



Si-substitutional defects on the α -Sn/Si(1 1 1)-($\sqrt{3} \times \sqrt{3}$) surface

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Abstract

We present a theoretical analysis of the atomic and electronic structure of Si-substitutional defects on the α -Sn/Si(1 1 1)-($\sqrt{3} \times \sqrt{3}$) surface. We use a first-principles DFT local-orbital method and analyze Si-defects on a large Sn/Si(1 1 1) surface unit-cell, corresponding to a defect concentration as low as 3.7%. We also calculate the theoretical STM images, and compare with the experimental results. We find that a single Si-defect induces an upward displacement of its six nearest Sn-adatoms that shows up in filled state STM images as a bright ring of adatoms around the defect. We also analyze the atomic structure and STM images associated with three nearby Si-defects. These results are compared with those found for the Sn/Ge(1 1 1) surface. We conclude that the atomic distortion induced by Si (Ge) substitutional defects is very local, the differences found for these two surfaces being basically due to their different ground state geometries.

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1. Introduction

The α - $\sqrt{3} \times \sqrt{3}$ phases formed when a coverage of 1/3 monolayer of Sn or Pb atoms are adsorbed on Ge(1 1 1) or Si(1 1 1) have recently attracted much attention due to the discovery, in Pb/Ge(1 1 1) [1], of a continuous transition to a new 3×3 phase when the temperature is lowered. This phase transition was soon also reported in Sn/Ge(1 1 1) [2]. In contrast, no evidence of this transition has been found in Sn/Si(1 1 1) for temperatures as low as 6 K [3].

The Sn/Ce(1 1 1) system has been thoroughly investigated. In the generally accepted model for the LT Sn/Ge(1 1 1)- 3×3 phase, Sn adatoms are adsorbed on T₄ sites and, out of the three Sn adatoms per 3×3 unit-cell, one is displaced upwards by

$\sim 0.3 \text{ \AA}$ w.r.t. the other two Sn adatoms [4–10]. The physical mechanism that leads to the stabilization of this 3×3 structure, and the origin and character of the phase transition, has been the subject of an intense scientific debate (see, for example, the review articles [11–14] for details). It was initially proposed that, as a result of Fermi surface nesting, the 3×3 phase was a two-dimensional realization of a charge density wave, although this idea was soon discarded [2]. Density functional theory (DFT) calculations predict that the 3×3 structure is only marginally lower in energy than the ideal $\sqrt{3} \times \sqrt{3}$ surface (by $\sim 5 \text{ meV}$ per Sn atom) [4,15], and that the 3×3 distortion is associated with the stabilization of a surface soft phonon [15,16]. In these calculations the 3×3 distortion leads to an electronic energy gain that overcomes the elastic energy spent in the deformation of the system. Ge-substitutional defects have been found to play an important role in the stabilization of the 3×3 structure [17,18]. In particular it has been found that

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these defects are ordered in the 3×3 structure, occupying preferentially positions that would correspond to “down” Sn adatoms on the 3×3 structure.

The character of the $\sqrt{3} \times \sqrt{3}$ phase presents also a puzzling problem. For example, PES experiments show a strikingly similar electronic structure of the $\sqrt{3} \times \sqrt{3}$ and 3×3 phases, with two inequivalent Sn-atoms on the surface, in clear contradiction with an ideal $\sqrt{3} \times \sqrt{3}$ geometry [4,19,20]. This puzzling situation has been explained by means of a dynamical fluctuations model, whereby Sn-atoms fluctuate in the surface between two different positions at high T , being frozen in the 3×3 geometry at low T [4,10,16,21].

In the case of the α -Sn/Si(1 1 1) surface, the STM images show a $\sqrt{3} \times \sqrt{3}$ symmetry for temperatures as low as 6 K [3]. On the other hand, photoemission spectroscopy (RT down to 40 K) [22,23] show two major components in the Sn 4d core-level lineshape and two surface state structures (one at E_F and the other one fully occupied), in similarity with the Sn/Ge(1 1 1) surface, suggesting the presence of two inequivalent types of Sn adatoms. Interestingly, the relative position of the major and minor components of the Sn 4d lineshape is reversed in Sn/Si(1 1 1) as compared with Sn/Ge(1 1 1) [14,22]. DFT calculations indicate that this surface does not present any stable 3×3 distortion, i.e. the ideal $\sqrt{3} \times \sqrt{3}$ structure is the stable structure. These calculations also show that the 3×3 phonon mode (the soft phonon that yields to the 3×3 reconstruction for Sn/Ge(1 1 1)) is a minimum of the phonon dispersion curve [15]. This result suggests that the atomic dynamics of this surface could be dominated by this mode, explaining the PES results.

Si-substitutional defects on the α -Sn/Si(1 1 1)- $\sqrt{3} \times \sqrt{3}$ surface have been investigated using STM and core-level PES [22–26]. These studies have been motivated by the proposal for the Sn/Ge(1 1 1) system, that the $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ phase transition is induced by Ge-substitutional defects and their interaction [11,17,18]. In this paper, we analyze theoretically the atomic and electronic structure of Si-substitutional defects on the α -Sn/Si(1 1 1)- $\sqrt{3} \times \sqrt{3}$ surface, in order to understand the similarities and differences between the Sn/Ge(1 1 1) and the Sn/Si(1 1 1) cases. We use an efficient DFT technique and analyze the electronic and atomic changes induced by Si-defects

on the α surface using a large 9×9 -Sn/Si(1 1 1) unit-cell. Using our first-principles Hamiltonian of the surface system, we also calculate theoretical STM images using the DFT local-orbital Hamiltonian of the surface together with a non-equilibrium Keldish Green function approach [27], and compare with the experimental results. We find that the distortion induced by Si-defects is very local. A single Si-defect induces an upward displacement (~ 0.05 Å) of its six Sn-adatoms nearest-neighbours (n.n.). This displacement is correlated with the transfer of one electron from the Si-DB to the six Sn-DBs. This structural and electronic effect shows up in filled state STM images as a bright ring of adatoms around the defect. In the case of two and three nearby Si-defects the distortion induced by the defects is, in a first approximation, the superposition of the displacements induced by independent defects [25,28]. Finally, we compare these results with the corresponding ones for the Sn/Ge(1 1 1) case [28], and relate their differences to their ground state geometries.

2. Total energy calculations

In order to analyze theoretically the atomic and electronic structure of Si-substitutional defects we have used an efficient first-principles total energy method (FIREBALL96) [29]. This technique has been successfully applied to the study of the similar α -Sn/Ge(1 1 1) system, and in previous studies of the Sn/Si(1 1 1) surface. The main advantage of this technique is that typically it presents a very favourable balance between accuracy and computational efficiency; this is related to the use of an *optimized* minimal basis set of confined atomic-like orbitals. Thus, it is important to choose first carefully this basis set. In this study we have tuned our atomic-like basis set using as a guide the plane-waves DFT analysis of the delicate energy balance associated with the 3×3 distortion [15].

Fig. 1a (circles) shows the total energy per 3×3 unit-cell as a function of the vertical displacement of one of the Sn adatoms (Sn_1) as calculated with the PW-code [15]. This is a key quantity, since it has been shown that in the case of Sn/Ge(1 1 1) this energy curve displays the soft-phonon behaviour that gives rise to the 3×3 reconstruction (which corresponds to

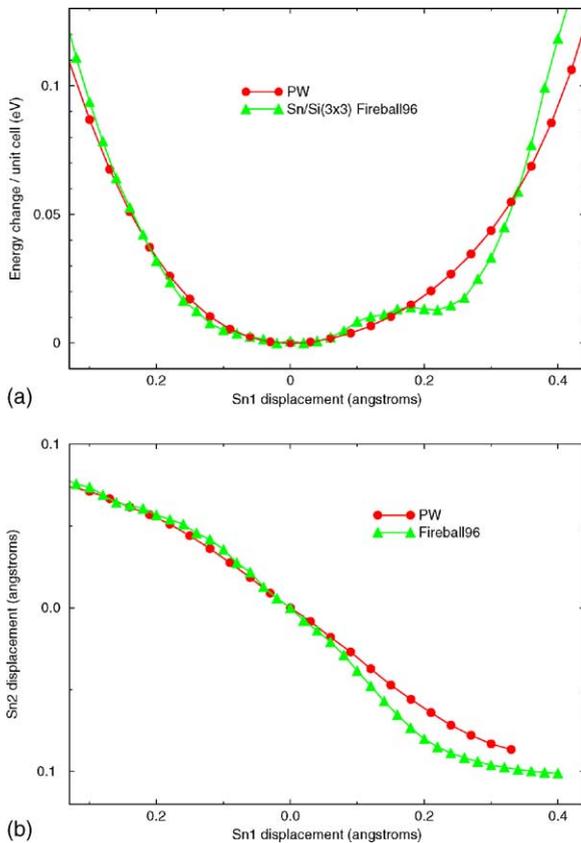


Fig. 1. (a) Total energy as a function of the Sn_1 for the $\text{Sn}/\text{Si}(1\ 1\ 1)$ surface as calculated with plane-waves (CASTEP) and local-orbitals (FIREBALL96 with a minimal basis defined by $R_c(\text{Si}) = 4.7$ a.u. and $R_c(\text{Sn}) = 5.2$ a.u.). The energy of the $\sqrt{3} \times \sqrt{3}$ structure is taken as the reference, (b) displacements (in Å) of the Sn_2 , Sn_3 atoms as a function of the Sn_1 displacement. All the displacements are referred to the $\sqrt{3} \times \sqrt{3}$ structure.

a shallow global minimum at ~ 0.18 Å in the corresponding energy curve). Notice that the total energy changes around the minimum are very small even for Sn_1 displacements as large as 0.2 Å. Fig. 1b shows the response of the other two Sn adatoms to the Sn_1 displacement: these atoms move in the opposite direction to the constrained Sn_1 displacement. Fig. 1 also shows the results obtained with FIREBALL96 (triangles) for the minimal basis set used in this work. Notice the shallow local minimum at ~ 0.2 Å in Fig. 1a, that indicates that the FIREBALL96 calculations might present (if any) an enhanced tendency to form 3×3 local structures, compared with the PW calculations. The results displayed in Fig. 1 show that we can achieve a

good description of the $\alpha\text{-Sn}/\text{Si}(1\ 1\ 1)$ surface using an optimized minimal basis set. This is a significant result, since it allows us to apply the efficient FIREBALL96 method to calculate the large $\text{Sn}/\text{Si}(1\ 1\ 1)$ surface unit-cells required to study the atomic and electronic structure of defects on this surface. In this paper we analyze Si-substitutional defects using a 9×9 surface unit-cell, which corresponds to a defect concentration as low as 3.7%.

The adatom relaxed structure corresponding to one Si-defect per 9×9 unit-cell is shown in Fig. 2a: the dark circle represents the Si-defect. The numbers in the circles indicate the vertical displacement (in Å) of

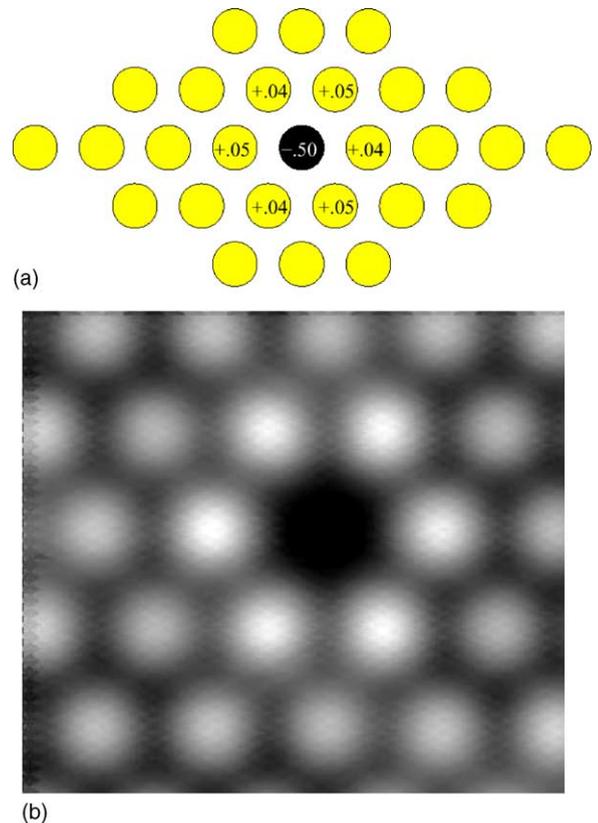


Fig. 2. (a) Adatom vertical displacements (in Å) for one Si-defect in a 9×9 unit-cell, with respect to Sn-adatoms positions in an ideal $\sqrt{3} \times \sqrt{3}\text{-Sn}/\text{Si}(1\ 1\ 1)$ surface. The black circle represents a Si-adatom and the grey circles correspond to Sn-adatoms. Vertical displacements which are smaller than ± 0.02 Å are not indicated, (b) theoretical STM filled-states image for one Si-defect in a 9×9 unit-cell, calculated using a Pt five-atom pyramidal tip in constant-height mode (tip-apex at 5 Å above the $\sqrt{3} \times \sqrt{3}$ surface) and a voltage of -0.5 V.

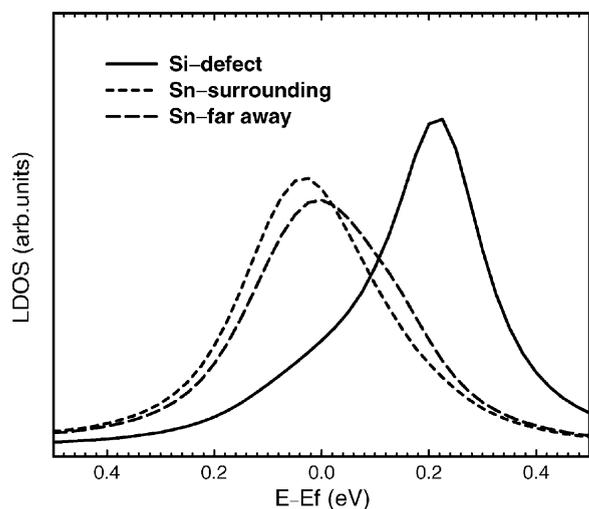


Fig. 3. Local density of states (LDOS) on the different adatoms for one Si-defect in a 9×9 unit-cell (see Fig. 2). One electron is transferred from the Si dangling bond to its six n.n. Sn adatoms.

the corresponding adatom w.r.t. the Sn-adatom position in an ideal $\sqrt{3} \times \sqrt{3}$ -Sn/Si(1 1 1) surface. The Si-adatom is displaced 0.50 \AA towards the surface (inwards), while the six Sn-adatoms nearest neighbours are displaced upwards by $\sim 0.05 \text{ \AA}$, forming a ring around the defect. It is interesting to mention that the slight threefold symmetry of this ring (0.05 \AA versus 0.04 \AA in Fig. 2a) is in resemblance with STM experimental results [25]. The other Sn-adatoms on the surface are basically not affected (within $\pm 0.02 \text{ \AA}$) by the presence of the Si-defect.

The rearrangement of charge in the dangling bonds due to the presence of the Si-defect is shown in Fig. 3. The dangling bond corresponding to the Si-defect is $\sim 0.2 \text{ eV}$ above the Fermi level. Since in the ideal $\sqrt{3} \times \sqrt{3}$ -Sn/Si(1 1 1) surface each Sn dangling bond is occupied by one electron, the Si-substitutional defect of Fig. 2a induces a total transfer of one electron to the six nearby Sn-adatoms dangling bonds (i.e. each dangling bond gains $\sim 1/6$ of electron). As shown in Fig. 3, these dangling bond states are slightly displaced to lower energies. The correlation between structural and electronic changes is clear: the upward displacement of these adatoms (Fig. 2a) is associated with the shift to lower energies of their corresponding dangling bonds [28].

It is interesting to compare at this point with the Sn/Ge(1 1 1) system. In this case the ideal surface

(with no defects) presents a 3×3 reconstruction: one-third of the Sn adatoms are displaced upwards, forming a hexagonal lattice, while the other Sn adatoms display a honeycomb pattern. A similar calculation for the atomic and electronic structure for a Ge-defect [28] indicates that Ge-defects occupy preferentially one of the honeycomb lattice positions. The perturbation induced by these defects is well localized, affecting only to the three Sn adatoms nearest neighbours in the honeycomb lattice. These adatoms are displaced upwards by $\sim 0.05 \text{ \AA}$, and their dangling-bonds gain $\sim 1/6$ electrons, very much in similarity to the values discussed above for the Sn/Si(1 1 1) surface.

We have also analyzed the case of two Si-defects in first, second and third nearest neighbours positions, and the case of three nearby defects. We find that the perturbation induced by the defects is basically the superposition of the perturbation induced by isolated defects (e.g. see Fig. 4a).

3. STM theoretical images

Fig. 2b shows the theoretical STM image (filled state) calculated for one Si-defect in a 9×9 unit-cell. The Si-defect appears as a dark spot: the Si-adatom is $\sim 0.5 \text{ \AA}$ below the average surface, and its dangling-bond is empty. On the other hand, Sn-adatoms surrounding the Si-defect appear brighter than the other Sn-adatoms, due to their increased dangling-bond charge and their slightly higher atomic position, in good agreement with experimental STM images [22,25].

Fig. 4a shows a configuration with three Si-defects that contains Sn-adatoms that are nearest neighbours to three, two and one Si-defects. This configuration has been analyzed in detail experimentally using STM (see Fig. 2a and b in Ref. [25]). In Fig. 4b and c we present the corresponding theoretical filled state STM image and profile. As shown in Fig. 4c, the Sn-adatom with three Si-defects nearest neighbours (atom A) is $\sim 0.3 \text{ \AA}$ higher than the average surface, while atoms B (two Si-defects n.n.) and C (one Si-defect n.n.) are ~ 0.2 and 0.15 \AA above the average surface. These numbers are to be compared with the experimental results 0.35 , 0.21 and 0.13 \AA , respectively [25]. In the theoretical STM profiles Si-defects induce a negative

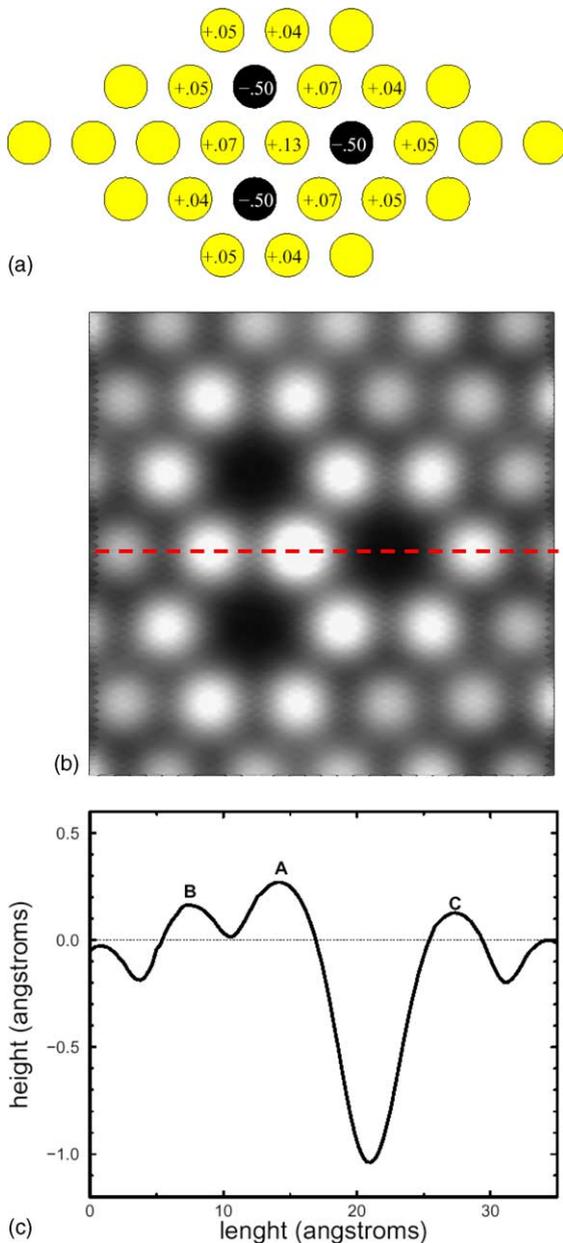


Fig. 4. (a) Same as Fig. 2a for the case of three nearby defects, (b) filled state STM image. (c) STM profile ($V_{\text{tip}} = 1.0$ eV, $I = 0.5$ nA) along the line shown in Fig. 4b. A, B, C correspond to Sn adatoms nearest-neighbour to three, two and one Si-defects, respectively. See Fig. 2 in Ref. [25] for the corresponding experimental result.

corrugation of 1.0 \AA , while in the experimental profile this corrugation is only 0.8 \AA . This difference is probably due to the idealized STM-tip used in the

theoretical calculation. The additive nature of the perturbation induced by Si-defects in nearest-neighbours Sn adatoms has also been observed in experimental STM images [25].

4. Conclusions

The presence of Si-substitutional defects on the $\alpha\text{-}\sqrt{3} \times \sqrt{3}\text{-Sn/Si}(1\ 1\ 1)$ surface induces structural and electronic changes in the surrounding Sn-adatoms. As shown in Fig. 3, there is a rearrangement of the charge in the dangling bonds: one electron is transferred from the Si-dangling bond to its six nearest-neighbours Sn-dangling bonds. In order to accommodate this extra charge, these Sn-adatoms lower their dangling-bond states by moving upwards ($\sim 0.05 \text{ \AA}$). This effect is clearly observed in filled state STM images, where a ring of six bright adatoms is observed around Si-defects, in good agreement with experiment. This six-fold symmetry around the Si-defect is in contrast to the threefold symmetry observed around Ge-defects on the Sn/Ge(1 1 1) surface [18,28]. This difference is related to the different ground state atomic structures: Sn/Ge(1 1 1) presents a 3×3 reconstruction while in Sn/Si(1 1 1) the ideal $\sqrt{3} \times \sqrt{3}$ is the lower in energy structure (see Fig. 1).

The structural distortion induced by a Si-defect affects basically only the Sn-adatoms nearest-neighbours to the Si-defect, in agreement with similar theoretical results [28] for the $3 \times 3\text{-Sn/Ge}(1\ 1\ 1)$ surface. This result suggests that the interaction between defects cannot be the main driving force for the $\sqrt{3} \times \sqrt{3} \leftrightarrow 3 \times 3$ phase transition.

Acknowledgements

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