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Structural prediction of stabilized atomically thin tin layers

Pedro Borlido¹, Ahmad W. Huran², Miguel A. L. Marques² and Silvana Botti¹

The family of group IV two-dimensional materials shows a rich variety of structural, electronic and topological properties. Only graphene is stable in the honeycomb structure, while buckling and dumbbell configurations stabilize silicene and germanene. Here we investigate from first principles the lowest-energy atomic arrangements of atomically-thin tin layers. Our calculations are performed with a very efficient method for global structural prediction, combined with constraints that enforce the desired one-dimensional confinement and include the effect of strain due to the substrate. We discover a series of new structures that span a large range of atomic densities and are considerably more stable than hexagonal single- or double-layer stanene, as well as dumbbell structures. The ground state, a metallic double layer with a square lattice that lies 295 meV/atom below honeycomb stanene and only 149 meV/atom above bulk α -tin, is akin to the atomic arrangement of a layer of romarchite tin oxide. Due to its enhanced stability with respect to honeycomb stanene, we propose that this structure can be easily synthesized on appropriate lattice-matched metallic substrates.

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INTRODUCTION

Since the discovery and characterization of graphene,^{1,2} two-dimensional (2D) materials have been the subject of an increasing body of research. In flatland we can find several interesting systems with exotic properties driven by quantum-size effects. Besides graphene, the 2D archetype, the most studied systems have been 2D polytypes of other group-IV elements (silicene, germanene, and stanene), hexagonal boron nitride, borophene, phosphorene, bismuthene, and transition-metal dichalcogenides.^{3,4}

Here we want to focus our attention on 2D tin. In fact, this system has particularly appealing properties. For example, few-layer stanene has been experimentally determined to be a superconductor with a critical temperature between 0.6 and 2 K (depending on the number of layers).⁵ The high reactivity of the buckled honeycomb monolayer has been predicted to offer low temperature trapping and dissociation of common air pollutants, such as NO_x, SO_x and CO_x.⁶ Moreover, due to the position of Sn in the periodic table, spin-orbit effects become relevant in tin crystals, opening the door for topological behavior. Theoretical studies have indeed predicted that buckled stanene is a quantum spin-Hall insulator,^{7,8} with a band gap of 0.1 eV that can be increased to 0.3 eV by chemical functionalization,⁹ allowing to preserve the topological properties up to almost room temperature.

Tin is a rather mundane chemical element belonging to the same group as carbon. However, due to the increasing size of the atomic core as we descend group-IV, the tetrahedral coordination, driven by sp^3 hybridization, becomes progressively more and more favored than sp^2 -like planar configurations. As such, there is in nature no silicon, germanium, or tin analog of bulk graphite, which hinders the preparation of atomically thin samples for these elements via exfoliation. Fortunately, more advanced preparation techniques have already led to the experimental realization of

honeycomb silicene, germanene, and stanene on adequate metallic substrates, e.g., on Ag or Au (111) surfaces.^{10–13}

The increase of sp^3 hybridization has a number of other consequences. For example, Si, Ge, and Sn planar honeycomb structures are dynamically unstable,¹⁴ hence these materials prefer to adopt a buckled hexagonal motif. Furthermore, the relative buckling height increases along the group from 0.44 Å¹⁴ for Si, to 0.64 Å¹⁴ for Ge, and finally to 0.85 Å¹⁵ for Sn. This also seems to justify the impossibility to experimentally build free-standing atomic sheets from group-IV elements other than carbon.¹⁶

Another direct consequence is that the stability of these elemental monolayers is greatly enhanced by the addition of adatoms or by building multi-layered structures. Indeed, in the case of silicene and germanene, the addition of atoms of the same element on top and under the 2D hexagonal plane, forming a so-called dumbbell, leads to motifs that can be 218 meV/atom lower in energy than the parent honeycomb structure.^{17,18} To some extent, tin exhibits a similar behavior, as some dumbbell configurations were shown to be at least 180 meV/atom lower than stanene.¹⁵ Additionally, a MoS₂-like structure was found to be even more stable, 230 meV/atom lower than stanene.¹⁵

Layer stacking also gives rise to a stabilization effect. This becomes evident if one considers buckled stanene as a reconstruction of an isolated α -tin (111) surface layer. In this picture, an α -tin-like supercell can be built from the AB stacking of buckled stanene with a layer separation of 2.88 Å. The AB stacked bilayer of buckled stanene is already 122 meV/atom below the monolayer. This effect could indeed explain the possibility of fabricating few-layer free-standing stanene.¹⁹

Interesting questions now arise: what happens when we add atoms to a stanene monolayer? Will they bond to the atoms of the honeycomb lattice in order to form dumbbells, or will a new layer of stanene be formed? Does tin prefer completely new

¹Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany and ²Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany

Correspondence: Silvana Botti (silvana.botti@uni-jena.de)

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geometrical arrangements, still unreported for the other group-VI compounds? Of course, the situation becomes even harder to predict if we want to account for the effect of substrate constraints.

RESULTS AND DISCUSSION

To shed light onto this intriguing problem, we decided to investigate extensively the possible morphological arrangements of tin layers with a thickness of few ångström. Our tool is global structural prediction,²⁰ and more specifically the minima-hopping method.^{21,22} This is an efficient and successful technique^{23,24} to perform a completely unbiased exploration of the Born-Oppenheimer potential-energy surface. Often global structural prediction algorithms input energies and forces from a density-functional theory (DFT) calculation. It is true that DFT is probably the best electronic structure method for solids on the market, as it combines an extraordinary precision with a rather modest computational effort. However, our runs require hundreds of thousands of energy and force evaluations, making the use of DFT exceedingly slow when the size of the unit cell increases. As a workaround, we use a two-step procedure. First, we perform global structural prediction runs with energies and forces calculated with density-functional tight-binding, as implemented in the DFTB+ package.²⁵ We then select the most relevant structures and re-optimize them with DFT.^{26,27}

Our results are summarized in Fig. 1, where we plot the DFT energy per atom as a function of the area for the most interesting structures stemming from the minima-hopping runs. More detailed structural data, together with band-structures, can be found as Supplementary Information. Each curve was calculated by applying an equibiaxial strain to the corresponding optimized structure. Colored curves represent the frontier of the phase diagram, and are labeled from Sn-I to Sn-IX in increasing order of the position of the minimum. The zero of energy is chosen to be Sn-I in mechanical equilibrium. For comparison, single-layer stanene appears very unstable, with an energy of 295 meV/atom above the ground state Sn-I and with an area per atom of 9.5 Å^2 /atom, buckled AB bilayer stanene is at 174 meV/atom with an area per atom of 4.5 Å^2 /atom, buckled ABA trilayer stanene lies at 98 meV/atom in this energy scale with an area per atom of 3.18 Å^2 /atom (outside the range displayed in Fig. 1). Note that bulk α -Sn is only 149 meV/atom more stable than Sn-I.

Fig. 1 Energy per atom as a function of the area per atom for two-atom thick tin structures. All values are plotted with respect to the energy minimum of Sn-I. Gray curves represent a selection of structures obtained from the minima-hopping method that do not form a boundary for the energy curve. Thickness is measured as the vertical distance between the top- and bottom-most atoms of each structure. For reference, the buckled honeycomb mono-, AB bi- and ABA trilayers of stanene are located 296, 174 and 98 meV/atom above Sn-I, respectively, while bulk α -tin is merely 149 meV/atom below it

From Fig. 1 we can immediately see how buckling stabilizes layered tin phases. In fact, the lowest energy structures are also the thicker ones. To obtain thinner layers requires larger areas/atoms, that can be achieved, e.g., through strain.

The most stable structure we found, i.e., the ground-state of a quasi-two-dimensional layer of tin, lies on the left of Fig. 1 with an area of 4.07 Å^2 /atom. This structure, that can be described by a square lattice with 8 atoms in the primitive unit cell, is a staggering 174 meV/atom *below* buckled bilayer stanene. Surprisingly, Sn-I does not exhibit the familiar hexagonal honeycomb arrangement of graphene, silicene, germanene, or stanene. Instead, it is a bilayer of corrugated squares (see Fig. 2), with an atomic arrangement akin to the one of Sn and O in a layer of the (layered) romarchite tin oxide. Each layer features tin atoms in a stretched tetrahedral coordination occupying alternating sites, while the other sites are occupied by atoms in a pyramidal configuration with a square base. The enhanced stability of Sn-I with respect to buckled stanene can be understood in light of the more favorable tetrahedral coordination of tin atoms. These tetrahedra are of lower symmetry than those that build up α -tin, as their faces are isosceles triangles rather than equilateral ones. We remark that Sn-I is more stable than both bilayer and trilayer buckled stanene, appearing therefore as an island of stability for atomically-thin films made of tin, in an area/atom range intermediate between the one of bilayer and trilayer structures.

As it turns out, Sn-I (like all the other phases discussed below) is an excellent conductor with a strong metallic character (see Fig. 3 and Supplementary Information), due to several bands crossing the Fermi energy. Not surprisingly, as there is no honeycomb lattice, no Dirac cone can be found at the Fermi level.

In ref.¹² the growth of an hexagonal bilayer of tin on a Bi_2Te_3 (111) surface is reported. We remember that buckled hexagonal bilayers of tin have an energy per atom 174 meV/atom higher than Sn-I, and more than 300 meV/atom higher than bulk α -Sn. Also silicene lies more than 400 meV/atom above the diamond phase, but it has been experimentally synthesized thanks to its stabilization on substrates. Supporting metallic substrates can indeed stabilize silicene by donating electrons, while preserving a moderately small interaction between the monolayer and surface atoms. We expect therefore that also Sn-I should be synthesizable on appropriate metallic substrates. In view of the in-plane square lattice displayed by Sn-I, we can suggest some possible metallic substrates with square surface lattices and a small lattice mismatch. Surfaces of Ag and Au remain good candidates if we replace the (111) surface with the (100) surface. Ag (100) and Au (100) squared lattices have a lattice mismatch of 2.7 and 2.9%, respectively, corresponding to an equivalent area/atom of 4.33 and 4.35 Å^2 /atom, very close to the stability minimum, and well inside the stability interval of Sn-I. Even closer to the equilibrium area/atom are Al (100) and Pt (100) surfaces, with lattice mismatches of 0.3 and 1.8% only.

To ascertain the dynamical stability of free-standing Sn-I we calculated the phonon band-structure using the finite differences method as implemented in the PHONOPY package.²⁸ We used the Perdew-Zunger²⁹ local-density approximation, as this functional was shown to outperform PBE for phonon-related properties.³⁰ Unlike the monolayer of romarchite tin oxide, which is dynamically unstable,³¹ Sn-I has only real phonon frequencies (see Fig. 3). As expected considering the large mass of Sn, phonon frequencies are rather low, and consistently within the same energy range of the phonon frequencies of α - or β -Sn.³²

The structural motif observed in Sn-I seems to be favored for structures with up to 4.5 Å^2 /atom. Sn-II, 19 meV/atom almost directly above Sn-I, displays a corrugation pattern modified along one of the in-plane directions, becoming asymmetric in a sort of sawtooth-like structure. Structural similarities to Sn-I are more apparent in Sn-III (27 meV/atom above Sn-I). This structure can be seen as a reconstruction of the Sn-I monolayer, exhibiting sharper

Fig. 2 Crystal structure of the polymorphs mentioned in the main text. Sn-IX is not shown since it has been extensively investigated in the literature. Atoms are colored using a scale from blue to red according to their relative position at the top or bottom of the structure, respectively

Fig. 3 **a** Side and **b** top views of Sn-I, together with the calculated PBE electronic band structure **c**, and phonon bands **d**

corrugation patterns but a smaller thickness of approximately 4.0 Å (compared to the 5.6 Å of Sn-I).

At lower values of atomic density, new types of structure becomes favored. The Sn-IV phase, 44 meV/atom above Sn-I, is composed of buckled hexagons. The buckling height is 2.57 Å, almost three times larger than the one of stanene. In this picture, Sn-IV can be seen as the result of a simple transformation of buckled stanene, namely, an increment in the buckling height accompanied with shrinkage of the lattice constant, forming what is usually known as the high-buckled (HB) honeycomb structure. Along the aforementioned transformation path, we estimated the internal energy barrier to be 227 meV/atom, with the transition structure exhibiting a buckling height of 1.66 Å. Unlike the dynamically unstable HB silicene and germanene,¹⁴ HB stanene is a true local minimum of the potential energy surface (see Supplementary Information). We note that the increased buckling is accompanied by an enhanced electron localization on the atomic sites.

Between 5.0 and 5.5 Å²/atom we find three structures: Sn-V, Sn-VI, and Sn-VII. The Sn-V phase, 43 meV/atom above Sn-I, consists of alternating corrugated sections that meet at distorted buckled

hexagons, similar to the ones encountered in Sn-IV. At slightly higher formation energies we find Sn-VI, formed by two shifted planar networks of rhombi. The following minimum, Sn-VII, is a 6-4 haeckelite double-layer, located 57 meV/atom above Sn-I. An interesting feature of this structure is that its monolayer analog is extremely unstable, as it lies 430 meV/atom above Sn-I. Therefore, the formation of the bilayer results in a 373 meV/atom stabilization.

Finally, we refer to the Sn-VIII and Sn-IX allotropes, which have geometrical elements in common. Sn-IX is found at around 7.0 Å²/atom, 115 meV/atom above Sn-I. This structure is well-known for 2D materials of group IV, and it is often called the large honeycomb dumbbell.¹⁷ Curiously, it is a low-energy structure for both silicon and germanium. Furthermore, previous studies on Sn predict it to be dynamically stable and also a quantum spin Hall insulator.³³ Sn-VIII can be derived from the Sn-IX structure, as it consists of a series of large honeycomb dumbbell ribbons (with the dumbbells along the edges), tilted collectively along their translational axis, and joined at the facing dumbbells (see Supplementary Information). The additional coordination deriving from dumbbell atoms is enough to lower this structure by 30 meV/atom with respect to Sn-IX.

We would also like to comment on one last structure of 2D-tin that has been recently proposed in the literature, specifically the MoS₂ stanene variant.¹⁵ This structure lies at 3.12 Å²/atom, circa 50 meV/atom below the large honeycomb dumbbell,¹⁵ but still 60 meV/atom above Sn-I (an energy range with a large density of possible structures).

In conclusion, we performed extensive global structural prediction calculations for quasi-two-dimensional tin, in a large range of atomic densities, focusing on a layer thickness comparable to the one of buckled bilayer stanene. More than 100 000 minima were found, from which we selected the most interesting for further analysis. Our results show a complex landscape, with several different geometrical arrangements competing in the low-energy regime. The most stable polymorph of 2D bilayer tin, that we named Sn-I, has a square lattice and metallic character, with several electronic bands crossing the Fermi level. Its structure is reminiscent of a layer of romarchite tin oxide, where both tin and oxygen sites are occupied in this case by tin. This arrangement allows for a tetrahedral coordination of the Sn atoms, therefore favoring a large sp^3 hybridization. Thanks to the much smaller energy difference to bulk α -tin (Sn-I is only 149 meV/atom higher) we believe that this structure could be produced

experimentally, using e.g., the stabilizing effect of almost lattice-matched Ag (100), Au (100), Pt (100), or Al (100) substrates.

METHODS

Crystal-structure prediction calculations

Crystal-structure prediction calculations were performed using a constrained version of the minima-hopping method.^{21,22} We have already successfully applied this constrained approach to investigate 2D polymorphs of carbon,³⁴ silicon,¹⁸ and germanium. Due to the amount of structures considered, forces and energies were first computed with density-functional tight-binding, as implemented in the DFTB+ package.²⁵ For this step, we used home-made high-quality Slater-Koster parameters, specifically fitted to obtain energies and forces with quasi-DFT precision.³⁵ The number of calculations also forced us to neglect spin-orbit coupling at this stage, although we verified *a posteriori* that this is acceptable (see below).

A systematic structural prediction of supported 2D tin, including explicitly its interaction with every possible substrate, is beyond our computational capabilities. We decided therefore to simulate the strain due to the substrate by constraining the unit-cell area of the free-standing tin layers. We performed structural prediction at fixed area, spanning values of the area/atom in a large interval that is compatible with the formation of both monolayer and bilayers of tin. This translates to inverse atomic densities ranging between 3.5 and 8 Å²/atom. We complemented then these fixed-area calculations with unconstrained ones. We considered unit cells containing 2 to 20 Sn atoms. All in all, we obtained more than 100 000 local minima, with layer thickness varying between 2.4–5.9 Å. At the end we searched for lattice-matched metallic substrates for the identified lowest-energy structures. In this way we assume that the stabilizing effect of the substrate is limited to the donation of electrons to the ultra-thin tin layer, while we neglect the formation of chemical bonds between stanene and the substrate. This choice is essential to make possible an exhaustive large-scale exploration of the most stable 2D crystal structures.

DFT calculations

The most relevant structures were re-optimized with DFT within the projector-augmented wave formalism, as implemented in VASP.^{26,27} The Perdew-Burke-Ernzerhof (PBE)³⁶ approximation to the exchange-correlation functional was used for geometry optimizations and band-structure calculations. In the direction perpendicular to the layer, we built supercells containing at least 15 Å of vacuum to isolate periodic copies, while in the plane we used a *k*-point set with a density corresponding to a 12 × 12 grid for stanene.

All these calculations were performed without taking into account spin-orbit coupling, mostly to reduce the computational cost. However, we know that tin is a rather heavy element, with a sizable spin-orbit interaction, that is important in certain contexts. As such, we repeated *a posteriori* DFT calculations for a series of structures including this term. We found that spin-orbit coupling does have a measurable effect in the formation energy. However, this energy shift is nearly constant for all 2D structures (55–59 meV/atom), thereby our assumptions are justified.

DATA AVAILABILITY

All data that support the findings of this study are available in the published article (and in its Supplementary Information files). The Crystal Information Files are also included in the Supplementary Information. Source data for figures are available from the corresponding author upon reasonable request. Supplementary material is available on the journal website.

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AUTHOR CONTRIBUTIONS

M.A.L.M. and S.B. designed and directed the project. A.H. computed Slater-Koster parameters. P.B. performed minima hopping and electronic structure calculations. All authors contributed to the analysis of the data and to the writing of the manuscript.

ADDITIONAL INFORMATION

Supplementary Information accompanies the paper on the *npj 2D Materials and Applications* website (<https://doi.org/10.1038/s41699-019-0103-9>).

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