Atomic and electronic structure of ideal and reconstructed \(\alpha\)-Sn (111) surface

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(November 2, 2018)

Abstract

We have carried out an \textit{ab-initio} study of \(\alpha\)-Sn (111), with the aim of predicting and understanding its structure, reconstructions, and electronic states. We consider a variety of structural possibilities, and optimize them by moving atoms according to Hellmann-Feynman forces. Our results indicate that the unreconstructed surface is highly unstable, while a variety of reconstructions compete for the true ground state. Extrapolated trends from diamond to Si to Ge are well borne out, with a \(2 \times 1\) \(\pi\)-bonded chain reconstruction prevailing in the absence of adatoms, and a \(c(4 \times 2)\) or \((2 \times 2)\) basic adatom-restatom unit reconstruction otherwise. Accompanying surface bucklings are in both cases larger than in Si and Ge, with consequently large ionic charge transfers predicted. Search for a \(\beta\)-Sn-like metallic state of the surface turned out to be inconclusive.
I. INTRODUCTION

Essentially all semiconductor surfaces are reconstructed. As is well known, this can be traced back to the strong covalency of their bulk band structure. In fact, the uniqueness of covalent systems, as opposed to, for example, regular metals, is that bulk covalent bonding is very directional and relatively inflexible. Consequently, it generally costs too much energy to locally rearrange the electron wave functions at the surface (as required by the presence of broken bonds), without some major lattice readjustments.

In the group-IV insulators and semiconductors, known to crystallize in the diamond structure, the best studied face by far is the (111), where well documented results are available for diamond, Si and Ge. Both experiment and theory indicate that a variety of different reconstruction mechanisms are realized. A summary is presented in Table I. One can see that all (111) surfaces possess a $\pi$-bonded chain $2 \times 1$ reconstructed state. As a true ground state, however, $\pi$-bonded chains only prevail in diamond, possibly reflecting the difficulty of obtaining well annealed adatoms on this surface. On Si and Ge (111), the adatom reconstructions, $(7 \times 7)$ [Ref. 1] and $c(2 \times 8)$ [Ref. 2] respectively, have lower energy, whereas the $2 \times 1$ $\pi$-bonded chain reconstruction remains well-defined, but energetically metastable.

In all cases: diamond, Si and Ge (111), the metallic character of the ideal, symmetrical $\pi$-bonded chain reconstruction is removed by some accompanying distortion. This distortion can consist either of a slight dimerization of the chain, as is probably the case in diamond, or of a vertical buckling, as in Si and Ge. Although experimental buckling data for diamond and Ge (111) are not yet available, \textit{ab-initio} calculations exist for these geometrical distortions. The size of the predicted chain bucklings exhibits an interesting trend, namely it is zero in diamond, about 0.4 Å in silicon (where experimental data confirm this magnitude), and 0.8 Å in germanium. The absence of buckling in carbon has been ascribed to the larger intra-atomic Coulomb repulsion, which prevents the ionic charge transfer implied by the buckling. The decrease of Coulomb repulsion with increasing atomic
number is consistent with the trend towards a larger buckling.

When adatoms are present, as in annealed Si and Ge (111), then an adatom-rest atom reconstruction prevails. Interestingly, the adatom reconstruction again implies surface ionicity, with an electron charge transfer between the adatom and the restatom.

Besides $\pi$-bonded chains and adatom-restatom reconstructed states, a third kind of state, namely the displacive $2 \times 1$ buckled reconstruction, originally proposed by Haneman, may also play a role. Although never found to be stable experimentally, and never stable theoretically either, it does make a brief appearance as a metastable transition state in the transformation path from ideal $1 \times 1$ to $2 \times 1 \pi$-bonded chain, in Si and Ge (111), as found by ab-initio molecular dynamics. This does not seem to occur on C (111), probably again because the Haneman state is ionic, and thus very costly in carbon.

Finally, the last entry in Table considers, as a fourth type of reconstruction, the possible transformation of a thin surface layer from semiconducting to metallic. This possibility is suggested by the bulk phase diagrams of Si, Ge and Sn, where fully metallic phases completely surround the semiconducting phases, under any combination of either high pressure or temperature. There is considerable evidence that surface metallization does in fact play a relevant role at high temperatures. The finite temperature behavior is however outside the scope of the present work. Although this transformation (as predicted, for example, in Ga) does not appear to prevail at $T=0$ K in Si and Ge, it could still take place in $\alpha$-Sn, which is closer to being metallic.

Throughout the literature, only the (100) surface of $\alpha$-Sn appears to have been considered so far. This paper is devoted to what is therefore a first study of the $\alpha$-Sn (111) surface. In particular, since there are no experimental data available, ab-initio calculations are required to compare the various possible reconstructions, and understand the trends relative to the other semiconductors just described. By extrapolating the trends of Table we are led to expect the following:

i) the $2 \times 1 \pi$-bonded chain reconstruction should be present also in $\alpha$-Sn(111), with an even more pronounced buckling than in Ge;
ii) This reconstruction will be in energetic competition with some adatom/restatom reconstructions, the latter being likely to prevail;

iii) A surface metallization mechanism is also possible because of the presence of the bulk metallic $\beta$-Sn phase, energetically very close to the $T = 0$ bulk ground state $\alpha$-Sn.

In this work we shall find that (apart from metallization, which turns out to be a harder problem) these trends are generally well borne out by ab-initio calculations. An adatom-restatom reconstruction is predicted to be the annealed ground state of $\alpha$-Sn (111). Although the exact periodicity cannot be predicted, our geometry and energetics based on an elementary $c(4 \times 2)$ or $2 \times 2$ unit should be fairly reliable.

This paper is organized as follows. First of all, we calculate electronic structure, total energy and optimal geometry of bulk Sn, both in the $\alpha$ semimetallic phase, and in the $\beta$ metallic phase. This is described in Section II. Next, in section III we use the same ingredients for a surface calculation in the usual slab geometry. We deal first with the ideal, unreconstructed $\alpha$-Sn (111) surface, whose properties we study without and with surface relaxation. We find partly filled dangling bond states in the ideal surface electronic structure, which as usual suggest that this is not a stable surface. This is confirmed in Section IV, where a $2 \times 1$ displacive reconstruction is shown to lower surface energy without energy barriers. The more interesting $\pi$-bonded chain reconstruction is considered in Section V. It is found that a very strongly buckled $2 \times 1 \pi$-bonded chain state exists for $\alpha$-Sn (111), its energy being better than that of the Haneman state. Section VI is devoted to the alternative possibility of adatom/restatom reconstructions. We find this latter possibility to be energetically the best, particularly in the $c(4 \times 2)$ local geometry. Lastly, in Section VII we briefly describe an attempt at finding a stable metallic reconstructed surface ground state, which however turns out to be inconclusive. Section VIII summarizes the main conclusions of this work on $\alpha$-Sn (111), confirming the trends extrapolated from diamond, Si and Ge, and stressing our predictions for future experimental work.
II. BULK PROPERTIES

The zero temperature structure of bulk Sn is the $\alpha$ phase with a diamond lattice of spacing 6.483 Å (at 90 K). As is well known, if the temperature is raised to 286 K at atmospheric pressure, semimetallic $\alpha$-Sn transforms into the fully metallic $\beta$-Sn phase. Under pressure, this transformation occurs at lower temperatures, extrapolating to T=0 K at a pressure of 5 Kbar. Total energy LDA (local density approximation) calculations confirm that at zero temperature and zero pressure the $\beta$ phase is energetically very close to the $\alpha$ phase, their energy difference being 44 meV/atom, with a predicted transition pressure to the $\beta$ phase of 8 Kbar. The relative success of LDA calculations in predicting very closely these extremely delicate differences provides confidence in extending this approach towards exploring surface properties.

In the present $ab$-initio calculations for $\alpha$-Sn (bulk and surface) and $\beta$-Sn (bulk) we model the electron-ion interaction with a norm-conserving pseudopotential in the Kleinman-Bylander form with $s$ and $p$ nonlocality, and use the standard LDA for the electron-electron interaction. We expand the Kohn-Sham orbitals in plane waves with an energy cutoff of 12 Ry in all calculations (bulk and surface) for consistency. For the $\alpha$-Sn bulk calculation, 10 special k-points are sampled in the Irreducible Brillouin Zone (IBZ) of the diamond phase. For the metallic $\beta$ phase, instead, we find that 160 k-points are needed to describe accurately the IBZ summations, with an additional gaussian spreading of 0.14 eV. We find a lattice constant $a = 6.446$ Å (exp. $a = 6.483$ Å) for $\alpha$-Sn and $a = 5.768$ Å (exp. $a = 5.812$ Å) for $\beta$-Sn (for simplicity, we fixed the c/a ratio to the experimental value of 0.546). We also find that the $\beta$-phase is disfavored with respect to the $\alpha$-phase by 17 meV/atom, with an $\alpha \rightarrow \beta$ transition pressure of 5 Kbar in excellent agreement with experiment. We have tested that increasing the energy cutoff to 35 Ry and the k-point integration to 200 points in the IBZ of the $\beta$-phase does not alter significantly these results. On the contrary, if the energy cutoff is less than 12 Ry, e.g. 10 Ry, the transition pressure becomes 2.5 Kbar and the energy difference drops to 9 meV/atom.
The electronic band structure of $\alpha$-Sn is reported in Fig. 1 and that of $\beta$-Sn in Fig. 2. As can be seen, in particular, the semimetallic character of the $\alpha$-phase (zero gap at $\Gamma$) and the fully metallic character of the $\beta$-phase are of course correctly borne out in our calculations.

III. THE RELAXED, UNRECONSTRUCTED $\alpha$-SN (111) SURFACE

We study the surface properties of $\alpha$-Sn (111) by a standard slab calculation. One of the two surfaces of the slab is frozen in its ideal geometry, together with the first three adjacent layers (a total of two rigid bilayers). The atoms belonging to the remaining layers are allowed to fully relax guided by the corresponding Hellmann-Feynman forces. Convergence is assumed when forces are less than 4 meV/Å. The number of atomic layers in the slab is fixed to a total of 12 layers (not including the adatom layer when present). Each layer consists of either one, two, or four Sn atoms, in correspondence to choosing $1 \times 1$, $2 \times 1$, and $2 \times 2$ [or $c(4 \times 2)$] surface cells, respectively. The number of “vacuum layers” is fixed to 6 (vacuum thickness $\sim 11$ Å), and the number of k points in the Irreducible Surface BZ (ISBZ) is chosen according to the size of the surface cell and its geometry, as described case by case. The initial atomic positions are chosen according to the calculated equilibrium bulk lattice spacing ($a_0 = 6.446$ Å). This guarantees that the forces on the atoms of the central layers are smaller than 4 meV/Å for all the surfaces studied. In all cases, surface energies $E_{\text{surf}}$ are given as $E_{\text{surf}} = E_{\text{slab}} - NE_{\text{bulk}} - E_{\text{ideal}}$, where $E_{\text{slab}}$ is the total energy of the slab, $E_{\text{bulk}}$ is the energy per atom of bulk $\alpha$-Sn as computed in section II [$E_{\text{bulk}} = -96.753$ eV/atom] above, $N$ is the total number of atoms in the slab. Furthermore $E_{\text{ideal}} = [E_{\text{ideal slab}} - NE_{\text{bulk}}]/2$ is the energy of the frozen ideal surface. Here $E_{\text{ideal}}$ is the total energy of a slab with both surfaces rigid and ideal, computed using the same supercell geometry and k-point set as $E_{\text{slab}}$. We thereby have to repeat ideal surface calculation several times in different supercells and k-point sets corresponding to different surface reconstruction slab calculations in order to compare different reconstructed surface energies. The convergence of our results with respect
to the k-points sampling has been tested for each surface by increasing the k-point number after the atomic relaxation. Accordingly, we can estimate our overall energy resolution to be about 10 meV/(1 × 1)cell. We also constructed the electronic band structure of the relaxed surfaces, by using the Kohn-Sham eigenvalues of a 10-layer slab, obtained by removing the seven bottom layers of the simulation slab and replacing them by the inverted image of the topmost five relaxed layers. The reason for this procedure is threefold. First, we get rid of the undesired states related to the bottom rigid ideal surface. Second, we increase the effective symmetry of the supercell, thus decreasing the computational effort of the band structure calculation. Third, although the interaction of identical surface states belonging to opposite surfaces generally lifts their degeneracy (again an undesired effect), their average energy still corresponds, to first order, to the noninteracting value in the ideal case of an infinite slab.

As a first case we have considered the (1 × 1) unreconstructed surface. Six special k-points in the hexagonal ISBZ have been used [24]. The electronic band structure of the ideal (1 × 1) surface is reported in Fig. 3. There are various surface states lying in the projected gaps. The surface states crossing the Fermi level inside the fundamental gap are clearly related to the presence of unsaturated surface dangling bonds. This feature is common to all the other group-IV insulator and semiconductors, and is responsible for the high grade of instability of the ideal (111) surface, as mentioned. The electron density corresponding to the surface state is analysed in Fig. 4, and reveals a high degree of surface localization as well as a clear dangling-bond character.

As the next step, we allowed the surface, i.e. all atoms in the eight topmost surface layers, to relax, according to Hellmann-Feynman forces, so as to reduce surface energy. Despite the presence of unsaturated dangling bonds, the result of this energy minimization shows that surface atoms do not relax significantly (see Table II), with a surface energy gain of only 7 meV/(1 × 1)cell, and a downward relaxation of the top layer of 0.02 Å. We also checked that increasing the k-point number from six to eighteen changed none of the above results.
IV. HANEMAN (2 × 1) “BUCKLED ATOM” RECONSTRUCTION

In the previous calculation, reconstruction was forbidden by symmetry. If the symmetry constraints imposed by the choice of a (1 × 1) cell are relaxed, the ideal surface is provided with a simple mechanism for the partial saturation of the dangling bonds. One such mechanism, first proposed by Haneman, consists of a simple in-out buckling of the topmost layer, resulting in a (2 × 1) displacive reconstruction. The inward motion of one surface atom implies an $sp^3 \rightarrow sp^2$ rehybridization, and a more $p_z$-like dangling bond for that atom. The outward motion of the other atom, by contrast, causes dehybridization, and a more $s$-like dangling bond. Since in the atom $E_s << E_{p_z}$, electrons will flow from the inward to the outward atom. This charge transfer empties and saturates respectively the two dangling bonds and therefore stabilizes the surface. This (2 × 1) reconstruction, although actually never observed, has been recently suggested to play the role of a transition state, a kind of “stepping stone” in the dynamical process leading from an unreconstructed state towards, e.g., a (2 × 1) $\pi$-bonded chain state. In order to study the possible occurrence of such a buckled atom reconstruction on $\alpha$-Sn (111), we have repeated our calculation in a larger (2 × 1) surface cell, using 4 special k-points in the rectangular (2 × 1) ISBZ. We find, indeed, that the surface spontaneously buckles as in the Haneman distortion, against which the ideal surface is therefore unstable, very much as Ge (111) does. The energy gain from the ideal to the optimal buckled geometry (Table II), is about 0.22 eV/(1 × 1) cell, measured relative to the energy of the ideal surface computed using the same (2 × 1) supercell and k-point set. The buckling of the top layer is found to be enormous, namely 1.23 Å. The final atomic coordinates of the relaxed top five atomic layers are given in Table III.

V. (2 × 1) $\pi$-BONDED RECONSTRUCTION

The instability of the ideal (111) surface against (2 × 1) buckling is interesting, but probably academic, except possibly in dynamics. In our pursuit of the true (111) ground state
surface structure, we consider next the surface reconstruction geometries which are experimentally observed in the other group-IV insulator and semiconductors. Here we consider the (111) $2 \times 1 \pi$-bonded chain reconstruction. In the lack of any experimental and theoretical data, we arranged the surface atoms in the structure proposed by Pandey$^3$. Pandey’s structure can be obtained by simultaneously depressing one surface atom into the second layer and correspondingly raising one second layer atom, so that i) the number of dangling bonds per surface atom is the same as before; ii) all bond lengths are set to the bulk value. The atomic coordinates in Pandey’s structure are given in Table IV. Subsequently, we allowed the atomic positions to relax according to their ab-initio forces, using the same supercell and same k-point sampling as in the previous section. At convergence, the energy gain of this $2 \times 1$ reconstruction, with respect to the ideal surface, is 0.24 eV/(1 $\times$ 1)cell (Table [V]), i.e., larger than that of the previous section. The optimal atomic coordinates of the top five atomic layers are given in Table [V]. The bond lengths within the $\pi$-bonded chain are 2.80 Å, only 0.4 % longer with respect to the ideal bulk bond length (2.79 Å). The chain buckling (1.15 Å) is however very large if compared with that of Si or Ge (0.4 Å$^6$, and 0.8 Å$^7$, respectively), fully confirming the trends discussed in Section I and listed in Table [I]. The magnitude of this buckling is so large, that the whole $\pi$-bonded chain is now lying onto an essentially vertical plane (see Fig. [5]). The large chain buckling is accompanied by a large electron transfer from the lowered to the raised chain atom, which largely saturates the raised atom dangling bond. This is clearly seen in Fig. [6], where the charge distributions of the highest occupied (panel (a)) and lowest unoccupied states (panel (b)) are shown. This charge rearrangement is accompanied by the opening of a large gap in the dangling bond surface state, as seen in the electronic structure of Fig. [6]. Here the highest occupied (lowest unoccupied) surface states correspond to raised (lowered) atom dangling bonds respectively. Finally, since the alternative possibility of a dimerization of the chain was excluded in our cell due to symmetry constraints, we tried slightly dimerizing the initial, unbuckled $\pi$-bonded chain, and also the final, fully buckled one (thereby doubling the number of k-points in the ISBZ). However, we found these configurations to be energetically disfavored with respect
VI. ADATOM / RESTATOM RECONSTRUCTIONS

As the next likely candidate for the reconstruction of $\alpha$-Sn (111), we now consider the adatom / restatom reconstruction, known to be the stable mechanism for both Si and Ge. Although this reconstruction shows up with rather more complex surface unit cells, such as the $(7 \times 7)$ DAS model in Si$^8$ and the $c(2 \times 8)$ in Ge$^9$, the building block of this class of reconstructions is simple. It is based on the presence of one adatom every four $(1 \times 1)$ first-layer atoms. The adatom sits in a threefold site, saturating three first-layer atoms, leaving one (the restatom) unsaturated. Of the two available threefold sites, namely $T_4$ (on top of a second-layer atom), and $H_3$ (hollow site), the adatoms prefer, at least in Si and Ge$^9$, the $T_4$ site. Moreover, the $T_4$ site adatoms may still be arranged in a $(2 \times 2)$ or $c(4 \times 2)$ geometry. For instance in Ge (111) $c(2 \times 8)$, they are stacked in alternated $(2 \times 2)$ and $c(4 \times 2)$ cells. In this work we assume the pure $(2 \times 2)$ [or pure $c(4 \times 2)$] $T_4$ structure as the prototype adatom / restatom reconstruction, restricting for simplicity our analysis to this case only. As for the $\pi$-bonded reconstruction case, we have no data to guide us. We start with an ideal $T_4$ position for the adatom (see Table V) such that the lengths of the adatom bonds with the three first-layer atoms are equal to the bulk bond-length. The relative positions of atoms are initially chosen according to the $(2 \times 2)$ [or $c(4 \times 2)$] case of Table V [or Table VI]. The $k$-point sampling of this larger supercell is restricted to a single special point (mean-value point) of the hexagonal $(2 \times 2)$ ISBZ$^4$. We then calculate Hellmann-Feynman forces, and let the atoms relax to the equilibrium positions. We also find that increasing the number of special $k$-points of the relaxed surface to three and six does not change the surface energy within 5 meV/(1 × 1)cell. As before we must also repeat the rigid ideal slab calculation using this larger supercell and $k$-point sampling. As shown in Table IV, the energy of the relaxed adatom-reconstructed surface turns out to be lower than all previous reconstructions by as much as 0.09 eV/(1 × 1)cell. This indicates that the
adatom / restatom reconstruction is the most efficient way of saturating the highly unstable dangling bonds of the clean (111) surface. The alternative choice of a $c(4 \times 2)$ adatom / restatom geometry (using the two k-points obtained from the refolding in the $c(4 \times 2)$ ISBZ of the four ones used in the above $(2 \times 1)$ reconstruction calculations) confirms this result, yielding an energy 16 meV/(1 $\times$ 1)cell lower than the $(2 \times 2)$ choice. This energy difference is however comparable with our overall energy resolution. Similarly, our calculation does not rule out the existence of more complex surface reconstructions. It does however suggest that, if this is the case, then the adatom / rest atom mechanism, either in a $(2 \times 2)$ or in a $c(4 \times 2)$ arrangement, is very likely to constitute their basic building block, as is the case in Si and Ge. Moreover, the advantage over the $\pi$-bonded chain reconstruction is larger in $\alpha$-Sn, confirming the Si-Ge trend.

In Table V we report the relaxed atomic coordinates of the $(2 \times 2)$ adatom-restatom reconstructed surface. Due to the symmetry constraint, the adatom and restatom only relax in the $z$ direction. The in-plane distance between the rest atom and its three neighbors shrinks by about 10 % with respect to the ideal bulk value. The rest atom moves outward from its initial bulk-like position by 0.8 Å, again a very large relaxation if compared with values in Si (0.3 Å), and in Ge (0.55 Å). Due to this relaxation, the rest atom has bond angles of 94.0°, a value closer to total $s$, $p$ dehybridization (90°) than to the original $sp^3$ one (109°), and bond lengths of 2.84 Å (bulk bond length is 2.79 Å). In turn, the adatom bond lengths with the three neighboring first-layer atoms are 2.97 Å, larger by 7 % than the bulk bond length, and the adatom bond angles are 93.4°. The second-layer atom under the adatom is pushed downward. Although its final distance from the adatom (2.99 Å) is comparable with the other adatom bond length, there is no bond-like accumulation of electronic charge between them, as can be seen in the total charge density reported in Fig. 4. Rather, most of the adatom charge is transferred to the restatom dangling bond. This charge transfer is not directly visible in the total charge density of Fig. 4, but shows up clearly in the band structure of Fig. 5. The half filled surface-localized band typical of unsaturated dangling bonds (see Fig. 3), is here split into a lower filled band with prevailing
rest-atom character, and an upper empty band manly localized onto the adatom. This charge transfer is known to be the fundamental mechanism for the stabilization of the adatom/rest atom reconstruction in Si and Ge\textsuperscript{25,26}, and does appear to be so even in Sn. A glance at the charge density associated with the lower and upper surface bands (see Fig. 9) confirms this expectation. The charge associated with the lower band, shown in the panel (a) of Fig. 9, has a strong rest-atom character and extends very little into the bulk, thus confirming its picture of saturated dangling bond. On the contrary, the upper unoccupied band (panel (b) of Fig. 9) has a strong adatom character, but extends largely below the adatom, and might therefore be thought to as a band of so called “floating bonds”\textsuperscript{27} associated with both the adatom and the five-fold coordinated atom immediately underneath.

The optimal atomic positions and electronic band structure of the c(4 × 2) adatom/restatom reconstruction are given in Table VI and Fig. 10. Differences in the atomic relaxations and charge densities are negligible with respect to the (2 × 2) case, and will not be re-discussed.

We have also verified that the $H_3$ site for the adatom is not energetically favored, the energy of this surface being higher than the one with adatoms in $T_4$ sites by about 70 meV/(1 × 1)cell. Its optimal atomic coordinates are given in Table VII.

VII. METALLIC OVERLAYERS

The presence of a metallic phase ($\beta$-Sn) energetically very close to the $\alpha$ phase, suggests that an insulator-to-metal transition might take place at the surfaces of $\alpha$-Sn, for example, through the formation of a thin $\beta$-Sn metallic overlayer. Such was proposed to be the case, e.g., in gallium\textsuperscript{21}, where based on calculations similar to these presented here a metallic bilayer of Ga-III was predicted to stabilize the surface of $\alpha$-Ga better than any other reconstruction. In our case, however, we encounter a problem, since no low-index $\beta$-Sn planes appear to match epitaxially the $\alpha$-Sn (111) lattice. In particular, we have calculated the surface energy of several structures obtained by covering the $\alpha$-Sn(111) surface with strained
epitaxial (100), (110), (111), and (221) planes of $\beta$-Sn. None of these surfaces gave a surface energy comparable, let alone lower, than the ideal (111) surface, all our results being higher with respect to the $(2 \times 2)$ adatom / restatom reconstruction by more than 0.45 eV/(1 x 1)cell. However, this negative result cannot of course be taken as a guarantee that metallic overlayers do not form at the $\alpha$-Sn surface, since other more complex configurations, beyond our present factory, might have to be considered. The situation with respect to metallization remains therefore open.

An indirect indication against metallization is however provided by surface energies. One can expect metallization to be favored, in fact, in cases where the metal has a lower surface free energy. In our case, however, the T=0 K energy of reconstructed $\alpha$-Sn (111), $E_{surf} \approx 540 \text{ mJ/m}^2$, is substantially lower than the free energy measured for $\beta$-Sn, namely 670 mJ/m$^2$. This suggests that metallization might not take place in the ground state, while it could be attained after deconstruction.

VIII. DISCUSSION AND CONCLUSIONS

From this ab-initio study, we predict that the (111) surface of $\alpha$-Sn should be unstable in its unreconstructed form, and can be stabilized by various types of reconstructions.

Among the reconstructions not involving adatoms, the $(2 \times 1)$ $\pi$-bonded chain model is energetically best, and is predicted to display a gigantic buckling above 1 Å in magnitude. This is in line with the trend towards increasing buckling in going from diamond to Si to Ge (111).

In the presence of adatoms, the adatom-restatom pair reconstruction is found to be energetically best, and is thus the strongest candidate for the true ground state of this surface. The relative energy gain over the $\pi$-bonded state is larger than in Si and Ge, again in line with trends. The actual optimal periodicity of the adatom-reconstructed $\alpha$-Sn (111) is however difficult to predict (as is the case in Si and Ge) because of many subtle factors, including possible coexistence and competition between the two different basic units, namely
(2 × 2) and \( c(4 × 2) \).

A search for a possible metallic state of \( \alpha \)-Sn (111), suggested by the proximity of \( \beta \)-Sn in the phase diagram, was so far inconclusive, and is disfavored by surface energy considerations.

The beginning of actual experiments on \( \alpha \)-Sn (111) is at this stage highly desirable, as we are not aware of any data so far. The present study makes rather strong predictions, both at the qualitative and the quantitative level. Qualitatively, we expect \( \pi \)-bonded chains to dominate on the adatom-free (e.g., cleaved) surface, and adatom-restatom reconstructions to appear after annealing, very much as for Si and Ge (111). At the quantitative level, we predict that buckling distortions and the associated dipole moments connected with intra-surface ionic charge transfers should be larger than in Si and Ge. This effect ought to be relevant to, e.g., surface vibrational spectroscopy. The corresponding band splittings should finally be observable in electron spectroscopies, including photoemission and optical absorption, particularly to optical conductivity for \( q \neq 0 \).

It is hoped that these results will stimulate newer efforts towards an understanding of the \( \alpha \)-Sn (111) surface, where hardly any data can presently be found.

**ACKNOWLEDGMENTS**

We would like to thank Dr. Marco Bernasconi for providing us the computer codes used in this work, and for his cooperation in the early stage of this work. This research was partly sponsored through EEC, contract ERBCHRXCT 930342, and by the Italian CNR, under projects “SUPALTEMP” and also under contract “95.01056.CT12”.

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TABLES

### TABLE I.

| Structure                                | C                        | Si                      | Ge                      |
|------------------------------------------|--------------------------|-------------------------|-------------------------|
| $2 \times 1 \pi$-bonded chains           | dimerized ($\ast$) (?)    | buckled                 | more buckled            |
| adatom/ rest atom                        | not found                | $7 \times 7$ DAS model ($\ast$) | c($2 \times 8$) adatom model ($\ast$) |
| $2 \times 1$ buckled                     | not found                | saddle-point            | saddle-point            |
| metallic                                 | graphitic $T \geq 2700K$ (?) | $T \geq 1500K$ (?)      | $T \geq 1050K$          |

($\ast$) Stable structure at $T = 0$.

(?) Pending confirmation.

### TABLE II. Calculated surface energies, absolute and relative, of different optimized reconstructions for $\alpha$-Sn (111) surface.

| Structure                        | $E_{surf}$ | $\Delta E$ | vert. relax. or buckling$^a$ |
|----------------------------------|------------|------------|------------------------------|
|                                  | [eV/(1×1 cell)] | [mJ/m$^2$] | [eV/(1×1 cell)] | (Å)       |
| ideal                            | 0.940      | 837        | 0.000                      | 0         |
| fully relaxed                    | 0.933      | 831        | -0.007                     | 0.02      |
| $2 \times 1$ buckled (Haneman)   | 0.732      | 652        | -0.217                     | 1.23      |
| $2 \times 1$ $\pi$-bonded chain | 0.697      | 621        | -0.243                     | 1.15      |
| $2 \times 2$-adatom ($H_3$)      | 0.696      | 620        | -0.244                     | 0.54 (restatom) |
| $2 \times 2$-adatom ($T_4$)      | 0.626      | 558        | -0.314                     | 0.81 (restatom) |
| $c(4\times2)$-adatom ($T_4$)     | 0.610      | 543        | -0.330                     | 0.74 (restatom) |
| metallized                       | $\geq 1.06$| 944        | $\geq 0.121$              |           |

$^a$Vertical relaxation is relative to initial bulk-like positions, and buckling is difference between relaxation of two atoms.
TABLE III. Ideal, and optimized atomic positions of the α-Sn (111) (2×1) buckled (Haneman) surface. In the rectangular supercell, coordinates are given by \( \mathbf{r} = c_1 \mathbf{a}_1 + c_2 \mathbf{a}_2 + c_3 \mathbf{a}_3 \), where \( \mathbf{a}_i \) is defined in the conventional cubic coordinate system as
\[
\mathbf{a}_1 = \left( \frac{a_0}{2} \right)(-1, 2, -1), \quad \mathbf{a}_2 = \left( \frac{a_0}{2} \right)(-1, 0, 1), \\
\mathbf{a}_3 = a_0(1, 1, 1) \text{ and } a_0 \text{ (} = 6.446 \text{ Å}) \text{ is the lattice parameter.}
\]

| Atom no. | Ideal | Optimal |
|----------|-------|---------|
|          | \( c_1 \) | \( c_2 \) | \( c_3 \) | \( c_1 \) | \( c_2 \) | \( c_3 \) |
| 1        | .000  | .000    | .000    | .009  | .000    | -.048   |
| 2        | .500  | .500    | .000    | .485  | .500    | .062    |
| 3        | .167  | .500    | .083    | .132  | .500    | .077    |
| 4        | .667  | .000    | .083    | .692  | .000    | .077    |
| 5        | .167  | .500    | .333    | .169  | .500    | .330    |
| 6        | .667  | .000    | .333    | .667  | .000    | .332    |
| 7        | .333  | .000    | .417    | .334  | .000    | .415    |
| 8        | .833  | .500    | .417    | .836  | .500    | .417    |
| 9        | .333  | .000    | .667    | .334  | .000    | .665    |
| 10       | .833  | .500    | .667    | .833  | .500    | .667    |

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TABLE IV. Initial (Pandey’s), and optimized atomic positions of the $\alpha$-Sn (111) \((2 \times 1)\) π-bonded surface. In the rectangular supercell, coordinates are given by \(r = c_1 a_1 + c_2 a_2 + c_3 a_3\), where \(a_i\) is defined in the conventional cubic coordinate system as \(a_1 = (a_0/2)(-1, 2, -1)\), \(a_2 = (a_0/2)(-1, 0, 1)\), \(a_3 = a_0 (1, 1, 1)\) and \(a_0 \approx 6.446 \text{ Å}\) is the lattice parameter.

| Atom no. | Pandey’s$^a$ | Optimal |
|----------|--------------|---------|
|          | \(c_1\)     | \(c_2\) | \(c_3\) | \(c_1\) | \(c_2\) | \(c_3\) |
| 1        | -.148        | .000    | .023    | -.167   | .000    | .060    |
| 2        | -.019        | .500    | .023    | -.020   | .500    | -.043   |
| 3        | .315         | .500    | .106    | .278    | .500    | .100    |
| 4        | .519         | .000    | .106    | .484    | .000    | .077    |
| 5        | .167         | .500    | .333    | .178    | .500    | .341    |
| 6        | .667         | .000    | .333    | .657    | .000    | .317    |
| 7        | .333         | .000    | .417    | .336    | .000    | .431    |
| 8        | .833         | .500    | .417    | .831    | .500    | .400    |
| 9        | .333         | .000    | .667    | .337    | .000    | .678    |
| 10       | .833         | .500    | .667    | .834    | .500    | .654    |

$^a$For corresponding bulk-like positions, see the ideal case of Table [I].
TABLE V. Initial, and optimized atomic positions of the $\alpha$-Sn (111) (2 x 2) adatom / re- 
statom ($T_4$ configuration) reconstructed surface. In the hexagonal supercell, coordinates are given 
by $r = c_1a_1 + c_2a_2 + c_3a_3$, where $a_i$ is defined in the conventional cubic coordinate system as 
$a_1 = (a_0/2)(-1, 2, -1)$, $a_2 = (a_0/2)(-1, 0, 1)$, $a_3 = (a_0/3)(1, 1, 1)$ and $a_0 (= 6.446 \text{ Å})$ is the lattice 
parameter.

| Atom no. | Initial | | | Optimal | | |
|---|---|---|---|---|---|---|
|   | $c_1$ | $c_2$ | $c_3$ | $c_1$ | $c_2$ | $c_3$ |
| 1 | .000 | .000 | 2.375 | .000 | .000 | 2.509 |
| 2 | -.167 | .500 | 2.125 | -.158 | .475 | 2.077 |
| 3 | .333 | .000 | 2.125 | .317 | .000 | 2.077 |
| 4 | -.167 | -.500 | 2.125 | -.158 | -.475 | 2.077 |
| 5 | .333 | -1.000 | 2.125 | .333 | -1.000 | 2.343 |
| 6 | .000 | .000 | 1.875 | .000 | .000 | 1.705 |
| 7 | .500 | .500 | 1.875 | .485 | .544 | 1.935 |
| 8 | .000 | -1.000 | 1.875 | .030 | -1.000 | 1.935 |
| 9 | .500 | -.500 | 1.875 | .485 | -.544 | 1.935 |
| 10 | .000 | .000 | 1.125 | .000 | .000 | .963 |
| 11 | .500 | .500 | 1.125 | .500 | .501 | 1.175 |
| 12 | .000 | -1.000 | 1.125 | .000 | -1.000 | 1.175 |
| 13 | .500 | -.500 | 1.125 | .500 | -.501 | 1.175 |
| 14 | .167 | .500 | .875 | .175 | .525 | .864 |
| 15 | .667 | .000 | .875 | .667 | .000 | .926 |
| 16 | .167 | -.500 | .875 | .175 | -.525 | .864 |
| 17 | .667 | -1.000 | .875 | .650 | -1.000 | .864 |
| 18 | .167 | .500 | .125 | .170 | .510 | .110 |
| 19 | .667 | .000 | .125 | .667 | .000 | .175 |
| 20 | .167 | -.500 | .125 | .170 | -.510 | .110 |
|   |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|
| 21 | 0.667 | -1.000 | 0.125 | 0.660 | -1.000 | 0.110 |
TABLE VI. Initial, and optimized atomic positions of the α-Sn (111) c(4 × 2) adatom / re-statom (T4 configuration) reconstructed surface. In the rectangular supercell, coordinates are given by $r = c_1 a_1 + c_2 a_2 + c_3 a_3$, where $a_i$ is defined in the conventional cubic coordinate system as $a_1 = (a_0/2)(-1, 2, -1)$, $a_2 = (a_0/2)(-1, 0, 1)$, $a_3 = (a_0/3)(1, 1, 1)$ and $a_0 (=6.446\text{Å})$ is the lattice parameter.

| Atom no. | $c_1$ | $c_2$ | $c_3$ | $c_1$ | $c_2$ | $c_3$ |
|---------|-------|-------|-------|-------|-------|-------|
| 1       | .000  | .000  | 2.375 | .004  | .000  | 2.527 |
| 2       | .167  | .500  | 2.125 | .158  | .469  | 2.083 |
| 3       | -.333 | .000  | 2.125 | -.313 | .000  | 2.102 |
| 4       | .167  | -.500 | 2.125 | .158  | -.469 | 2.083 |
| 5       | -.333 | -1.000 | 2.125 | -.341 | -1.000 | 2.325 |
| 6       | .000  | .000  | 1.875 | -.006 | .000  | 1.716 |
| 7       | -.500 | .500  | 1.875 | -.489 | .525  | 1.941 |
| 8       | .000  | -1.000 | 1.875 | -.027 | -1.000 | 1.945 |
| 9       | -.500 | -.500 | 1.875 | -.489 | -.525 | 1.941 |
| 10      | .000  | .000  | 1.125 | .001  | .000  | .975  |
| 11      | -.500 | .500  | 1.125 | -.501 | .501  | 1.178 |
| 12      | .000  | -1.000 | 1.125 | .005  | -1.000 | 1.182 |
| 13      | -.500 | -.500 | 1.125 | -.501 | -.501 | 1.178 |
| 14      | -.167 | .500  | .875  | -.174 | .525  | .880  |
| 15      | -.667 | .000  | .875  | -.650 | .000  | .874  |
| 16      | -.167 | -.500 | .875  | -.174 | -.525 | .880  |
| 17      | -.667 | -1.000 | .875 | -.665 | -1.000 | .907  |
| 18      | -.167 | .500  | .125  | -.169 | .509  | .127  |
| 19      | -.667 | .000  | .125  | -.661 | .000  | .123  |
| 20      | -.167 | -.500 | .125  | -.169 | -.509 | .127  |
| 21 | -0.667 | -1.000 | 0.125 | -0.668 | -1.000 | 0.149 |
TABLE VII. Initial, and optimized atomic positions of the α-Sn(111) (2 × 2) adatom / re- 
statom (H₃ configuration) reconstructed surface. In the hexagonal supercell, coordinates are given 
by \( \mathbf{r} = c_1 \mathbf{a}_1 + c_2 \mathbf{a}_2 + c_3 \mathbf{a}_3 \), where \( \mathbf{a}_i \) is defined in the conventional cubic coordinate system as 
\( \mathbf{a}_1 = (a_0/2)(-1, 2, -1), \mathbf{a}_2 = (a_0/2)(-1, 0, 1), \mathbf{a}_3 = (a_0/3)(1, 1, 1) \) and \( a_0 (= 6.446 \text{ Å} ) \) is the lattice 
parameter.

| Atom no. | Initial c₁ | Initial c₂ | Initial c₃ | Optimal c₁ | Optimal c₂ | Optimal c₃ |
|----------|-------------|-------------|-------------|-------------|-------------|-------------|
| 1        | .167        | .500        | 2.375       | .167        | .500        | 2.525       |
| 2        | -.167       | .500        | 2.125       | -.142       | .500        | 2.090       |
| 3        | .333        | .000        | 2.125       | .321        | .037        | 2.090       |
| 4        | -.167       | -.500       | 2.125       | -.167       | -.500       | 2.271       |
| 5        | .333        | -1.000      | 2.125       | .321        | -1.037      | 2.090       |
| 6        | .000        | .000        | 1.875       | -.015       | -.046       | 1.848       |
| 7        | .500        | .500        | 1.875       | .531        | .500        | 1.848       |
| 8        | .000        | -1.000      | 1.875       | -.015       | -.954       | 1.848       |
| 9        | .500        | -.500       | 1.875       | .500        | -.500       | 1.984       |
| 10       | .000        | .000        | 1.125       | .000        | -.001       | 1.102       |
| 11       | .500        | .500        | 1.125       | .501        | .500        | 1.102       |
| 12       | .000        | -1.000      | 1.125       | .000        | -.999       | 1.102       |
| 13       | .500        | -.500       | 1.125       | .500        | -.500       | 1.199       |
| 14       | .167        | .500        | .875        | .167        | .500        | .861        |
| 15       | .667        | .000        | .875        | .663        | -.012       | .883        |
| 16       | .167        | -.500       | .875        | .175        | -.500       | .883        |
| 17       | .667        | -1.000      | .875        | .663        | -.988       | .883        |
| 18       | .167        | .500        | .125        | .167        | .500        | .105        |
| 19       | .667        | .000        | .125        | .665        | -.006       | .133        |
| 20       | .167        | -.500       | .125        | .171        | -.500       | .133        |
|    | 21  | .667 | -1.000 | .125 | .665 | -.994 | .133 |
|----|-----|------|--------|------|------|-------|------|

FIGURES

FIG. 1. Electronic structure of bulk $\alpha$-Sn. The zero in energy corresponds to the Fermi level.

FIG. 2. Brillouin zone and electronic structure of bulk $\beta$-Sn. The zero in energy corresponds to the Fermi level.

FIG. 3. Surface electronic structure of the ideal $\alpha$-Sn(111) surface reported along high-symmetry lines of the $(1 \times 1)$ hexagonal irreducible Brillouin zone. Shaded areas correspond to surface-projected bulk states, while thicker lines correspond to surface states. The surface Brillouin zone is given in the inset. Note that the dangling bond surface state crosses the fermi level $E_F$.

FIG. 4. Electron density contour of the highest occupied state of the ideal $(1 \times 1)$ surface at $\bar{K}$, on the (110) plane passing through top atoms. Full circles correspond to Sn atoms, and thicker straight lines to bonds among Sn atoms. Contour lines are separated by 0.0005 (a.u.). Note the dangling bond character of this state.

FIG. 5. Electron density contours of the highest occupied state (panel (a)) and of the lowest unoccupied state (panel (b)) in the $(2 \times 1)$ $\pi$-bonded chain reconstruction at $\bar{J}$, on the (110) plane passing through the up (down) atom. In panel (b) atoms are labelled according to the optimal positions of Table IV. Contour lines are separated by 0.0005 (a.u.).

FIG. 6. Surface electronic structure of the $(2 \times 1)$ $\pi$-bonded chain reconstructed surface reported in the $(2 \times 1)$ rectangular irreducible Brillouin zone (see inset). Shaded areas correspond to surface-projected bulk states, while thicker lines correspond to surface states. The original dangling bond is now split into two.

FIG. 7. Geometry, and electron density contour of the $(2 \times 2)$ adatom / restatom reconstruction, on the plane passing through the adatom and the rest atom. Contour lines are separated by 0.005 (a.u.). Note the strong outward relaxation of the restatom, and the strong inward relaxation of the second and third layer atoms beneath the adatom. (R: restatom, A: adatom)
FIG. 8. Surface electronic structure of the $(2 \times 2)$ adatom / restatom reconstructed surface reported in the $(2 \times 2)$ hexagonal irreducible Brillouin zone (see inset). Shaded areas correspond to surface-projected bulk states, thicker lines correspond to surface states, dotted lines to surface resonances. The $\sim 1$ eV splitting of the surface state reflects the adatom-restatom electron transfer.

FIG. 9. Electron density contours of the highest occupied state (panel (a)) and of the lowest unoccupied state (panel (b)) in the $(2 \times 2)$ adatom / restatom reconstruction at $\bar{K}$, on the same plane as in Fig. 7. In panel (b) atoms are labelled according to the optimal positions of Table V. Contour lines are separated by 0.0004 (a.u.). Note the strong restatom / adatom characters, with a larger penetration of the adatom empty state.

FIG. 10. Surface electronic structure of the $c(4 \times 2)$ adatom / restatom reconstructed surface reported in the $c(4 \times 2)$ rectangular irreducible Brillouin zone (see inset). Shaded areas correspond to surface-projected bulk states, thicker lines correspond to surface states, dotted lines to surface resonances.
