of the Sn monolayer deposited on the Au substrate and (c) total density of states of the Au_{43} tip.



Fig. 8 The STM images at constant current mode (1 nA) with an applied bias of 50 mV of a Sn monolayer on a Au(111) substrate. The minima (darker areas) correspond to the holes in the hexagonal monolayer lattice.

account for the broadening arising due to its semi-infinite nature. Note that the lifetime broadening of the electrons of a cluster deposited on a surface is found to be of the order of or greater than 0.2 eV.^{35}

We calculated the tunneling current with the STM tip aligned with a Sn atom, separated by 5 Å of vacuum. Fig. 7(a) shows the I-V characteristics in the range of -0.5 V to 0.5 V. The tunneling current shows an Ohmic response for both positive and negative values of the external bias. Fig. 7(b) and (c) show total density of states of stanene over the Au(111)surface and the Au₄₃ cluster mimicking the cap configuration of the tip, respectively. The modification of Sn orbitals due to the interaction with surface Au atoms established the presence of the hybridized states near the Fermi level, which eventually become the primary conducting channels for the system. Finally, we depict (Fig. 8) the constant current mode STM images calculated at 50 mV and 1 nA. We find that individual Sn atoms are subtly visible, but the image is dominated by the circular minima, corresponding to the 'holes', which are characteristic of a hexagonal lattice.

4. Conclusion

In summary, using first principles theory we have investigated the growth motif and stability of a graphene-like stanene on the Au(111) support. For Sn atom adsorption, we find that the hollow hcp site of the Au(111) substrate is preferred over other well defined sites. For the dimer, an 'in-plane' configuration parallel to the surface is preferred. Moreover, the dimer formation of Sn₂ on the substrate is more energetically preferred than two Sn atoms adsorbed at a distance. Importantly, the most stable structure of the Sn₁₀ cluster on the Au(111) surface shows planar fused hexagon geometry, indicating a graphenelike growth motif for this system. For the dimer, Sn atoms prefer to form planar structures. In the Sn/Au(111) heterostructure, significant charge transfer occurs from Sn atoms to the substrate. The stabilization of graphene-like planar stanene on the Au(111) substrate is explored further. While free standing stanene shows buckled structure as the lowest energy configuration, on the Au(111) support the planar graphene-like structure becomes the most stable. This structural transition is attributed to the participation of Sn-p_z orbitals in bonding with surface Au atoms. The electron transport behavior of the adsorbed stanene has been evaluated which showed Ohmic tunneling current through the sheet. Moreover, the calculated STM images revealed distinctly the so-called 'holes' in the hexagonal lattice of stanene.

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‡ Binding energy = $E_{(Sn@Au111)} - E_{Au(111)} - E_{Sn monolayer(planar)}$. To test the accuracy, similar calculations have been carried out using higher cutoff (500 eV) as well as more fixed layers (3 relaxed and 3 fixed layers), which resulted binding energy of 5.83 eV and 5.84 eV, respectively.

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